

Rainer Kimmich

Principles of Soft-Matter Dynamics

Basic Theories, Non-invasive Methods,
Mesoscopic Aspects

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To Herta

Preface

Soft-matter physics – one might ask, is that plainly the counterpart of *solid-state physics*, so to speak the more complex, elusive part of condensed-matter science? Referring to solid-state physics, we have a clear notion what sort of subjects is covered, namely the application of mature theoretical concepts to predominantly crystalline materials. In books on solid-state physics, one usually expects chapters on lattice dynamics, electronic band theory, magnetism, superconductivity, etc. Solid-state physics is defined by a certain class of phenomena and their theoretical explanation, not so much by the chemical nature of the materials. This appears to be in contrast to soft-matter science. The scope of books and scientific journals in this field is often adumbrated by a list of systems considered to form classes of their own: colloids, polymers, liquid crystals, amphiphiles etc. In principle, there could be independent monographs for each of these fields, and quite a few of them exist indeed. But, what is the conceptual span of the global field? What dynamical features do all these systems have in common, or – at least – what dynamical principles form the concerted basis?

One of the most prominent pioneers of soft-matter science, the Physics Nobel Laureate P. G. de Gennes, whose work inspired my own studies in the past so much, had the bold visions needed to establish theoretical guidelines how to treat problems in this multifaceted field. He converted our notion of the field from ‘what it is not’ to ‘what it could be or should be’ in the sense of a framework of formal principles. His Nobel lecture in Stockholm in 1991 (http://nobelprize.org/nobel_prizes/physics/laureates/1991/gennes-lecture.pdf), even though embroidered with a series of references to typical compounds forming soft systems, beautifully delineates the seminal ideas behind.

In this sense, I aspired to a book outlining fundamental and well-established formalisms of dynamic processes in the field. This refers to theoretical principles, standard experimental techniques, and typical applications. The focus will be on the treatment of basic concepts that can be calculated with reasonable effort by non-experts. Qualitative descriptions and mere listings of facts are avoided as far as possible.

The level of the treatise corresponds to the lectures and seminars I held at the University of Ulm for graduate students. Accordingly, the typical readership the book aims at ranges from Master and Ph.D. students to scientists working in this field. Paying tribute to the interdisciplinary character of soft-matter applications, all important formalisms are developed in a detailed step-by-step manner and should be comprehensible even with moderate mathematical training. To my experience as a teacher, tracing laws back to first principles is elucidating and supports understanding. On this basis, the reader should be enabled to do independent research in soft-matter science in the most promising way, namely by combining experiment, analytical theory, and computer simulation. Corresponding examples will be demonstrated.

In principle, the book is founded on three pillars: *Fundamental phenomena*, *methods* and *applications*. The chapters referring to the first two categories have largely the character of textbooks. That is, the simplest scenarios of dynamic phenomena and their experimental detection are described and are theoretically established. Real applications are far more complex. The specific methodological features will therefore be outlined in chapters devoted to certain material classes.

One of the problems researchers in soft-matter science are often facing is that it may be rather cumbersome to relate and compare results obtained with different molecular-dynamics methods. The main reason is that data are “encoded” in terminologies specific for the diverse techniques. What has the *loss angle* in dielectric relaxation to do with the *spin-lattice relaxation time* in NMR? How does the *double-differential cross-section* of incoherent neutron scattering compare with the *echo attenuation function* in field-gradient NMR diffusometry? In *Chap. 1, Introduction*, it will be pointed out that there is a category of dynamic functions that is in use and is consequently understood commonly by all methodological communities, namely *temporal correlation functions*. A correlation function terminology will be introduced as a sort of lingua franca of molecular dynamics. In a multi-disciplinary, multi-methodological field such as soft-matter science, this is expected to facilitate communication among scientists referring to different methods. In the subsequent chapters, the reader will frequently be reminded of these “common denominators” of dynamic techniques.

Chapter 2, Basic Phenomena and Definitions, is to provide fundamental information such as interaction forces, equations-of-motions, and translational and rotational categories of molecular dynamics. To some degree, this material can be found in other textbooks as well. However, the ambition was to have a closed representation in a nomenclature consistent with the subsequent applications. Moreover, a number of less common topics such as Casimir and depletion forces will be addressed as well in view of the attention these subjects attracted in the context of colloidal suspensions and micro-electro-mechanical systems (MEMS).

Coherent and incoherent particle motions, translational and rotational molecular dynamics, these are the global classifications one has certainly in mind when speaking of soft-matter dynamics. The methodology permitting the exploration of these phenomena is of paramount importance for the whole field. *Chapter 3, Non-invasive Methods*, comprises the most common techniques suitable for soft-matter studies. ‘Non-invasive’ means that the sample materials can be examined in

their native form without modifications such as labeling with probe molecules. One and the same sample can in principle be subjected to different and complementary investigations with different techniques, while the microstructure remains undistorted by any label compounds. Unavoidably, this chapter is relatively long due to the fact that no adequate compendium comprising this particular methodology exists in the literature. Paying tribute to the conceptual philosophy of this book, the specific features of the methods will be presented with particular reference to correlation functions and with a consistent symbolism throughout.

Treatments of molecular dynamics in general and especially if they are based on Langevin equations-of-motions are hardly possible without referring to hydrodynamics, a field addressing coherent rather than incoherent particle motions. Basic hydrodynamic concepts such as Stokes' friction law of particles in a viscous medium are ubiquitously employed in molecular dynamics. It is therefore not so far off to include the relatively short *Chap. 4, Fluid Dynamics*, in the frame of the present book. Hydrodynamics is a classical discipline addressed by numerous textbooks and other monographs in the literature. Nevertheless, the present treatise is unique in the sense that it juxtaposes the principles of the analytical formalism in the form of computer simulations with real experiments. If the topology of objects is known or predetermined by special sample preparations, hydrodynamics can be simulated and measured under identical conditions. This option opens a promising application field of utmost importance for chemical engineering. Little has been done in this respect so far.

The term *fluid dynamics* is moreover understood in a generalized sense. Apart from pressure driven flow, a wealth of related *transport phenomena* will be addressed in this chapter. The scope covers examples as different as the spatially resolved probing of thermal convection, heat conduction, electro-osmosis, and ionic currents. The application potential and the information promised by comparative studies of the diverse transport species offer enormous prospects.

Concepts based on equation-of-motion treatments can favorably be exemplified with polymers. On the other hand, polymer science is usually considered to be an independent research field of its own. Owing to a certain heterogeneity of representation, the accessibility of the standard polymer literature appears to be rather limited for beginners starting at the graduate student level. Sacrificing any ambition of completeness, I therefore focused in *Chap. 5, Molecular Dynamics in Polymers*, on the treatment of suitably modified versions of the Langevin equation introduced in *Chap. 2*. The Langevin equation-of-motion concept will be taken as a general basis for analytical explanations of dynamic polymer phenomena of central interest. The reader is thus led straightforwardly from the dynamics of *freely-draining* polymer chains as the simplest case to *entangled-chain* phenomena and finally to *confinement* effects. Langevin equation based treatments will be supplemented step by step by taking into account additional force terms specific for the diverse scenarios. The relaxation-mode solutions obtained in this way will be expressed in the form of predictions for diverse experimental techniques outlined in *Chap. 3*.

In a sense, liquid crystals are strongly related to polymers as concerns molecular dynamics. Analytical treatments result again in solutions based on collective

relaxation modes. This will be delineated in *Chap. 6, Molecular and Collective Dynamics in Liquid Crystals and Other Mesophases*. The chapter is kept relatively short since the field is well represented in the introductory literature. Molecular dynamics in lipid bilayers, often considered as biological model membranes, and other layered structures are further examples belonging to this category.

Finally, in *Chap. 7, Dynamics at Fluid-Solid Interfaces: Porous Media and Colloid Particles*, molecular motions in complex media will be examined in detail. Such systems may be defined by the existence of fluid-solid interfaces. Surface-related phenomena are therefore of central interest. There is an endless list of examples belonging to this category: Rocks, foams, wood, ceramics, porous glass, bone, bricks, cement, skin, fabrics, soil, zeolites, membranes, agglomerates of fine-particle and globular macromolecules, paper, foodstuff, tissue, bead packs, sponges, aerogels, filters, lung, polymers, leather, sediment formations, granular beds, micro-electro-mechanical systems, lubrication films, colloid suspensions and many more other natural and technical products form a system class of its own. The predominant purpose of this chapter is to elaborate a well-classified scheme of the key mechanisms determining molecular dynamics in the presence of fluid-solid interfaces. Effects due to fluid-wall interactions on the one hand and, on the other hand, owing to geometric confinement in mesoscopic pore spaces will thoroughly be discriminated. Chapter 7 completes the series of applications of the methods described in *Chap. 3*. With the material-specific examples considered in the last four chapters of the book, the reader will be led from *coherent* transport over *collective* relaxation modes to *unconcerted* molecular motions.

To a great deal, this book is the outcome of my research and teaching work in the field over several decades. I enjoyed numerous fruitful co-operations and discussions with my friends, colleagues and coworkers helping me to advance my view of the subject. To mention only a few representative names, among these are Esteban Anordo, Ioan Ardelean, Nail Fatkullin, Farida Grinberg, Yujie Li, Carlos Mattea, Siegfried Stapf, Markus Weber. It is my pleasure to express my sincere thanks to all of them, mentioned by name or not, for the invaluable support.

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Chapter 1

Introduction

Abstract It will be pointed out that there is a category of dynamic functions that is used and consequently understood commonly by all methodological communities, namely, *temporal correlation functions*. A correlation function terminology will be introduced as a sort of lingua franca of molecular dynamics. In a multidisciplinary, multi-methodological field such as soft-matter science, this is expected to facilitate communication among scientists employing different methods in studies of molecular dynamics. In the subsequent chapters, the reader will frequently be reminded of these “common denominators” of dynamic techniques. As further key concepts of pivotal importance, linear-response theory and the fluctuation-dissipation theorem will be outlined.

The subject of this book, molecular dynamics in soft matter, is a rather general one and in principle ranges as far as from hydrodynamics to thermal motions. The former type of dynamics refers to coherent or concerted displacement of particles, the latter to diffusive, that is, incoherent translations and rotations of molecular entities.¹

The systems of interest in soft-matter science are *complex* by tendency, an attribute reminding of any sort of *anisotropy*, *obstruction*, and *confinement* the molecules under consideration are subjected to. Relative to bulk, isotropic, low-molecular materials, complex molecular dynamics arises as a consequence of microstructured and heterogeneous compositions. Typical examples are temporary or permanent wall adsorption of fluid molecules at surfaces in porous media,

¹ Molecular vibration and rotation states are excluded from detailed considerations here. Such excited molecular quantum states are subject of molecular spectroscopy of gases which is beyond the scope of this book.

alignment in liquid crystal domains, and orientation constraints of polymer segments due to chain connectivity.

Molecular dynamics in general comprises *translational* and *rotational* fluctuations of particles. One is tempted to take these two features as two sides of the same phenomenon being strongly correlated. It is seemingly equivalent to study either translational or rotational dynamics depending on which method and which facility is at hand. This conclusion may be valid for isotropic low-molecular fluids in bulk but will most likely fail with complex systems.

As an illustration, let us first consider a small solvent molecule in isotropic bulk environment as a simple example. The translational self-diffusion coefficient, D , can be estimated on the basis of the *Stokes/Einstein equation* (see Eq. 2.197):

$$D = \frac{k_B T}{6\pi\eta a_h} \quad (1.1)$$

where η is the (dynamic) viscosity of the medium, a_h is the hydrodynamic radius of the molecule, k_B is Boltzmann's constant, and T is the absolute temperature. Modeling translational diffusion by a random walk with a mean step time τ_{trans} and a root mean-square step length equal to the hydrodynamic radius a_h leads to the alternative expression

$$D \approx \frac{1}{6} \frac{1}{\tau_{trans}} a_h^2 \quad (1.2)$$

In the frame of the assumptions inherent to Eqs. (1.1 and 1.2), one obtains by comparison:

$$\tau_{trans} \approx \frac{\pi\eta a_h^3}{k_B T} \quad (1.3)$$

for the time scale of translational elementary steps.

On the other hand, the *Debye correlation time* for rotational fluctuations is given by

$$\tau_{rot} = \frac{4\pi\eta a_h^3}{3k_B T} \quad (1.4)$$

for spherical harmonics of order $l = 2$ (see Eq. 3.206). Equations (1.3 and 1.4) suggest the proportionality

$$\tau_{rot} \propto \tau_{trans} \quad (1.5)$$

that is, an equivalence of the time scales of rotational and translational fluctuations (apart from an insignificant numerical proportionality factor). This conclusion

would make sense for low-molecular fluids in bulk. However, it is totally misleading for the examples outlined below in the chapters on polymers, liquid crystals, and fluids confined in mesoscopic porous media. The commutability of the two variants of molecular fluctuations is no longer valid under the complex conditions intrinsic to those systems. In the following, it will be shown how tremendously versatile molecular dynamics in complex systems can manifest itself. Actually, this is a field demonstrating the applicability of a wealth of different theoretical principles. At the same time, the reader will hopefully be attracted by the beauty of formalisms crystallizing the essence of most complex scenarios in terms of straightforward model treatments of molecular-dynamics scenarios.

1.1 Correlation Functions as a Link Between Different Experimental Techniques

In Chap. 3, the most important noninvasive techniques for studies of incoherent molecular dynamics will be described in some detail. This in particular refers to rotational and translational fluctuations of molecules in situations expected to be relevant in soft-matter scenarios. A major problem of methodological literature reports is that the performance and the results of the techniques in use are expressed in rather specific technical terms. Comparisons of data acquired with different methods are therefore often cumbersome even if they refer to the same materials and the same processes of molecular dynamics. To give an example, researchers devoting their work to incoherent neutron scattering will usually not be aware of the fact that the scattering function evaluated in such experiments is of exactly the same nature as the echo attenuation function considered by NMR experimenters studying translational diffusion, and vice versa. As a consequence, the different methodological communities tend to “talk” more or less to themselves as recently complained in the foreword of a methodological special issue of the journal *ChemPhysChem* [1]. In the present context, it is therefore desirable to use a terminology common to all techniques, so that communication among the diverse communities is facilitated.

As will be demonstrated later on, the common basis of practically all techniques probing molecular dynamics must be sought on the time-correlation function level. Correlation functions are the natural means to characterize molecular fluctuations, and they are in use with all methodological communities dealing with molecular dynamics. Even though it will be unavoidable to practice the specific technical terms in the derivations of the individual methods, we will always try to remind of the correlation function basis shared by the techniques.

Time-correlation functions describing rotational and translational fluctuations are generally of the form

$$G(\tau) = \langle A(t + \tau) \cdot B^*(t) \rangle \quad (1.6)$$

where $A(t)$ and $B(t)$ are (possibly complex) functions of the molecular position $\mathbf{r} = \mathbf{r}(t)$ and/or of the molecular orientation specified by the polar and azimuthal angles $\vartheta(t)$ and $\varphi(t)$, respectively. These angles are spanned by a molecular axis relative to a direction fixed in the laboratory frame. B^* is the complex conjugate of B . The triangular brackets indicate an ensemble average for a given time t and a fixed interval τ or – according to the ergodic principle – equivalently represent an average over time t for a given molecule and again for a fixed interval τ . If the functions $A(t)$ and $B(t)$ represent identical physical quantities, one speaks of *autocorrelation* functions. The *correlation time* as a characteristic of the correlation decay can be defined by

$$\tau_c = \frac{1}{G(0) - G(\infty)} \int_0^\infty [G(\tau) - G(\infty)] d\tau \quad (1.7)$$

Truly stochastic fluctuations are subject to two fundamental properties, namely, *stationarity* and *time-reversal invariance*. The first of these conditions means that the correlation function $G(\tau)$ merely depends on the interval τ but is independent of the absolute time t . The latter is therefore often set equal to 0 for simplicity. The second property states that it is irrelevant which of the two times to be compared is first. Time-correlation functions are therefore *even* functions of the interval τ , so that $G(\tau) = G(-\tau) = G(|\tau|)$. In the following two sections, we will focus on two outstanding categories of molecular dynamic correlation functions, namely, (a) *orientation correlation functions* and (b) *dynamic structure factors*.

1.1.1 Orientation Correlation Functions

Molecular reorientations are best expressed in terms of spherical harmonics $Y_{l,m}(t)$ of degree l and order m . They consist of sine and cosine terms depending on the polar and azimuthal angles $\vartheta(t)$ and $\varphi(t)$, respectively. The angles are defined in Fig. 1.1 and refer to an external and method-specific field such as the magnetic-flux density $\mathbf{B}$ (in the case of nuclear magnetic relaxation experiments) or the electric field strength $\mathbf{E}$ (relevant for dielectric relaxation). The spherical harmonics of the first two nontrivial degrees are given by

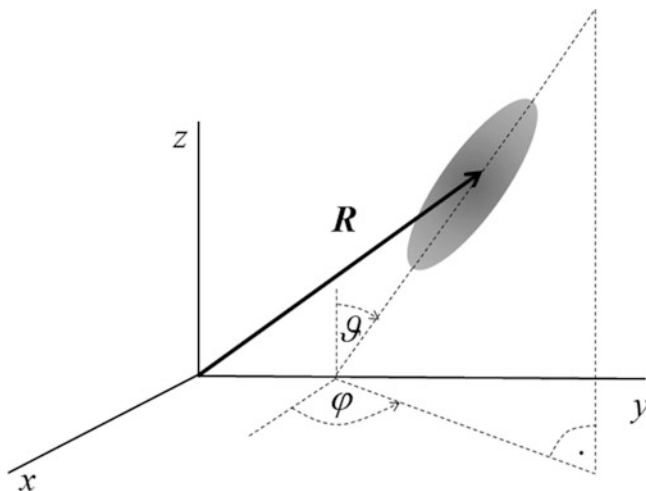


Fig. 1.1 The polar and azimuthal angles ϑ and φ , respectively, defining the orientation of a molecular axis relative to an external field. The center-of-mass position of the molecule is given by the vector $\mathbf{R}$

$$\begin{aligned}
 Y_{1,0} &= \sqrt{\frac{3}{4\pi}} \cos \vartheta \\
 Y_{1,\pm 1} &= \mp \sqrt{\frac{3}{8\pi}} \sin \vartheta e^{\pm i\varphi} \\
 Y_{2,0} &= \sqrt{\frac{5}{16\pi}} (3\cos^2 \vartheta - 1) \\
 Y_{2,\pm 1} &= \mp \sqrt{\frac{15}{8\pi}} \cos \vartheta \sin \vartheta e^{\pm i\varphi} \\
 Y_{2,\pm 2} &= \sqrt{\frac{15}{32\pi}} \sin^2 \vartheta e^{\pm 2i\varphi}
 \end{aligned} \tag{1.8}$$

On this basis, *orientation correlation functions* can be defined by the expression

$$G_{l,m}(t) = 4\pi(-1)^m \langle Y_{l,m}(t) Y_{l,-m}(0) \rangle \tag{1.9}$$

where the subscripts l and m specify the spherical harmonics relevant for the experimental technique under consideration. The numerical factor 4π is a normalization constant. That is, orientation correlation functions decay from the initial value $G_{l,m}(0) = 1$ under isotropic conditions to zero in the long-time limit. In anisotropic systems, the asymptotic value may be finite, that is, $G_{l,m}(\infty) = \text{const} < 1$.

Temporal autocorrelation functions of the type Eq. (1.9) describe *rotational* fluctuations of molecules or molecular systems. Typical methods probing such

fluctuations are spin–lattice relaxation ($l = 2, m = \pm 1, \pm 2$) [2] in particular if probed by the field-cycling technique [3], transverse relaxation ($l = 2, m = 0, \pm 1, \pm 2$) [4, 5], multiple-quantum buildup NMR ($l = 2, m = 0$) [6, 7], and dielectric relaxation ($l = 1, m = 0$) [8, 9].

1.1.2 Dynamic Structure Factors

The correlation function describing translational fluctuations of particles is the *incoherent dynamic structure factor*. It refers to *self-diffusion* and is defined according to

$$\begin{aligned}\mathcal{G}_{\text{inc}}(t) &= \left\langle e^{-i\mathbf{q}\cdot\mathbf{R}(0)} e^{i\mathbf{q}\cdot\mathbf{R}(t)} \right\rangle \\ &= \left\langle \exp\{-i\mathbf{q} \cdot [\mathbf{R}(0) - \mathbf{R}(t)]\} \right\rangle \\ &= \left\langle \exp\{i\mathbf{q} \cdot \mathbf{r}_{\text{self}}\} \right\rangle\end{aligned}\tag{1.10}$$

$\mathbf{R}(0)$ and $\mathbf{R}(t)$ are the position vectors of the diffusing reference particle at times 0 and t , respectively, so that $\mathbf{r}_{\text{self}} = \mathbf{R}(t) - \mathbf{R}(0)$ is the particle displacement by self-diffusion in the interval t (for an illustration, see Fig. 2.20). The wave vector $\mathbf{q}$ is defined specifically for the method under consideration. In the simplest case, the *propagator* of the diffusion process is a *Gaussian function* (see Sect. 2.5.1). The correlation function can then be expressed in terms of the mean-square displacement $\langle r_{\text{self}}^2 \rangle = 6Dt$, where D is the translational self-diffusion coefficient and $\langle r_{\text{self}}^2 \rangle$ is the second moment of the propagator:

$$\mathcal{G}_{\text{inc}}(t) = \exp\left\{-\frac{1}{6}q^2\langle r_{\text{self}}^2 \rangle\right\}\tag{1.11}$$

Well-known techniques probing incoherent dynamic structure factors are field-gradient NMR diffusometry in its different variants [10–12] (Sect. 3.2) and incoherent (quasi-elastic) neutron scattering [13] (Sect. 3.6). The incoherent variant of neutron scattering dominates for protons which possess a particularly strong incoherent scattering cross-section. In this case, the wave vector $\mathbf{q}$ reflects the momentum transfer in the scattering process:

$$\hbar\mathbf{q} = \hbar\mathbf{k}_{\text{incident}} - \hbar\mathbf{k}_{\text{scattered}}\tag{1.12}$$

The quasi-elastic character of the phenomenon is manifested by the approximate equality of the wave vector magnitudes of the incident and the scattered neutrons, $k_{\text{incident}} \approx k_{\text{scattered}}$. That is, no higher quantum states of the target nuclei are excited upon scattering.

In the case of field-gradient NMR diffusometry, the quantity $\mathbf{q}$ is formally termed “wave” vector as well although no propagating waves are considered in this case.² It is defined by

$$\mathbf{q} = \gamma \delta \mathbf{g} \quad (1.13)$$

where the interval δ is the spatial encoding time by the gradient $\mathbf{g}$ of the external magnetic field (for details, see Refs. [5, 10–12], for instance, and Sect. 3.2). Apart from this definition, the dynamic structure factor Eq. (1.10) probed as the spin echo attenuation curve is formally identical to the function acquired by incoherent neutron scattering [14].

Translational displacements of particles *relative to each other* can be described by the *coherent dynamic structure factor*. This correlation function is of the form³

$$\begin{aligned} G_{\text{coh}}(t) &= \frac{1}{N} \sum_{j,l=1}^N \left\langle e^{-i\mathbf{q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{q} \cdot \mathbf{R}_l(t)} \right\rangle \\ &= \frac{1}{N} \sum_{j,l=1}^N \left\langle \exp \left\{ -i\mathbf{q} \cdot (\mathbf{R}_j(0) - \mathbf{R}_l(t)) \right\} \right\rangle \\ &= \frac{1}{N} \sum_{j,l=1}^N \left\langle \exp \left\{ i\mathbf{q} \cdot \mathbf{r}_{j,l}(t) \right\} \right\rangle \end{aligned} \quad (1.14)$$

It correlates displacements of particle pairs j, l in an ensemble of N particles relative to each other, $\mathbf{r}_{j,l}(t) = \mathbf{R}_j(t) - \mathbf{R}_l(0)$. The particles can be located on the same or on different molecules depending on the system under investigation. That is, one can distinguish intra- and intermolecular coherent dynamic structure factors. In the latter case and if the molecules diffuse independently of each other, a Gaussian propagator of the relative displacements, $\mathbf{r}_{j,l}(t)$, can be assumed under simple conditions. The intermolecular coherent dynamic structure factor can then be approached by

$$G_{\text{coh}}(t) \underset{\text{propagator}}{\overset{\text{Gaussian}}{\approx}} \frac{1}{N} \sum_{j,l=1}^N \exp \left\{ -\frac{1}{6} q^2 \left\langle r_{j,l}^2(t) \right\rangle \right\} \quad (1.15)$$

²Note however that the magnetization grating generated in the course of such experiments is characterized by a modulation with a “wave” length corresponding to $\mathbf{q}$. For an illustration, see Fig. 3.26.

³The static counterpart, that is, the *static structure factor*, is defined by $S(\mathbf{q}) = G_{\text{coh}}(0)$. Note also that the terminology “relative pair diffusion” often used in this context should be taken only *cum grano salis* since the double sums in Eq. (1.14) imply the cases $j = l$, that is, self-diffusion.

In the intermolecular case, the information inherent to the coherent dynamic structure factor can be examined with the aid of isotopic dilution NMR relaxometry, that is, by typically studying proton NMR in partially deuterated samples as it was demonstrated in Ref. [15], for example. The intramolecular variant of the coherent dynamic structure factor can be acquired with the aid of coherent (quasi-elastic) neutron scattering [13]. Owing to the fact that the coherent scattering cross-section of deuterons is significantly stronger than that of their incoherent contribution, coherent neutron scattering can be identified and evaluated with the aid of deuterons as scattering centers in isolated perdeuterated species. In this context, Eq. (1.14) is also called *coherent-scattering function*.

1.1.3 Exponential Correlation Functions

Soft matter often consists of complex, heterogeneous, and locally anisotropic molecular systems. Correlation functions will reflect all the intricacies inherent to such scenarios. Therefore, no simple expressions can be expected. Nevertheless, elementary (mono-)exponential functions are often assumed in first-approach treatments. A justification may be that dynamic principles can be elucidated on this basis without necessarily concealing the essence of the treatment in lengthy formalisms. Let us therefore discuss shortly what the exponentiality of a correlation function means.

The rate with which a random process occurs be $1/\tau_c$. We are interested in the probability that the process does *not* take place in a period t . Let us subdivide this period in N equal intervals Δt so that $t = N\Delta t$. The probability that the process takes place in a given interval is then $\Delta t/\tau_c$. The complementary probability, namely, that the process does *not* take place in that interval, is consequently $1 - \Delta t/\tau_c$. Considering now the whole period $t = N\Delta t$ leads to the probability

$$\left(1 - \frac{\Delta t}{\tau_c}\right)^N = \left(1 - \frac{\Delta t}{\tau_c}\right)^{t/\Delta t} = \left[\left(1 - \frac{\Delta t}{\tau_c}\right)^{-\tau_c/\Delta t}\right]^{-t/\tau_c} \quad (1.16)$$

that the process did not yet take place. The expression becomes exact in the limit $\Delta t \rightarrow 0$ which gives the mono-exponential correlation function⁴

⁴ We use the calligraphic symbol $\mathcal{G}(t)$ throughout for *normalized* (or synonymously: *reduced*) correlation functions obeying the property $\mathcal{G}(0) = 1$. Otherwise, Roman symbols like $G(t)$ will be employed.

$$G(t) = \lim_{\Delta t \rightarrow 0} \left[\left(1 - \frac{\Delta t}{\tau_c} \right)^{-\tau_c/\Delta t} \right]^{-t/\tau_c} = \left[\lim_{\Delta t \rightarrow 0} \left(1 - \frac{\Delta t}{\tau_c} \right)^{-\tau_c/\Delta t} \right]^{-t/\tau_c} = e^{-t/\tau_c} \quad (1.17)$$

This derivation elucidates the meaning of this sort of correlation function: It is nothing else than the *probability* that the initial state is still retained. Consequently, it takes the value 1 for $t = 0$. According to Eq. (1.7), the *correlation time* τ_c ,

$$\tau_c = \int_0^{\infty} e^{-t/\tau_c} dt \quad (1.18)$$

can be considered as the *mean lifetime* of the initial state.

Fluctuations characterized by this sort of statistics are called *Poisson* or *Markoff processes* [16]. The former name reminds of the fact that the process takes place with the same probability in any time interval of the same length. The latter classification alludes to the condition that there is no memory effect involved in the fluctuations. The probability for the event merely depends on the present state of the system, while the prehistory is irrelevant.

1.1.4 The Long-Tail Detectability Problem

Unlike isotropic low-molecular liquids in bulk, correlation functions characterizing molecular dynamics in complex systems tend to be intrinsically non-exponential. It is therefore most important to probe these functions in a time range as wide as technically possible. Moreover, there is some tendency that short-time (i.e., short-range or local) fluctuations dominate most of the correlation decay, whereas the more system-specific (i.e., long-range) part of the information is contained in a small, slowly decaying tail comprising only a small fraction of the total correlation loss. Since one is usually interested in features specific for the system, a corresponding measuring capability should be ensured. This means firstly an experimental time window wide enough to include the long-time tail and secondly a detection sensitivity and a signal-to-noise ratio permitting the record of minute residual correlations.

Several scenarios illustrating these requirements of the experimental setup will be described in the course of the following chapters. A typical example is the dynamic correlation function of small solvent molecules confined in mesoscopic porous media. On a time scale too short to permit contacts with the pore walls, molecular dynamics will be the same as in bulk. By contrast, the long-time tail recorded with the required sensitivity contains all the information expected with respect to solvent/wall interaction and exchange processes. Likewise, short-time

dynamics of polymer chains is governed by short-range modes insensitive to confinement or entanglement effects. The wavelengths of chain modes susceptible to such effects are much longer. They can only be probed by techniques sensitive to correspondingly long times and correspondingly small correlations.

1.2 Linear-Response and the Fluctuation-Dissipation Theorem

Fluctuations of dynamic quantities in thermal equilibrium are best described by time-correlation functions as exemplified in the previous sections. The most important tools for studies of molecular dynamics are the various relaxation experiments to be described later in detail. The essence of relaxation experiments is that a *nonequilibrium* state is first generated and that the system responds by irreversible relaxation toward *equilibrium*. This can be done in a sequential way so that a free relaxation interval follows the initial perturbation pulse or step. It can also be performed in a “dynamic” way in the sense that the system reacts via relaxation to a periodic perturbation. In any case, the question is how the macroscopic response of the system to a perturbation can be related to the spontaneous microscopic fluctuations in equilibrium. Under certain circumstances, the answer is provided by the *fluctuation-dissipation theorem* which is closely related to Onsager’s regression hypothesis. A good representation of this formalism can be found in Ref. [17].

Consider a spontaneously fluctuating quantity $A(t)$ in a system in thermal equilibrium. Typical examples are the (local) polarization which will be referred to in the case of dielectric relaxation and the (local) stress relevant in the context of mechanical relaxation experiments. The fluctuations $\delta A(t)$ are characterized by the time-correlation function

$$G(t) = \langle A(0)A(t) \rangle - \langle A \rangle^2 \equiv \langle \delta A(0)\delta A(t) \rangle \quad (1.19)$$

where the quantity $A(t)$ is assumed to be a real scalar for simplicity. In the vectorial case, the product in Eq. (1.19) needs simply to be replaced by a scalar product. The special form of Eq. (1.19) ensures that the correlation function decays from $G(0) = \langle A^2 \rangle - \langle A \rangle^2$ to $G(\infty) = 0$. That is, we restrict ourselves to the fluctuating part $\delta A(t)$ of $A(t)$ and subtract the stationary contribution.

In a relaxation experiment, thermal equilibrium is distorted by a “force” $f(t)$ in the generalized sense. This can be an electric field of strength $E(t)$ in the dielectric case or a shear rate $\dot{\gamma}(t)$ with mechanical relaxation, for instance. The *macroscopic response* of the system to this disturbance is designated by the dynamical variable $\Delta A(t)$. Depending on the relaxation experiment, this can be the electric polarization of the sample, shear stress, etc. The relation between the macroscopic response and the perturbation will in general be quite complicated. It can however be treated if the deviation from thermal equilibrium remains small enough. The approach that

will become applicable under such circumstances is the *linear-response theory*. As the name says, there will be a *linear* relationship of the dynamical variable $\Delta A(t)$ to the generalized force $f(t')$ perturbing the system on the time scale $t' \leq t$. The integrated response $\Delta A(t)$ to the generalized force $f(t - \tau)$ acting at a period τ before t is

$$\Delta A(t) = \int_0^{\infty} \psi(\tau) f(t - \tau) d\tau + O(f^2) \quad (1.20)$$

Restricting ourselves to the linear term on the right-hand side, Eq. (1.20) is accurate to an error of the order $O(f^2)$ which indicates that this *linear-response formula* is based on a first-order Taylor series approximation. It is adequate for correspondingly *small* perturbations.

According to this linear-response formula, the response $\Delta A(t)$ is additively related to the prehistory of the generalized force $f(t - \tau)$ prior to the time t . The link is the *response function*⁵ $\psi(\tau)$, where τ is a period preceding the time t . The essence of the linear-response theory is that the response function $\psi(\tau)$ is an *equilibrium* property of the system. It is independent of the applied perturbation $f(t - \tau)$ at any time.

In principle, the response function can be interpreted as the response to an impulsive disturbance having occurred at a time $t' = t - \tau$:

$$f(t') = f_0 \delta(t') \quad (1.21)$$

where $\delta(t')$ is Dirac's delta function with the properties $\delta(t' \neq 0) = 0$, $\delta(0) = \infty$, and $\int_0^{\infty} \psi(\tau) \delta(t - \tau) d\tau = \psi(t)$. Inserting this into Eq. (1.20) gives

$$\Delta A(t) = f_0 \psi(t) \quad (1.22)$$

The response function consequently decays according to

$$\psi(t) = \frac{\Delta A(t)}{f_0} \quad \text{for } t \geq t' \quad (1.23)$$

From a more application-oriented point of view, the response function can be expressed in terms of the *equilibrium time-correlation function* Eq. (1.19) by making use of the *fluctuation-dissipation theorem* in the representation

⁵ Sometimes, the response function is also (and possibly misleadingly) called *generalized susceptibility*.

$$\psi(\tau) = \begin{cases} -\frac{1}{k_B T} \frac{d}{d\tau} \langle \delta A(0) \delta A(\tau) \rangle & \text{for } \tau > 0 \\ 0 & \text{otherwise} \end{cases} \quad (1.24)$$

k_B is Boltzmann's constant and T is the absolute temperature. As suggested by the factor $(k_B T)^{-1}$, Eq. (1.24) is the result of the lowest nontrivial order of a series expansion of the Boltzmann factor characterizing the equilibrium populations of the energy states. That is, we are again dealing with a *linear* approximation as justified for small deviations from equilibrium. Later, particularly in the frame of the linear-response treatments of dielectric and mechanical relaxation, this expression will turn out to be of outmost utility.

1.3 A Word on Classical and Quantum-Mechanical Treatments

The world of atoms and molecules is usually considered to be the realm of quantum mechanics. This is certainly true for electronic properties and phenomena at extremely low temperatures. By contrast, the equations of motion for the description of molecular dynamics to be discussed in the course of the following chapters are based on classical mechanics. What is the justification for that?

The crossover from quantum mechanics to classical approaches is characterized by the *correspondence principle*: In the large-quantum-number limit, quantum-mechanical laws converge to classical laws which can therefore be taken as an approach getting better the larger the quantum number. A typical example with which this can be demonstrated is the well-known treatment of the harmonic oscillator (see, e.g., Ref. [18]).

It may be a bit unspecific to argue with large quantum numbers of systems as complicated as liquid crystals or polymers. Let us therefore try another argument. Consider a free particle such as a molecule in a gas in thermal equilibrium. The de Broglie wavelength is given by

$$\lambda = \frac{h}{p} \quad (1.25)$$

where h is Planck's quantum of action and p is the particle momentum. The mean momentum in thermal equilibrium is

$$p_{\text{th}} = mv_{\text{th}} = \sqrt{3k_B T m} \quad (1.26)$$

where v_{th} is the mean thermal velocity, k_B is Boltzmann's constant, T is the absolute temperature, and m is the particle mass. At temperatures typically relevant for soft matter, the particle velocity is nonrelativistic of course. The mean de Broglie wavelength thus becomes

$$\bar{\lambda} = \frac{h}{\sqrt{3k_B T m}} \quad (1.27)$$

The decisive role of the molecular mass and the temperature is obvious. Taking $m \approx 10^{-25}$ kg as a typical order of magnitude for the mass of relatively small molecules and $T \approx 300$ K, we estimate

$$\bar{\lambda} \approx 1.9 \times 10^{-11} \text{ m} \quad (1.28)$$

where we have used the known constants $h = 6.6 \times 10^{-34}$ J s and $k_B = 1.38 \times 10^{-23}$ J K⁻¹. With that short wavelengths, it is obvious that wave properties such as diffraction or interference will hardly be observable.⁶ Under usual conditions, molecular dynamics of molecules in soft matter can therefore reliably be treated on the basis of classical mechanics.

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⁶ Actually, quantum-mechanical diffraction of relatively large molecules has indeed been demonstrated as reported in Ref. [19]. However, it is not only the so-called decoherence that makes an influence on soft-matter dynamics unlikely. The conditions required for successful detection of diffraction of wave functions are far away from anything relevant for soft matter.

Chapter 2

Basic Phenomena and Definitions

Abstract This chapter provides a compilation of the basic concepts on which soft-matter dynamics is founded. This implies interaction forces, equations of motions, and translational and rotational categories of molecular dynamics. The objective is to have a closed representation in a nomenclature consistent with the subsequent applications. Moreover, a number of less common topics such as Casimir forces and other electrochemical effects will be addressed as well in view of the attention these subjects are attracting in the context of colloidal suspensions and micro-electromechanical systems (MEMS).

2.1 Molecular and Particle Interactions on Length Scales from Å to μm

What forces keep soft matter in the condensed state, and what is the fundamental origin of material properties both of a static and a dynamic nature? Any answer to this basic question unavoidably refers to interactions among objects such as atoms, molecules, mesoscopic particles, surfaces, and interfaces. Interactions can be attractive or repulsive. That is, the respective interaction potential energy decreases or increases when the interaction partners approach each other. The superposition of attractive and repulsive interaction potentials leads to a minimum defining the stable “equilibrium” distance of the interacting particles. A general principle of physics is that systems always tend to adopt the structure of minimum potential energy. The colloquial terminology is that it is “energetically more favorable” if a system resides in a potential minimum associated to certain structural parameters.

Referring to nonmetallic, nonionic, and non-electrolytic substances, *intramolecular* interactions are normally dominated by covalent bonding in contrast to *intermolecular* van der Waals forces and hydrogen bonds. The binding energies of *intermolecular* interactions are weaker than those of covalent bonds by typically one order of magnitude in the case of hydrogen bonds and two orders of magnitude for van der Waals interactions. The bond or interaction strength is characterized by

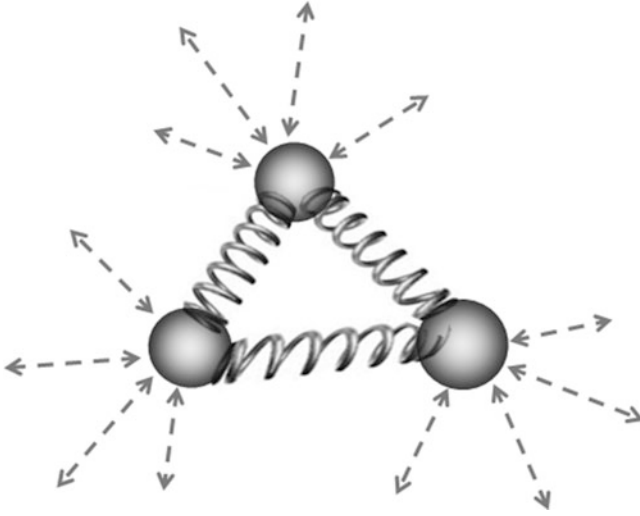


Fig. 2.1 Schematic illustration of intra- and intermolecular interactions. The *balls* are to represent three atoms of a fictitious molecule. The (strong) intramolecular couplings are represented by springs and (weak) intermolecular forces by *double arrows*

the binding (or dissociation) energy ε . Orders of magnitude per particle are 10^{-19} J (covalent bond), 10^{-20} J (hydrogen bond), and 10^{-21} J (van der Waals interaction).

Figure 2.1 schematically illustrates the couplings among atoms of a molecule and the distinction of intra- and intermolecular interactions.

When speaking of intermolecular forces, it may be adequate to tacitly imply also interactions among different chemical groups of the same molecule provided that these groups are not directly covalently bound to each other. Such intergroup interactions are particularly relevant in the case of flexible macromolecules where structurally remote groups can approach and interact with each other without being directly bound. Later, we will also extend the concept of particle–particle interactions to the continuum limit, that is, to particle–surface or surface–surface interactions. Such larger entities can be the pore walls in porous media or the solvent/particle interfaces of colloids.

As mentioned before, interactions among atoms and molecules are characterized by the interplay of attractive and repulsive forces strongly depending on the separation distance r of the interaction partners. A very well-known and typical ansatz for the interaction potential energy is the *Lennard/Jones potential* formally represented by the relationship

$$W(r) = 4\varepsilon \left\{ \left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right\} \quad (2.1)$$

with the parameters ε and r_0 . A graphical representation of Eq. (2.1) can be found in Fig. 2.2. In this case, the repulsive part scales proportional to r^{-12} and is positive,

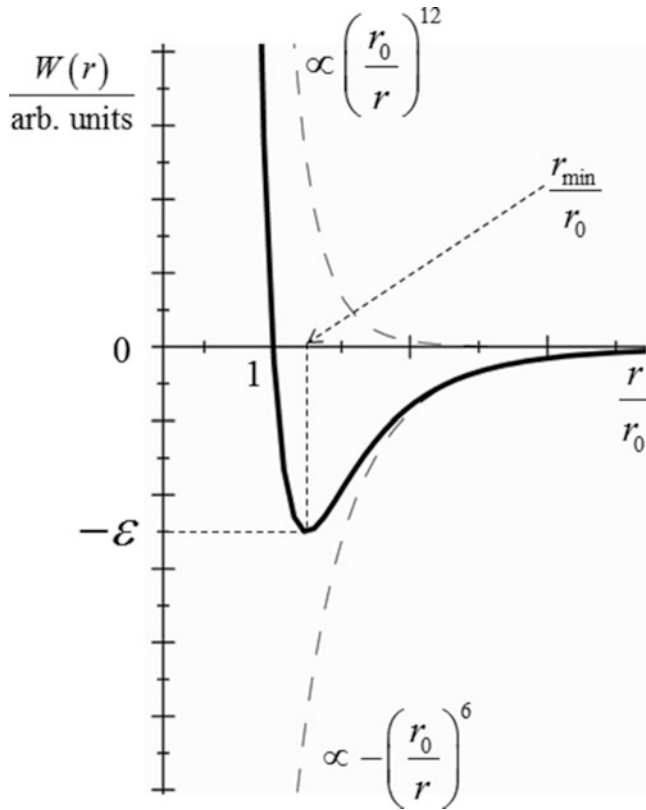


Fig. 2.2 Lennard/Jones potential $W(r)$ as a function of the distance r of the interacting particles in units r_0 (see Eq. 2.1)

whereas the attractive contribution is negative and proportional to r^{-6} . The superposition of both types of potentials leads to a minimum at a particle distance $r = r_{\min}$ indicating the equilibrium distance of the interaction partners.

The force between the two bodies is given by

$$F = -\frac{dW}{dr} = 24\epsilon \left\{ 2 \frac{r_0^{12}}{r^{13}} - \frac{r_0^6}{r^7} \right\} \quad (2.2)$$

It takes a positive sign if it acts along the positive r axis, that is, if $r < r_{\min}$ (see Fig. 2.2). A negative sign, on the other hand, indicates $r > r_{\min}$. The interaction force vanishes for $r = r_{\min}$,

$$F(r_{\min}) = 24\epsilon r_0^6 \left\{ 2 \frac{r_0^6}{r_{\min}^{13}} - \frac{1}{r_{\min}^7} \right\} = 0 \quad (2.3)$$

so that

$$r_{\min} = 2^{1/6} r_0 \quad (2.4)$$

The *binding energy* ε is the depth of the potential well, that is, a positive quantity, whereas the equilibrium value of the potential, $W(r_{\min}) = -\varepsilon$, is negative. For the particle distance $r = r_0$, attractive and repulsive terms cancel each other, so that $W(r_0) = 0$. Minimization of the total potential energy is the general stabilization principle of the microstructure of a system. In the following chapters, we will encounter numerous examples for this maxim.

If the system has many degrees of freedom, the term “potential” is usually understood in the thermodynamic sense because entropic contributions must then be taken into account. Distinct thermodynamic potentials adopting minimal values at equilibrium are in particular the *Helmholtz free energy* (adequate for isochoric state variations) and the *Gibbs free energy* (adequate for isobaric state variations).

The physical nature of all couplings discussed in the following is based on Coulomb interactions (attractive or repulsive) and the Pauli principle for the occupation of electron states (repulsive interaction). Let us begin with the discussion of the former contribution.

2.1.1 Coulomb Interaction

The well-known Coulomb formula for the potential energy of a point charge q_1 in the electric field $\mathbf{E}_{q_2} = (4\pi\varepsilon_0 r^2)^{-1} q_2 \mathbf{u}$ of a second point charge q_2 is

$$W_{\text{Coul}} = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{r} \quad (2.5)$$

$\mathbf{u}$ is the unit vector pointing from q_2 to q_1 . The electric field constant is represented by ε_0 , and r is the distance between the point charges. The Coulomb force acting on q_1 is then

$$\mathbf{F}_{\text{Coul}}(q_1) = q_1 \mathbf{E}_{q_2} = -\frac{dW_{\text{Coul}}}{dr} \mathbf{u} = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{r^2} \mathbf{u} \quad (2.6)$$

Likewise, the Coulomb force the point charge q_2 is subjected to is $\mathbf{F}_{\text{Coul}}(q_2) = -\mathbf{F}_{\text{Coul}}(q_1)$. The charges attract each other if they are of opposite sign (i.e., $W_{\text{Coul}} < 0$) and repel each other otherwise ($W_{\text{Coul}} > 0$). The relatively weak distance dependences $W_{\text{Coul}} \propto r^{-1}$ and $F_{\text{Coul}} \propto r^{-2}$ suggest that the interaction of ionized groups ranges over long distances compared to electric dipole interactions as we will see in the following.

2.1.2 Van der Waals Attractions¹

The most important intermolecular force in nonmetallic and non-electrolytic soft-matter materials is the *van der Waals interaction* which is based on Coulomb couplings of permanent or induced electric dipoles. Van der Waals interactions are subdivided into the special cases “interactions of permanent molecular dipoles” (*Keesom interaction*), “interactions of a permanent dipole and an induced dipole” (*Debye interaction*), and “interactions of two induced dipoles” (*dispersion* or *London interaction*).

A molecule forms an electric dipole if the center of positive charges (i.e., of the nuclei) and the center of negative charges (i.e., of the electron clouds) do not coincide permanently or temporarily. If q is the magnitude of the net charge at either center of charge and ℓ is the distance vector connecting the negative with the positive center of charge (see Fig. 2.3), the electric dipole moment is defined by

$$\mu = q\ell \quad (2.7)$$

where the vector direction is from the negative to the positive pole. The SI unit of the electric dipole moment is Cm (Coulomb times meter). However, one still finds the old unit 1 Debye (D) = 3.33564×10^{-30} Cm in the literature for historical reasons.

The question is now: What is the potential energy of an electric dipole in the electrostatic field of another electric dipole. That is, we will deal with the *interaction energy* of a dipole pair.

2.1.2.1 Interaction “Permanent Dipole”–“Permanent Dipole” (Keesom Interaction)

Two dipoles can be represented by four-point charges so that six pairs of interacting point charges can be formed. Since intra-dipole couplings are not of interest here, only four interdipole interaction pairs remain. A linear alignment of the two dipoles is the simplest arrangement as shown in Fig. 2.4. The total interdipole potential energy of such an arrangement is given by the sum of the binary Coulomb interactions (see Eq. 2.5):

$$W = \frac{1}{4\pi\epsilon_0} \left(-\frac{q_1q_2}{r+\ell} + \frac{q_1q_2}{r} - \frac{q_1q_2}{r-\ell} + \frac{q_1q_2}{r} \right) \quad (2.8)$$

¹ We restrict ourselves to the treatment of two-particle interactions. Three- or more-particle contributions can be finite but are practically (and didactically) of minor importance. References [1–3] are recommended for further reading in this matter. For crude estimations, it suffices to sum up all possible pair interactions and assume that these binary contributions are independent of each other. This is called the *pairwise additivity approximation* providing the total potential energy in the system with an accuracy of about 10%.

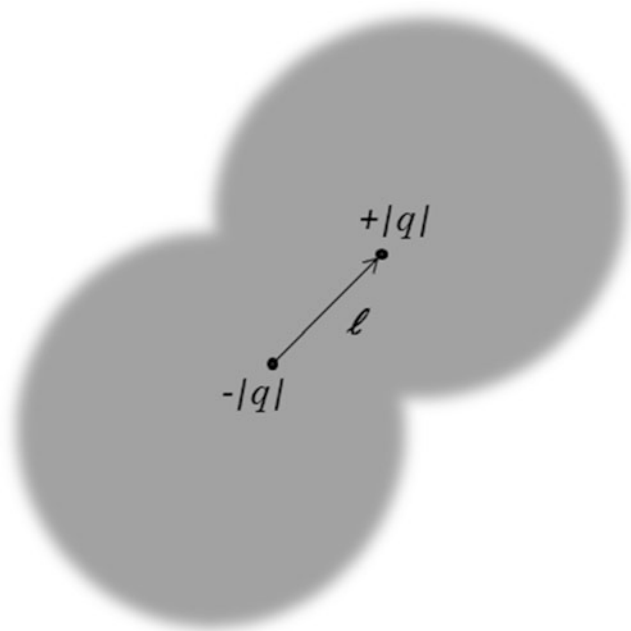


Fig. 2.3 Schematic illustration of an electric dipole formed by the negative and positive centers of charge in a fictitious molecule

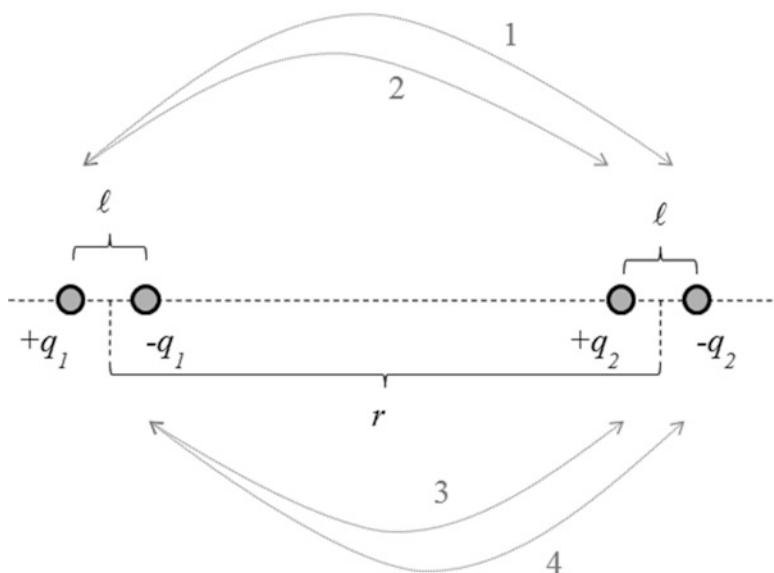


Fig. 2.4 In the simplest mutual arrangement, two electric dipoles are aligned along a *straight line*. The *four bent double arrows* indicate the Coulomb couplings between the four-point charge relevant for the interdipole interaction energy

Introducing the relative quantity $x = \ell/r$, that is, $\ell = xr$, converts this expression into

$$\begin{aligned} W &= \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r} \left(\frac{1}{1+x} - 2 + \frac{1}{1-x} \right) \\ &= \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r} \left\{ (1-x+x^2-\dots) - 2 + (1+x+x^2+\dots) \right\} \end{aligned} \quad (2.9)$$

where the terms $(1+x)^{-1}$ and $(1-x)^{-1}$ have been replaced by geometric power series. In the limit of long interdipole distances, $r \gg \ell$ or $x \ll 1$, the first nontrivial, that is, nonvanishing, approximation is

$$W \approx -\frac{1}{4\pi\epsilon_0} \frac{2x^2}{r} q_1 q_2 = -\frac{1}{4\pi\epsilon_0} \frac{2\mu_1 \mu_2}{r^3} \quad (2.10)$$

$\mu_1 = q_1 \ell$ and $\mu_2 = q_2 \ell$ are the magnitudes of the interacting dipole moments. Generalizing this result to arbitrary (long-distance) arrangements and to arbitrary orientations of the dipole moment vectors leads to the *dipole–dipole interaction energy*:

$$W_{12} = \frac{1}{4\pi\epsilon_0} \left(\frac{\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2}{r^3} - \frac{3(\mathbf{r} \cdot \boldsymbol{\mu}_1)(\mathbf{r} \cdot \boldsymbol{\mu}_2)}{r^5} \right) \quad (2.11)$$

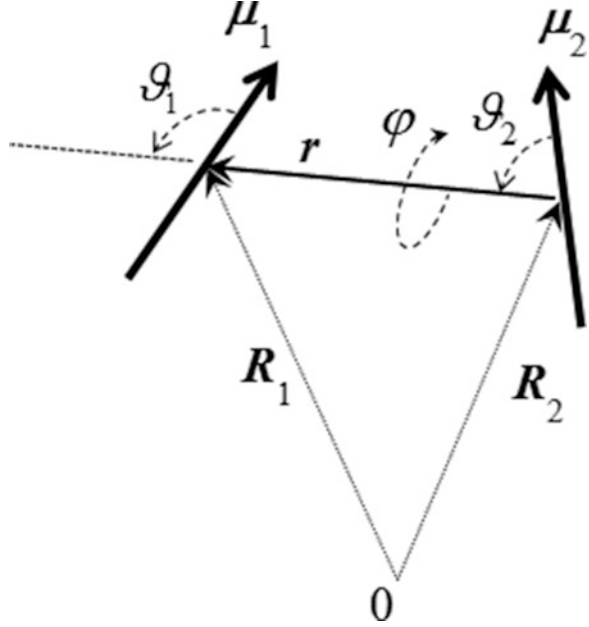
In terms of the angles defined in Fig. 2.5, this expression can be rewritten as

$$W_{12}(r, \varphi, \vartheta_1, \vartheta_2) = -\frac{1}{4\pi\epsilon_0} \frac{\mu_1 \mu_2}{r^3} (2 \cos \vartheta_1 \cos \vartheta_2 - \sin \vartheta_1 \sin \vartheta_2 \cos \varphi) \quad (2.12)$$

Obviously, the special case represented by Eq. (2.10) can immediately be reproduced on this basis for $\boldsymbol{\mu}_1 \parallel \mathbf{r}$, $\boldsymbol{\mu}_2 \parallel \mathbf{r}$, and $\boldsymbol{\mu}_1 \parallel \boldsymbol{\mu}_2$, that is, $\vartheta_1 = \vartheta_2 = 0$.

Molecules in liquid materials are normally subject to rotational diffusion due to thermal motion. The orientation of the dipoles consequently fluctuates relative to each other, and the interaction energy, Eqs. (2.11) or (2.12), must be averaged over all possible dipole alignments in terms of the angles ϑ_1 , ϑ_2 , and φ . If all relative dipole orientations would be equally distributed, this average would vanish. This is however not the case because the dipolar interaction energy is a function of the orientations of the dipoles relative to each other. For example, parallel orientation of the vectors $\boldsymbol{\mu}_1$, $\boldsymbol{\mu}_2$, and $\mathbf{r}$, that is, $\vartheta_1 = \vartheta_2 = 0$, leads to a *negative* (i.e., energetically favorable) interaction potential $W_{12}(r, \varphi, 0, 0) = -(2\pi\epsilon_0 r^3)^{-1} \mu_1 \mu_2$, as we have already seen in Eq. (2.10). This is in contrast to the opposite orientations, that is, $\vartheta_1 = \pi$ and $\vartheta_2 = 0$, which lead to a *positive* and therefore energetically unfavorable interaction energy $W_{12}(r, \varphi, \pi, 0) = (2\pi\epsilon_0 r^3)^{-1} \mu_1 \mu_2$. As a consequence, the average must be calculated in weighted form with the aid of an orientation distribution function.

Fig. 2.5 Electric dipole–dipole interaction: The interdipole vector is defined by $\mathbf{r} = \mathbf{R}_1 - \mathbf{R}_2$. The orientation of the dipole moments $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ relative to $\mathbf{r}$ is defined by the angles ϑ_1 and ϑ_2 , respectively. The angle between the planes spanned by the vector pairs $\boldsymbol{\mu}_1, \mathbf{r}$ and $\boldsymbol{\mu}_2, \mathbf{r}$ is designated by φ



The statistical weight for a certain relative orientation of the dipole moments $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ is given by the Boltzmann factor

$$p(\mathbf{r}, \varphi, \vartheta_1, \vartheta_2) = \exp\{-W_{12}(\mathbf{r}, \varphi, \vartheta_1, \vartheta_2)/k_B T\} \quad (2.13)$$

where k_B is Boltzmann's constant and T is the absolute temperature. In the high-temperature limit, $k_B T \gg W_{12}$, Eq. (2.13) can be approximated in first order by

$$\begin{aligned} p(\mathbf{r}, \varphi, \vartheta_1, \vartheta_2) &= 1 - \frac{W_{12}(\mathbf{r}, \varphi, \vartheta_1, \vartheta_2)}{k_B T} + \frac{1}{2!} \left(\frac{W_{12}(\mathbf{r}, \varphi, \vartheta_1, \vartheta_2)}{k_B T} \right)^2 \mp \dots \\ &\approx 1 - \frac{W_{12}(\mathbf{r}, \varphi, \vartheta_1, \vartheta_2)}{k_B T} \end{aligned} \quad (2.14)$$

On this basis, the weighted average of Eqs. (2.11) or (2.12) over the whole ranges of the angles φ , ϑ_1 , and ϑ_2 results in

$$\begin{aligned} \langle W_{12}(\mathbf{r}, \varphi, \vartheta_1, \vartheta_2) \rangle &= \int_{\varphi=0}^{2\pi} \int_{\vartheta_1=0}^{\pi} \int_{\vartheta_2=0}^{\pi} p(\mathbf{r}, \varphi, \vartheta_1, \vartheta_2) W_{12}(\mathbf{r}, \varphi, \vartheta_1, \vartheta_2) d\varphi \sin \vartheta_1 d\vartheta_1 \sin \vartheta_2 d\vartheta_2 \\ &\approx -\frac{1}{4\pi\epsilon_0} \frac{\mu_1 \mu_2}{r^3} \int_{\varphi=0}^{2\pi} \int_{\vartheta_1=0}^{\pi} \int_{\vartheta_2=0}^{\pi} \left(1 + \frac{1}{4\pi\epsilon_0} \frac{\mu_1 \mu_2}{r^3} \frac{1}{k_B T} (2 \cos \vartheta_1 \cos \vartheta_2 - \sin \vartheta_1 \sin \vartheta_2 \cos \varphi) \right) \\ &\quad \times (2 \cos \vartheta_1 \cos \vartheta_2 - \sin \vartheta_1 \sin \vartheta_2 \cos \varphi) d\varphi \sin \vartheta_1 d\vartheta_1 \sin \vartheta_2 d\vartheta_2 \\ &= -\frac{1}{24\pi^2 \epsilon_0^2} \frac{1}{k_B T} \frac{\mu_1^2 \mu_2^2}{r^6} \end{aligned} \quad (2.15)$$

for a given separation r . This expression describes the *Keesom interaction energy* of a single pair of permanent molecular dipoles subject to rotational diffusion in the high-temperature limit. Multiplying it with Avogadro's number gives the interaction energy per mol which is of the order -10 kJ/mol for typical molecules. The sign is negative so that the potential is attractive. The distance law is $\langle W_{12} \rangle \propto r^{-6}$. The attractive force correspondingly obeys $\langle F_{12} \rangle = -d\langle W_{12} \rangle/dr \propto r^{-7}$. This is to be compared with the much slower decays of the purely ionic interactions predicted by Eqs (2.5) and (2.6), respectively. A typical example of polar molecules where Keesom interaction dominates is $\text{HCl} \dots \text{HCl}$, where the permanent dipole moment of a HCl molecule is 3.4×10^{-30} Cm.

2.1.2.2 Interaction “Permanent Dipole”–“Induced Dipole” (Debye Interaction)

If a polar molecule, that is, a permanent dipole with the moment μ_{perm} , interacts with a nonpolar molecule, the electric field of the permanent dipole will induce a dipole moment μ_{ind} in the nonpolar molecule. The induced dipole moment depends linearly on the electric field strength E_{perm} produced by the permanent dipole at the position of the nonpolar molecule:

$$\mu_{\text{ind}} = \alpha E_{\text{perm}} \quad (2.16)$$

α is the polarizability of the nonpolar molecule. In the long-distance limit relative to the permanent-dipole length ℓ_{perm} , that is, $r \gg \ell_{\text{perm}}$, the magnitude of the electric field strength is given by (for definitions, see Fig. 2.6)

$$E_{\text{perm}}(r, \vartheta) \approx \frac{1}{4\pi\epsilon_0} \frac{\mu_{\text{perm}}}{r^3} \sqrt{1 + 3\cos^2\vartheta} \quad (2.17)$$

so that the magnitude of the induced dipole moment reads

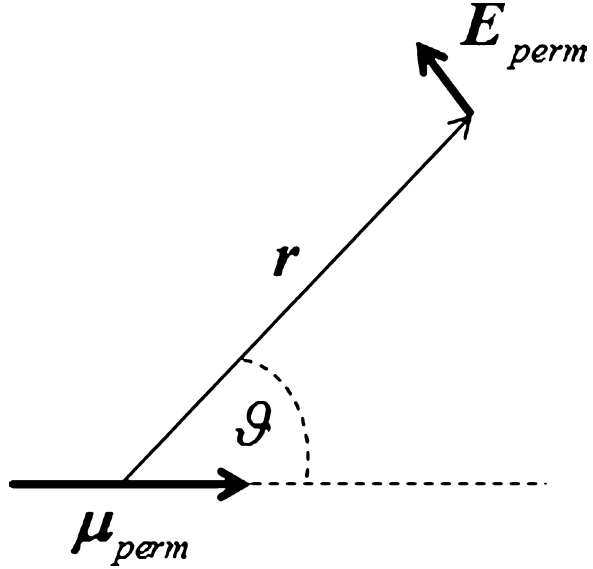
$$\mu_{\text{ind}} = \alpha E_{\text{perm}} \approx \alpha \frac{1}{4\pi\epsilon_0} \frac{\mu_{\text{perm}}}{r^3} \sqrt{1 + 3\cos^2\vartheta} \quad (2.18)$$

According to Eq. (2.16), the local vector directions are parallel to each other, $\mu_{\text{ind}} \parallel E_{\text{perm}}$. The (attractive) electrostatic force acting on the induced dipole at long distances r can consequently be derived as

$$\begin{aligned} \mathbf{F}(\mathbf{r}) &= q_{\text{ind}} \mathbf{E}_{\text{perm}}(\mathbf{r}) - q_{\text{ind}} \mathbf{E}_{\text{perm}}(\mathbf{r} + \ell_{\text{ind}}) \approx q_{\text{ind}} \ell_{\text{ind}} \frac{\partial}{\partial r} E_{\text{perm}}(\mathbf{r}) \\ &= \mu_{\text{ind}}(\mathbf{r}) \frac{\partial}{\partial r} E_{\text{perm}}(\mathbf{r}) \end{aligned} \quad (2.19)$$

where $\mu_{\text{ind}}(\mathbf{r}) = q_{\text{ind}} \ell_{\text{ind}}$ (see the scenario depicted in Fig. 2.7).

Fig. 2.6 Electric field strength of a permanent dipole μ_{perm} in a distance r



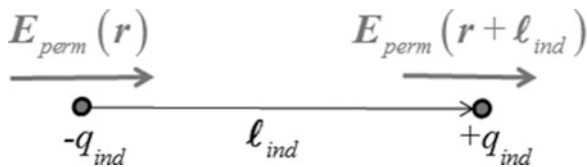
On this basis, the potential energy of the induced dipole in the electric field of the permanent dipole is readily obtained as

$$\begin{aligned}
 W(r, \vartheta) &= - \int_{\infty}^r \mathbf{F}(r') \cdot d\mathbf{r}' \\
 &= - \int_{\infty}^r \mu_{\text{ind}}(r') \frac{\partial}{\partial r'} E_{\text{perm}}(r') dr' \\
 &= - \int_0^{E_{\text{perm}}} \mu_{\text{ind}}(E'_{\text{perm}}) dE'_{\text{perm}} \\
 &= - \alpha \int_0^{E_{\text{perm}}} E'_{\text{perm}} dE'_{\text{perm}} = - \frac{1}{2} \alpha E_{\text{perm}}^2 \quad (2.20)
 \end{aligned}$$

The potential $W(r, \vartheta)$ is the energy gained upon moving the induced dipole from the infinite to the position r , where a radial integration path has been chosen in the above calculation. Inserting Eq. (2.17) gives

$$\begin{aligned}
 W(r, \vartheta) &= - \frac{1}{2} \alpha \left(\frac{\mu_{\text{perm}}}{4\pi\epsilon_0} \frac{1}{r^3} \sqrt{1 + 3\cos^2\vartheta} \right)^2 \\
 &= - \frac{\alpha \mu_{\text{perm}}^2}{32\pi^2 \epsilon_0^2} \frac{1}{r^6} (1 + 3\cos^2\vartheta) \quad (2.21)
 \end{aligned}$$

Fig. 2.7 Induced dipole in the electric field E_{perm} of a permanent dipole in a distance r (see Eq. 2.19)



This expression must now be averaged over all angles ϑ . In particular, using $\langle \cos^2 \vartheta \rangle = 1/3$ results in

$$\langle W(r, \vartheta) \rangle = -\frac{\alpha \mu_{\text{perm}}^2}{32\pi^2 \epsilon_0^2} \frac{1}{r^6} (1 + 3\langle \cos^2 \vartheta \rangle) = -\frac{\alpha \mu_{\text{perm}}^2}{16\pi^2 \epsilon_0^2} \frac{1}{r^6} \quad (2.22)$$

This is the potential of the so-called *Debye interaction*. It is again of an attractive nature, and the distance dependence scales proportional to r^{-6} . The typical order of magnitude is -1 kJ/mol. An example is the interaction between a HCl molecule and a noble gas atom such as Ne. Note that Debye interaction occurs between molecule pairs with permanent dipoles as well, that is, in addition to Keesom interaction.

2.1.2.3 Interaction “Induced Dipole”–“Induced Dipole” (Dispersion² or London Interaction)

This variant of van der Waals interactions is the most general one. It acts in addition to the couplings mentioned before but is particularly important for neutral and nonpolar particles and even applies to noble gases. Actually, the fact that liquid phases of noble gases exist is a manifestation of this sort of interaction. The fundamental origin is due to quantum-electrodynamic fluctuations making nonpolar molecules transiently polar in close analogy to the better known zero-point oscillations of harmonic oscillators. In order to avoid too complicated formalisms, we will try a semiclassical description leading, apart from a numerical factor, to the same analytical result as the more rigorous quantum-electrodynamic treatment.

The interacting particles are assumed to be neutral and their electron clouds be distributed around their nuclei with spherical symmetry bare of any permanent dipole moment. Quantum-electrodynamic fluctuations of the electron cloud break the spherical symmetry so that electric dipole moments (and higher-order multipole moments) arise. As a consequence, the nucleus and the charge center of the electron cloud will be temporarily separated. On the axis of the transient dipole generated in this way, the electric field strength produced by this dipole – let us label it as $\mu_{\text{ind},1}$ – is in the far-field limit:

$$E_1(r) \approx \frac{1}{4\pi\epsilon_0} \frac{2\mu_{\text{ind},1}}{r^3} \quad (2.23)$$

²The term “dispersion” alludes to the fact that this interaction is mainly due to the weakly bound electrons that are responsible for dispersion of light.

In the interaction partner in a distance r , this field in turn induces a dipole moment which we will label by number “2”:

$$\mu_{\text{ind},2} = \alpha E_1(r) \approx \alpha \frac{1}{4\pi\epsilon_0} \frac{2\mu_{\text{ind},1}}{r^3} \quad (2.24)$$

α is the polarizability of the atoms. Vice versa, the same sort of induction effect is produced in particle “1” by the electric field of the induced dipole moment in particle “2.” As a consequence of the induction phenomenon, the two dipole moments are correlated in the sense that they are aligned along the same direction. The interaction energy is accordingly

$$W_{1,2}(r) = -\mu_{\text{ind},2}E_1 = -\alpha E_1^2 = -\left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{4\alpha\mu_{\text{ind},1}^2}{r^6} \quad (2.25)$$

Since the two particles are assumed to be identical, we may omit the subscripts 1 and 2 which have originally been introduced to distinguish the interaction partners.

The dipole moment induced in an atom in this way can be expressed as

$$\mu_{\text{ind}} = q\ell \quad (2.26)$$

where ℓ is the distance between the positive and negative charge centers and q is the charge of the nucleus. The polarizability α of a spherical atom can be estimated from the equilibrium between the magnitude of the internal force $|F_{\text{internal}}| = q^2(4\pi\epsilon_0\ell^2)^{-1}$ due to Coulomb interaction between the respective charges $\pm q$ of the nucleus and the electron cloud, and, on the other hand, the magnitude of the external force $|F_{\text{external}}| = qE_{\text{external}}$ caused by an electric field E_{external} the particle is subjected to

$$\begin{aligned} |F_{\text{external}}| &= |F_{\text{internal}}| \\ qE_{\text{external}} &= \frac{q^2}{4\pi\epsilon_0\ell^2} \\ &= \frac{q}{4\pi\epsilon_0\ell^3} \mu_{\text{ind}} = \frac{q}{4\pi\epsilon_0\ell^3} \alpha E_{\text{external}} \end{aligned} \quad (2.27)$$

Solving this equation for the polarizability α gives

$$\alpha = 4\pi\epsilon_0\ell^3 \quad (2.28)$$

For quantitative estimations, the distance ℓ can roughly be equated with the Bohr radius a_0 of the lowest electron orbital,

$$\ell \approx a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e_0^2} \quad (2.29)$$

where m_e is the electron rest mass and e_0 is the elementary charge.

Combining Eqs. (2.25), (2.26), (2.27), (2.28), and (2.29) finally leads to

$$W(r) \approx -\frac{1}{4} \left(\frac{1}{\pi \epsilon_0} \right)^2 \frac{\alpha q^2 a_0^2}{r^6} \quad (2.30)$$

Analytically, this expression is equivalent to London's exact quantum-mechanical result for the corresponding expectation value [4]. It merely deviates by a different numerical factor. The dispersion interaction energy is thus again negative, that is, attractive, and follows a distance law $\propto r^{-6}$.

The latter statement anticipates that the distance r between the interacting bodies is short enough to neglect retardation effects. Typically, this will be the case for $r \ll 50$ nm. For longer distances, the finite (vacuum) velocity of light, $c_0 \approx 3 \times 10^8$ m/s, must be taken into account. The interaction is communicated between the interacting dipoles via photons, the elementary quanta of electromagnetic radiation. The time a photon takes to travel a distance of, say, 100 nm from particle "1" to particle "2" is $t = 10^{-7} \text{ m} / c_0 \approx 3 \times 10^{-16}$ s. On the other hand, this is the time scale of the fluctuations of electron clouds. That is, at the time when the photon response of the induced dipole μ_2 comes back, the original dipole moment may have changed already, so that $\mu_1(t) \neq \mu_1(0)$. The consequence of this loss of correlation of the fluctuating dipoles is a weakening of the interaction resulting in a stronger distance dependence of the dispersion interaction energy more realistically given by

$$W(r) \propto r^{-7} \quad (2.31)$$

The retardation effect specifically concerns London interaction, but is irrelevant for the other types of van der Waals attractions.

2.1.3 Repulsive Interaction and Total Potential

When the interacting molecules approach each other so that the electron orbitals start to overlap more and more, repulsive interactions come into play and will dominate at the end. Apart from Coulomb repulsion of the electron clouds, the reason can be traced back to the Pauli exclusion principle. Electron orbital states are characterized by sets of certain quantum numbers specifying atomic shells, orbital angular momentum, and spin states. Overlap of electron clouds means that electrons being in identical states in the same space region interfere. Since this is quantum mechanically not permitted, at least one of the overlapping electron orbitals is forced to adopt a higher-energy state that is not yet occupied. As a consequence, the potential energy is steeply raised upon squeezing molecules together.

At long distances, orbital wave functions tend to decay exponentially. The repulsive interaction energy may therefore be approached by

$$W_{\text{rep}}(r) = C \exp\left\{-\frac{r}{a}\right\} \quad (2.32)$$

where C is a (positive) constant and a characterizes the extension of the orbital. This is the so-called *Born repulsive interaction*. Usually this expression is approached by the power law:

$$W_{\text{rep}}(r) = 4\varepsilon \left(\frac{r_0}{r}\right)^{12} \quad (2.33)$$

where ε is the binding energy. Combining $W_{\text{rep}}(r)$ with the respective van der Waals attractive potentials given in Eqs. (2.15) (*Keesom*), (2.22) (*Debye*), and (2.30) (*London*) leads to the Lennard/Jones (or shortly 12/6) potential given already in Eq. (2.1):

$$W(r) = 4\varepsilon \left\{ \left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6 \right\} \quad (2.34)$$

A graphical representation is shown in Fig. 2.2.

2.1.4 Hydrogen Bonds

Hydrogen bonds are predominantly electrostatic in nature but retain some elements of covalent bonding. This sort of interaction refers to pairs of electronegative atoms. The pairs consist of the *donor* X and the *acceptor* Y, with a hydrogen atom in between. The mean distance of the hydrogen atom from the donor is shorter than the mean separation to the acceptor. This is formally represented by the scheme $\text{XH} \cdots \text{Y}$. The interaction can be of an intra- or an intermolecular nature, and it is fairly directional. Typical donor and acceptor atoms are N, O, and F. The binding energy ranges from 5 to 30 kJ/mol, that is an order of magnitude less than the energy of ordinary covalent bonds, but an order of magnitude larger than that of van der Waals interactions. Important examples for hydrogen bonds are $\text{OH} \cdots \text{O}$ in water and $\text{NH} \cdots \text{O}$ in proteins as intermolecular and intramolecular variants, respectively. The former example is responsible for the peculiar properties of water (and ice) and the latter for the secondary structure of proteins. The origin of hydrogen bonds cannot be traced back to a single principle. Straightforward analytical treatments are hardly feasible. Disregarding the importance for soft-matter structure and dynamics especially in bio-systems, we therefore refrain from any attempt of explicit derivations. Empirically, the attractive part of the interaction potential of hydrogen bonds scales with the donor–acceptor distance roughly as $\propto -r^{-2}$. For more detailed information, the reader is referred to Ref. [5].

As concerns the binding energy of hydrogen bonds, the following remark appears to be appropriate for soft-matter applications: The order of magnitude

given above refers to the gaseous state. In most cases of interest here, and this does not only refer to biological systems, we are dealing with condensed phases in *aqueous* environments. That is, the dissociation of a hydrogen bond between intra- or intermolecular solute groups will be accompanied by the instantaneous formation of a follow-up hydrogen bond to an adjacent water molecule. The *effective* dissociation energy, that is, the difference between the respective binding energies, is therefore much less than the nominal binding energy of a solute acceptor–donor pair. This is a crucial prerequisite for the relatively high reaction rates of hydrogen-controlled processes in biopolymers.

2.1.5 *Hydrophobic Interaction as an Entropic Force*

Strictly speaking, the so-called hydrophobic interaction is not a self-contained coupling mechanism. In a sense, it is the negation of hydrogen bonding between solute and solvent molecules. It refers to nonpolar solutes such as hydrocarbon chains in water. Hydrophobic species are not able to form hydrogen bonds, so that it is thermodynamically more favorable if they associate with each other rather than with water.

At first sight, one might suspect that this segregation is the direct consequence of the reduction of the number of hydrogen bonds among water molecules due to the presence of the nonpolar solute molecules. However, the effect is primarily not of an enthalpic nature. Rather, the fluctuating hydrogen bond network around the solute molecules is rearranged in such a way that the solute molecules will be encaged by solvation shells in which hydrogen bonds tend to be directed tangentially to the solute molecules, while the number of hydrogen bonds in the water is more or less maintained. The formation of solvation shells of this sort is accompanied by a loss of mobility of the water molecules in the shells. This in turn reduces entropy and is therefore thermodynamically unfavorable. Maximum entropy is thus reached by aggregation of the hydrophobic species keeping the formation of aqueous solvation shells at a minimum: The hydrophobic effect is predominantly of an *entropic* nature.

The most obvious phenomena following from the hydrophobic effect are the structures formed by amphiphilic molecules in aqueous environments. Amphiphilic molecules consist of hydrophobic and hydrophilic moieties. As a consequence, they are arranged in such a way that the hydrophilic groups are exposed to water and “screen” in this way the hydrophobic parts. Examples are micelles, vesicles, lipid bilayers, and other self-association phenomena. A detailed treatise on hydrophobic-interaction phenomena can be found in Ref. [6].

The hydrophobic effect may also interfere with cooperative transitions such as the helix–coil transition of polypeptides in solution. In the α -helix conformation, the configurational entropy of the polypeptide chain is much lower than in the random-coil conformation. On the other hand, the random-coil conformation exposes nonpolar polypeptide groups to the (polar) solvent in contrast to α -helices.

The hydrophobic effect is therefore increased. Whether the helix or the random-coil conformation prevails is then a question of whether the *increase* by conformational degrees of freedom is outbalanced by the *decrease* of entropy by the hydrophobic effect or not [7].

2.1.6 From Molecular to Interfacial (“Casimir”) Interactions

Emulsions, colloid dispersions, porous media, liquid crystal domains, and even micro-electromechanical systems (MEMS) are examples for heterogeneous structures where mesoscopic objects of a dimension from nanometers up to many micrometers perceptibly exert forces on each other. Hydrophobic interaction discussed in the previous section is already a first case where such coarse-grained aggregates and molecular ensembles play a role. Instead of particle interactions, one speaks of forces on or between surfaces and interfaces. The topology of such surfaces is often modeled by simple geometric objects such as planes, spheres, and cylinders [1, 2].

The principles of intermolecular interactions discussed above are again valid. That is, forces among supramolecular objects are of an electrodynamic nature and refer to electric multipoles. As mentioned above, London interaction is the consequence of quantum-electrodynamic fluctuations. There is a connatural phenomenon known as the *Casimir effect* [8] which is again due to quantum-electrodynamic fluctuations, namely, those of vacuum. Since it is related in this sense to van der Waals interaction, it is often quoted in the literature as a possibility to demonstrate quantum-electrodynamic-fluctuation effects with objects that can be handled macroscopically.³

In 1948, Casimir predicted an attractive force between two perfectly conducting metal plates, that is, perfect mirrors, facing each other in vacuum. The lateral extension of the plates was assumed to be large relative to the separation. This attractive Casimir force can be explained in the following way. Heisenberg’s uncertainty principle in the energy/time version tells us that vacuum energy can adopt values ΔW in transient time intervals Δt according to

$$\Delta W \Delta t \geq \frac{\hbar}{2} \quad (2.35)$$

³In this context, it should be mentioned that there is a certain analogy to forces based on fluctuations of a *non*-quantum-electrodynamic nature: The *critical Casimir force* between colloid particles and surfaces is the result of concentration fluctuations at the critical point of fluid mixtures [9]. At the critical point, the correlation length of such fluctuations diverges. Depending on the chemical nature of the confining surfaces, the forces can be attractive or repulsive.

where $\hbar$ is Planck's constant h divided by 2π . In vacuum, the fluctuation energy ΔW manifests itself in the form of electromagnetic radiation quanta or photons:

$$\Delta W = h\nu = \frac{hc_0}{\lambda} \quad (2.36)$$

where ν , λ , and c_0 are the frequency, the wavelength, and the light velocity, respectively. The shorter the lifetime Δt of the photons is, the larger the energy ΔW can be in full accordance with the conservation law of energy. The mean energy of vacuum fluctuations corresponds to half the photon energy at the respective frequency.

In free space, there is no limitation of the wavelength. However, steady waves propagating perpendicular to the plates can only exist between the metal plate state if integer multiples of half of their wavelength match the plate distance. One speaks of electromagnetic *modes* of the resonator formed by the two mirrors. Photons fulfilling this condition can form standing waves, whereas all other wavelengths cancel. The argument is not unlike Planck's well-known treatment of black-body radiation. The consequence of this restriction is that merely a selection of photons complying with the wavelength condition can exist between the plates while there is no such restriction in the outside space.

Remember now that photons carry a momentum $p = h/\lambda$, so that perpendicular reflection of photons at the plates is connected with a momentum transfer of $2h/\lambda$. The mean force acting on a plate from one side is given by the number of photons reflected per unit time times the momentum transfer of a single impact. Since the plates are hit by more photons from outside than from inside, there will be a net force attracting the plates. This is the Casimir force.⁴ It is closely related to the London dispersion force among molecules.

The relative selectivity of modes permitted to exist between the mirrors increases with decreasing plate spacing d . The consequence is that the Casimir force scales as $F \propto Ad^{-4}$ where A is the surface area of the plates. It is therefore not surprising that the experimental demonstration of the Casimir experiment succeeded only with plate separations as low as micrometers.

The setup of parallel metal plates in vacuum as originally proposed is not the sort of system one expects to be relevant in heterogeneously structured soft matter. A first generalization to continuous dielectric media was established later by Lifshitz [10]. On this basis, expressions can be derived for the forces acting between dielectric objects of arbitrary, but well-defined geometries immersed in dielectric media.

⁴ An analogous and illustrative wave phenomenon is the following example familiar to everybody: A piece of timber floating in harbor water apparently tends to "stick" to the quay wall. It is literally "attracted" because water waves steadily existing between wall and timber are restricted with respect to the wavelength. The nature and origin of the waves are totally different in this case, of course.

The problem of any such analysis is that van der Waals forces from surface molecule to surface molecule are not additive. Mere summation over all molecular pairs between the two objects would therefore be misleading. Rigorously, triple and multiparticle interactions would have to be taken into account as well [11]. This intricacy is avoided by Lifshitz's continuum treatment which is based on material parameters such as the relative dielectric permittivity ϵ_r and the relative magnetic permeability μ_r .

In the present context, the following coarse-grained approach may be useful and instructive although it is of a more qualitative nature. The interaction of neutral mesoscopic objects is estimated as the sum of van der Waals interactions between all pairs of volume elements of the objects. Since the volume elements are assumed to be much larger than molecules, the nonadditivity is more or less implicitly taken into account in the volume element – volume element interaction via a constant and unspecified factor C .

In the treatment of London dispersion forces, retardation effects due to the finite phase velocity of electromagnetic radiation should furthermore be considered as mentioned above. The consequence of such effects is a tendency toward a stronger distance dependence of the interaction energy. However, retardation can be neglected if we restrict our derivation to distances short relative to the extension of the interacting objects. For more elaborate theories, the reader is referred to Refs. [1, 2].

2.1.6.1 Particle–Wall Interaction

The most important issue in the context of interacting mesoscopic objects is the *reduction* of the distance dependence relative to the London interaction of molecular dipoles (Eq. 2.30). As a first example, let us consider a small, practically pointlike particle attracted by a planar, infinitely extended surface of an infinitely thick wall, that is, a *half space*. A practical example approaching this scenario is the force acting on the tiny tip of an atomic force microscope close to the surface of a planar sample.

The dimension of the particle is assumed to be negligible relative to the particle–surface distance. The attractive potential between the particle and a volume element dV of the wall in a distance R is given by the van der Waals relationship:

$$dW = -C \frac{\rho}{R^6} dV \quad (2.37)$$

where C is an unspecified positive constant and ρ is the mass density of the wall material. The distance of the particle from the wall surface be z_0 . Integration over the whole wall volume can be performed by integrating over infinitesimal circular rings of radius r , radial thickness dr , and vertical thickness dz as illustrated in

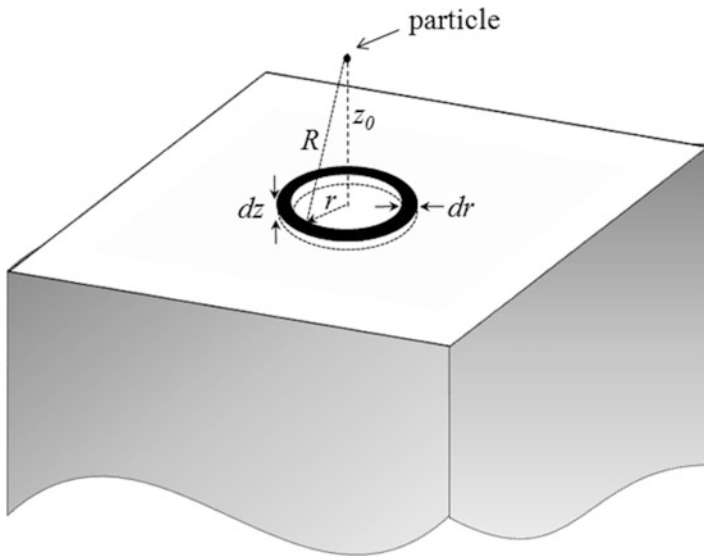


Fig. 2.8 Definition of the quantities needed for the treatment of the interaction between a small particle and a planar wall. The half-space wall is assumed to be “infinitely” thick and “infinitely” extended in lateral direction

Fig. 2.8. Taking such infinitesimal rings as volume elements $dV = 2\pi r dr dz$ and using the relation $R^2 = r^2 + z^2$ lead to the total attractive potential:

$$W = -2\pi C\rho \int_{z_0}^{\infty} dz \int_0^{\infty} dr \frac{r}{(r^2 + z^2)^3} = -\frac{1}{2}\pi C\rho \int_{z_0}^{\infty} dz z^{-4} = -\frac{1}{6}\pi C\rho \frac{1}{z_0^3} \quad (2.38)$$

Remarkably, the distance dependence thus turns out to be $\propto z_0^{-3}$ in contrast to the sixth power characteristic for the law in Eq. (2.37). That is, the range of influence of the potential Eq. (2.38) is extended over much longer distances. Accordingly, the attractive force obeys

$$F = -\frac{\partial W}{\partial z_0} = -\frac{1}{2}\pi C\rho \frac{1}{z_0^4} \quad (2.39)$$

If the size of the particle is no longer negligible relative to z_0 and if it exceeds molecular dimensions by far (as it is the case with colloid particles, for instance), we must additionally integrate over the particle volume. Assuming a sphere of radius $R_p \gg z_0$, where z_0 is defined as the distance between the particle-center and the wall-surface, we find

$$W = -\frac{1}{6}\pi^2 C R_p \rho_p \rho_w \frac{1}{z_0} = -\frac{1}{6} R_p A_{\text{Ham}} \frac{1}{z_0} \quad (R_p \gg z_0) \quad (2.40)$$

where ρ_p and ρ_w are the densities of the particle and wall materials, respectively. The quantities C and A_{Ham} are constants. The latter, the so-called *Hamaker constant*, is typically of the order 10^{-19} J. It is characteristic for the materials of the interacting objects. We note that the distance dependence predicted by Eq. (2.40), $W \propto z_0^{-1}$, is again reduced relative to the laws in Eqs. (2.37) and (2.38). This underlines the long-range character of van-der-Waals-based interactions between mesoscopic objects. The attraction force is

$$F = -\frac{\partial}{\partial z_0} W = -\frac{1}{6} R_p A_{\text{Ham}} \frac{1}{z_0^2} \quad (R_p \gg z_0) \quad (2.41)$$

A spectacular demonstration of the efficiency of van-der-Waals-based forces on mesoscopic length scales is the ability of geckos to walk along ceilings even if the surface is absolutely smooth. Gecko toes are covered with a tuft of hair providing contact to the surface close enough for sufficiently strong attraction forces. The total force by which a gecko is attracted to a surface can be about 250 N depending on the relative dielectric permittivity of the surface material. Another animal species taking advantage of van der Waals enforced grip are spiders. A third example where van der Waals forces matter in biology is the well-known cylindrical stacks of erythrocytes. Although being negatively charged, erythrocytes attract each other on the basis of van der Waals interactions. In the literature, these phenomena are often somewhat vaguely referred to as special cases of the Casimir interaction.

2.1.6.2 Interaction Between Spheres

As a further scenario possibly relevant in the soft-matter field, let us consider the van-der-Waals-based interaction between two solid spheres of radii R_1 and R_2 , mass densities ρ_1 and ρ_2 , and a center-to-center distance z_0 (Fig. 2.9). The spheres can be considered to model colloid particles or lipid vesicles in liquid dispersions, for instance. Integration analogous to the procedure described above leads to the attractive potential

$$W = -\frac{1}{6} \pi^2 C \rho_1 \rho_2 \frac{R_1 R_2}{R_1 + R_2} \frac{1}{z_0} = -\frac{1}{6} A_{\text{Ham}} \frac{R_1 R_2}{R_1 + R_2} \frac{1}{z_0} \quad (R_1, R_2 \gg z_0) \quad (2.42)$$

and the attraction force

$$F = -\frac{\partial}{\partial z_0} W = -\frac{1}{6} A_{\text{Ham}} \frac{R_1 R_2}{R_1 + R_2} \frac{1}{z_0^2} \quad (R_1, R_2 \gg z_0) \quad (2.43)$$

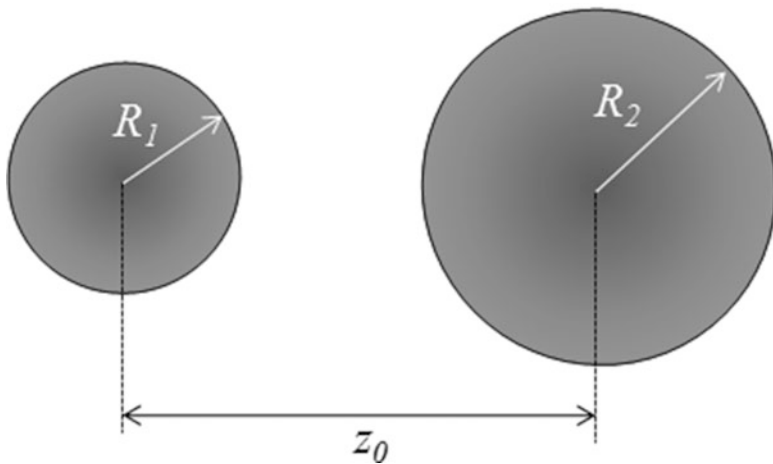


Fig. 2.9 Interaction between two solid spheres of densities ρ_1 and ρ_2 and radii R_1 and R_2 in a distance z_0

2.1.6.3 Interaction Between Parallel Lamellae

Finally, the van der Waals interaction energy per unit area, W/A , between two parallel and infinitely extended slabs or lamellae of thickness a in a spacing z_0 is found to be

$$\frac{W}{A} = -\frac{1}{12\pi} A_{\text{Ham}} \left(\frac{1}{z_0^2} - \frac{2}{(z_0 + a)^2} + \frac{1}{(z_0 + 2a)^2} \right) \quad (2.44)$$

The (attractive) force per unit area is given by

$$\frac{F}{A} = -\frac{\partial W/A}{\partial z_0} = \frac{1}{6\pi} A_{\text{Ham}} \left(\frac{1}{z_0^3} - \frac{2}{(z_0 + a)^3} + \frac{1}{(z_0 + 2a)^3} \right) \quad (2.45)$$

Practical examples where the two-slab scenario is expected to be relevant are smectic aggregates of mesogenic molecules and stacked lipid bilayers as illustrated in Fig. 2.10. The repulsive interactions counteracting this attractive force are due to surface charges and/or to increasing overlap of electronic orbitals. The nature of the latter effect is the same as outlined in Sect. 2.1.3.

2.1.7 Depletion Forces

Typical systems where depletion forces can arise are emulsified droplets and colloids suspended in a solvent or in non-adsorbing polymers. In all cases, the system consists of a dispersion of particles of substantially deviating size. A schematic illustration is depicted in Fig. 2.11a. A few large particles are dispersed

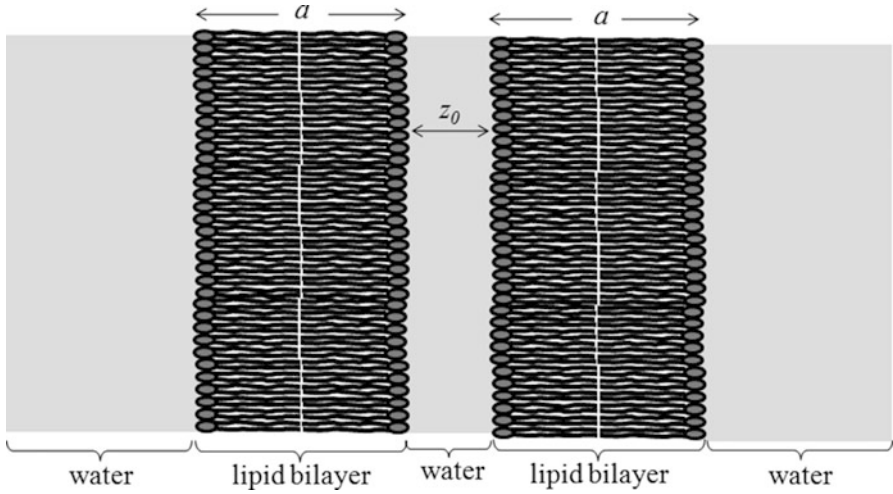


Fig. 2.10 Schematic representation of lipid bilayers as an example that approaches the scenario underlying Eqs. (2.44) and (2.45). Note that the surfaces of such associations of amphiphilic molecules are charged. The repulsive forces arising on these grounds will be discussed in Sect. 2.1.8

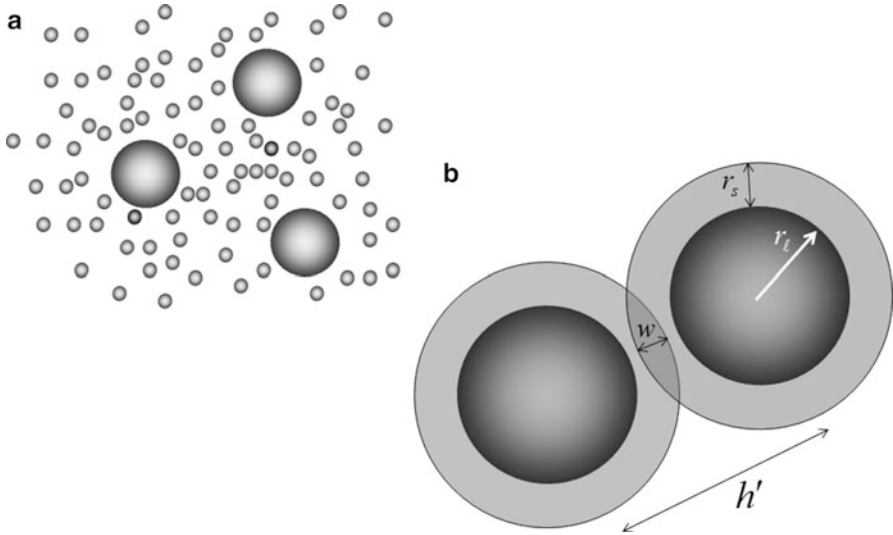


Fig. 2.11 (a) Schematic illustration of a system giving rise to depletion forces. It consists of a mixture of small and large particles with radii r_s and r_l , respectively. (b) A shell of thickness r_s around the large particles is inaccessible to the centers of the small particles and forms a volume excluded for the small particles. If two such *depletion zones* overlap, the excluded volume will be reduced by a lens-shaped volume of width w . The distance of the centers of the large particles is denoted by h'

in a medium consisting of relatively small molecules. In the case of colloids or emulsified droplets, “large” refers to the mesoscopic length scale. It is then a matter of statistical physics that the mere presence of small particles effectively produces an attractive force between the large particles even in cases where the large particles do not interact directly with other particles, neither with each other nor with the small particles [12].

The basis of depletion forces is the dependence of the Helmholtz free energy of the small particles on the mutual distance h' of the large particles, $A_H = A_H(h')$. Provided a relationship of this sort exists, a force

$$F = - \left(\frac{\partial A_H}{\partial h'} \right)_T \quad (2.46)$$

among the large particles is expected. The subscript on the right-hand side of Eq. (2.46) indicates that isothermal conditions are anticipated. The force will be attractive if $A_H(h')$ increases with the separation h' of the large particles and repulsive in the opposite case. The problem is now to examine the potential relationship $A_H = A_H(h')$.

The statistical nature of depletion forces can be explained on the basis of the scheme shown in Fig. 2.11b. The large particles are assumed to be spherical with a diameter $d_\ell = 2r_\ell$. They are considered to be diluted in a solvent consisting of $N_s \gg N_\ell$ small spherical particles with diameters $d_s = 2r_s$. Let us now consider a volume V containing a large number N_s of small particles but only $N_\ell = 2$ large particles. Due to the presence of the large particles, the volume available for the centers of the small particles is reduced according to

$$V_{\text{avail}} = V - V_{\text{ex}} \quad (2.47)$$

where V_{ex} is the excluded volume.

The large particles are surrounded by so-called *depletion zones*, that is, spherical shells of thickness r_s . The depletion zones are defined by the nearest distance the centers of the small particle can approach the surface of the large particles. If the depletion zones do not overlap, that is, if the distance between the two large particles obeys $h' \geq d_\ell + d_s$, the excluded volume will be $V_{\text{ex}} = \pi(d_\ell + d_s)^3/3$. This is twice the spherical volume of a large particle including its depletion zone.

On the other hand, if the two large particles approach each other so that their depletion zones start to overlap, as it will be the case for distances $d_\ell < h' < d_\ell + d_s$, the excluded volume will be reduced. The volume V_{avail} available for the small particles will therefore *increase* by the volume formed by the overlap “lens” of width w (see Fig. 2.11b). In the following, the argument will be that an increase of the available volume is accompanied by an increase of entropy, which is thermodynamically more favorable. The consequence will be an attractive force between the large particles.

The volume of the overlap lens between the two large particles can be calculated with the aid of the known formula as twice the volume of spherical calottes of height $w/2$:

$$V_{\text{lens}} = \frac{\pi w^2}{12} [3(d_\ell + d_s) - w] = \frac{\pi}{12} (d_\ell + d_s - h')^2 (2d_\ell + 2d_s + h') \quad (2.48)$$

where $w = d_\ell + d_s - h'$. In the case of overlapping depletion zones, the excluded volume will consequently be reduced by the lens volume $V_{\text{ex}} = \pi(d_\ell + d_s)^3/3 - V_{\text{lens}}$. In summary, the respective volumes excluded for the centers of the small particles can thus be represented by

$$V_{\text{ex}}(h') = \begin{cases} \frac{\pi}{3} (d_\ell + d_s)^3 & \text{for } h' \geq d_\ell + d_s \\ \frac{\pi}{3} (d_\ell + d_s)^3 - \frac{\pi}{12} (d_\ell + d_s - h')^2 (2d_\ell + 2d_s + h') & \text{for } d_\ell < h' < d_\ell + d_s \end{cases} \quad (2.49)$$

for the non-overlap and overlap cases.

For simplicity, let us now assume ideal conditions in the sense that merely hard-core interactions among the small particles as well as between small and large particles exist. The only attractive force that can arise under such conditions is then the depletion force Eq. (2.46) between the large particles. The point is that the Helmholtz free energy of the small particles varies as a consequence of the presence of the large particles. Since there is no direct interaction energy among the particles, the variation of the Helmholtz free energy is exclusively of an entropic nature. The entropy $S = S(h')$ can be calculated on the basis of Boltzmann's famous entropy formula. Referring to the ratio of the available volume and the total volume, the Helmholtz free energy can be determined analogously to the known formalism for ideal gases according to

$$\begin{aligned} A_H(h') &= -N_s T S(h') = -N_s k_B T \ln \frac{V_{\text{avail}}(h')}{V} \\ &= -N_s k_B T \ln \left(1 - \frac{V_{\text{ex}}(h')}{V} \right) \approx N_s k_B T \frac{V_{\text{ex}}(h')}{V} \end{aligned} \quad (2.50)$$

where k_B is Boltzmann's constant. Here, we have approximated the logarithm linearly, which is justified in view of $V \gg V_{\text{ex}}$.

Finally, inserting Eq. (2.49) gives the desired relationship between the Helmholtz free energy and the distance of the large particles. Since the excluded volume $V_{\text{ex}}(h')$ decreases with the distance h' as long as $d_\ell < h' < d_\ell + d_s$, the Helmholtz free energy will decrease as well. That is, an attractive force

$$F(h') = - \left(\frac{\partial A_H}{\partial h'} \right)_T \approx - \frac{\pi n_s k_B T}{4} [(d_\ell + d_s)^2 - h'^2] \quad (2.51)$$

among the large particles is predicted from Eq. (2.46) in this particular distance range, while the force vanishes for larger distances. The quantity $n_s = N_s/V$ is the mean number density of small particles in the system.

The attractive character of this force leads to numerous phenomena relevant in praxis. One of these is the so-called depletion flocculation of emulsions as discussed in Refs. [13, 14], for instance. Due to depletion forces, there will be a general aggregation tendency of large particles suspended in low-molecular solvents. This tendency will be increased by further interactions which potentially play an additional role in real systems [15].

2.1.8 Charged Surfaces and the Electric Double Layer

Whenever phases of different polar media form an interface, some charge separation will take place. This in particular refers to solid or solid-like surfaces of polar materials exposed to water or aqueous electrolyte solutions [16, 17]. Examples are colloid particles and the walls of porous media surrounded by water. The polarity of the surface charges depends on the nature of the constituents of the system. The main reasons for this phenomenon are (1) preferential adsorption of one ion species due to different chemical affinity and (2) the dissociative ionization of surface groups. Examples for the latter case are acidic groups such as $-\text{COOH} \rightarrow \text{COO}^- + \text{H}^+$ and basic groups such as $-\text{OH} \rightarrow \oplus + \text{OH}^-$, producing negatively and positively charged surfaces, respectively. Surface charges are particularly strong in electrolyte solutions since then both mechanisms are effective. The surface charges will be balanced by counterions attracted (together with their solvation shells) by the charged surface as schematically illustrated in Fig. 2.12.

Charged colloid particles are subject to van der Waals attractions in the same way as neutral molecules. In addition, Coulomb interactions are superimposed as a consequence of the net charges. In the simplest case, that is, two-point charges, the Coulomb coupling is described by Eqs. (2.5) and (2.6). The situation of charged colloid particles dispersed in an electrolyte solution is more complicated. There are always sufficient counterions screening the charge of the colloid particle. It is therefore favorable to solve problems of this sort by assuming continuum conditions for the charge distribution.

Ions in electrolyte solutions are freely movable and will therefore be distributed near charged surfaces according to thermal equilibrium criteria. The consequence is the formation of the so-called *electric double layer* as illustrated in Figs. 2.12 and 2.13. The double layer consists of the charged surface, the *compact (or Stern) layer* of immobilized counterions, and the *diffuse layer* of mobile counterions. In order to balance the charged surface, the counterions outnumber the co-ions in the compact and diffuse layers so that a net charge exists in these areas. The joint face of the two layers is termed the *shear (or outer Helmholtz) plane*. The electrostatic potential $\Phi(\mathbf{r})$ at the shear plane is the so-called *zeta potential*, $\Phi(0) = \zeta$. The thickness of the

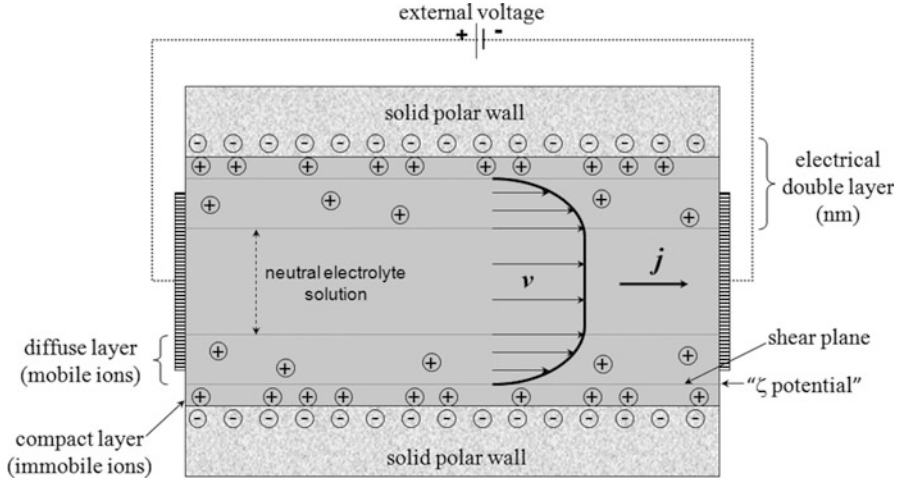


Fig. 2.12 Schematic cross section through a cylindrical pore filled with an electrolyte solution as an illustration of the *electric double layer*. Negatively charged surfaces are assumed. The positive charge carriers are the excess counterions balancing the negative surface charges. The thickness of the *compact layer* is determined by the counterions together with the hydration shells of the wall and the surface. If a potential difference is applied to (permeable) electrodes on both sides of the channel, an ionic current will arise with the current density j . The consequence will be *electro-osmotic flow* with the peculiar velocity distribution $v = v(r)$ schematically represented by a “plug-like” profile. Details of electroosmotic flow will be discussed in Sect. 4.9.5

diffuse layer and the concentration of excess counterions in it depend on the temperature according to a Boltzmann equilibrium distribution.

The spatial distribution of the electrostatic potential $\Phi(r)$ in the diffuse layer can be calculated by solving Poisson's equation

$$\nabla^2 \Phi = -\frac{1}{\epsilon_0 \epsilon_r} \rho_c \quad (2.52)$$

with the boundary conditions $\Phi(\infty) = 0$ infinitely away from the surface and $\Phi(0) = \zeta$ at the shear plane. ϵ_r is the relative dielectric permittivity of the electrolyte solution, and ϵ_0 is the electric field constant. The charge density ρ_c is distributed in the diffuse layer according to a Boltzmann factor as a function of the electrostatic potential:

$$\rho_c = e \sum_i n_{i0} z_i \exp \left\{ -\frac{z_i e \Phi}{k_B T} \right\} \quad (2.53)$$

e is the positive elementary charge; n_{i0} and z_i are the bulk number density and the valence of the i -th ionic species, respectively; k_B is Boltzmann's constant; and T is the absolute temperature.

Inserting Eqs. (2.53) into (2.52) gives the nonlinear *Poisson/Boltzmann equation*

$$\nabla^2 \Phi(\mathbf{r}) = -\frac{1}{\varepsilon_r \varepsilon_0} e \sum_i n_{i0} z_i \exp\left\{-\frac{z_i e \Phi(\mathbf{r})}{k_B T}\right\} \quad (2.54)$$

It can be linearized in the *Debye/Hückel* or *high-temperature approximation* for $|z_i e \Phi| \ll k_B T$ as

$$\nabla^2 \Phi(\mathbf{r}) \approx -\frac{1}{\varepsilon_r \varepsilon_0} e \sum_i n_{i0} z_i \left(1 - \frac{z_i e \Phi(\mathbf{r})}{k_B T}\right) \quad (2.55)$$

In this way, analytical solutions become feasible for simple surface geometries. Furthermore, assuming a single pair of symmetrical ionic species simplifies Eq. (2.55) to

$$\nabla^2 \Phi(\mathbf{r}) \approx \frac{2e^2 n_0 z^2}{\varepsilon_r \varepsilon_0} \frac{1}{k_B T} \Phi(\mathbf{r}) = k^2 \Phi(\mathbf{r}) \quad (2.56)$$

where

$$k^2 = \frac{2z^2 e^2 n_0}{\varepsilon_r \varepsilon_0 k_B T} \quad (2.57)$$

is the *Debye/Hückel parameter*. n_0 is the bulk number density of the counterions (or co-ions), and $\pm z$ represents their valences.

2.1.8.1 Uniformly Charged Plane

The electrostatic potential in the diffuse layer of a uniformly charged plane, that is, the one-dimensional problem depicted in Fig. 2.13a, can be calculated with the aid of the one-dimensional version of Eq. (2.56):

$$\frac{\partial^2}{\partial x^2} \Phi(x) = k^2 \Phi(x) \quad (2.58)$$

The x -axis is defined perpendicular to the surface with the origin at the shear plane. The solution is

$$\Phi(x) = \zeta \exp\{-kx\} \quad (2.59)$$

Starting with the ζ potential at the shear plane, that is, $\Phi(0) = \zeta$, the electrostatic potential decays exponentially in the diffuse layer. The mean width of the diffuse

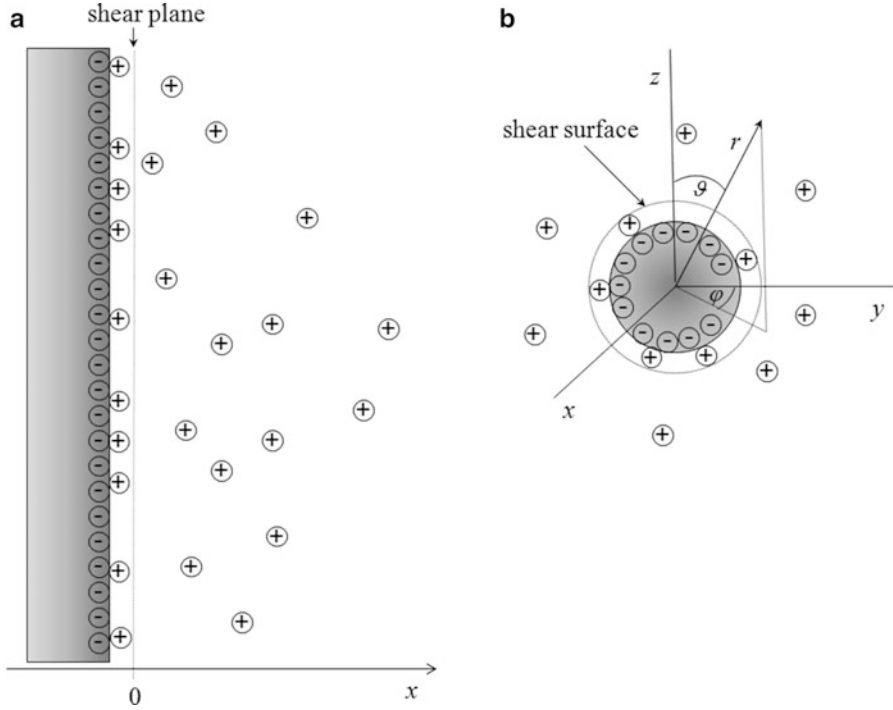


Fig. 2.13 Double layers around (a) a charged plane and (b) a charged sphere

layer in terms of the distance from the shear plane weighted with the electrostatic potential is thus

$$\bar{x} = \frac{\int_0^\infty x' \Phi(x') dx'}{\int_0^\infty \Phi(x') dx'} = \frac{1}{k} \quad (2.60)$$

$\bar{x}$ is also called the *Debye (screening) length*. According to the Debye/Hückel parameter in Eq. (2.57), it decreases with the inverse square root of the bulk number density n_0 of the ions and increases with the square root of the absolute temperature T . Typically, the mean width ranges from a few nanometers in concentrated electrolyte solutions to micrometers in pure water. The distribution of the excess charge density in the diffuse layer can be calculated with the aid of Eq. (2.53) using the Debye/Hückel high-temperature approximation, $|z_i e \Phi| \ll k_B T$, and assuming a single pair of symmetric ionic species again:

$$\rho_c(x) = e \sum_i n_{i0} z_i \exp \left\{ -\frac{z_i e \Phi(x)}{k_B T} \right\} \approx \frac{2e^2 n_0 z^2}{k_B T} \Phi(x) \quad (2.61)$$

With the electrostatic potential given in Eq. (2.59), the charge density becomes

$$\rho_c(x) = \frac{2e^2 n_0 z^2 \zeta}{k_B T} \exp\{-kx\} \quad (2.62)$$

That is, the charge density of the excess counterions decays exponentially in the diffuse layer in the same way as the electrostatic potential does.

2.1.8.2 Uniformly Charged Surface of a Sphere

We now turn to the situation depicted in Fig. 2.13b. The electrostatic potential in the diffuse layer around the uniformly charged surface of a sphere can be calculated analogously to the case of a charged plane by expressing the Poisson/Boltzmann equation in polar coordinates, namely, the azimuth angle φ , the polar angle ϑ , and the radial distance r from the sphere center as defined in Fig. 2.13b. In terms of these coordinates, the Laplace operator reads (see, e.g., [18])

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{1}{r^2 \sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} \quad (2.63)$$

Because of the spherical symmetry of the present problem, all derivatives with respect to the angles vanish, so that the operator is reduced to the radial form:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) = \frac{2}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} \quad (2.64)$$

Combining Eqs. (2.56) and (2.64) gives

$$\frac{2}{r} \frac{\partial \Phi}{\partial r} + \frac{\partial^2 \Phi}{\partial r^2} = k^2 \Phi \quad (2.65)$$

with the boundary conditions $\Phi(r \rightarrow \infty) = 0$ and $\Phi(r = R_{\text{shear}}) = \zeta$. The radius of the shear surface is denoted by R_{shear} . The solution of Eq. (2.65) is

$$\Phi(r) = \zeta \frac{R_{\text{shear}}}{r} \exp\{-k(r - R_{\text{shear}})\} \quad (2.66)$$

As concerns the attractive part, the interaction of two- or more-charged colloid particles is again governed by van der Waals dispersion forces. On the other hand, if charged colloid particles approach each other, the diffuse layers ultimately start to overlap more and more. The consequence is that the counterion clouds repel each other due to Coulomb forces with the tendency to recombine the counterions with the co-ions on the surfaces. This in turn reduces the configurational entropy of the

diffuse layers, so that a repulsive “osmotic force” arises. It may shortly be addressed as *double-layer interaction*. A detailed analysis of this phenomenon with respect to the distance dependence can be found in Ref. [1].

In total, the interaction of charged colloid particles or surfaces is determined by the superposition of attractive van der Waals dispersion and repulsive double-layer interactions. At long distances relative to the Debye length, the attractive and repulsive forces can balance each other. However, when the charged surfaces of colloid particles approach each other, the attractive van der Waals dispersion force tends to dominate. In combination with the depletion force discussed above, this will cause colloid coagulation and flocculation.

In the case of fast motions of charged colloid particles in electrolytic solutions, part of the diffuse layers will be stripped off. The hydrodynamic radius effective under such conditions is thus determined by the remaining compact layer. The electrostatic potential at this reduced hydrodynamic radius is the zeta potential, which therefore plays a crucial role for all electrokinetic effects [16, 17].

2.2 Remarks on Conservative Forces and Microreversibility

From the classical point of view, that is, in the absence of quantum-mechanical effects, all molecular forces are *conservative* on atomistic length scales. “Conservative” means that the forces $F(\mathbf{r})$ can be calculated as the negative gradient of the associated potential W :

$$F(\mathbf{r}) = -\nabla W \quad (2.67)$$

as it was already practiced above in the context of the van der Waals forces. For instance, in a one-dimensional harmonic potential along the x -axis, $W = Kx^2/2$, characterized by a quadratic dependence on the position x of the particle, the force on the particle obeys the linear Hooke relation $F = -Kx$, where K is the force constant. The minus sign indicates that the force always counteracts the deviation x from the equilibrium position.

Another definition of conservative forces is that the potential at a position $\mathbf{r}$ is independent of the path along which the position was reached. The work needed to transfer the particle from the infinite to the position $\mathbf{r}' = \mathbf{r}$ is then

$$W(\mathbf{r}) = - \int_{\infty}^{\mathbf{r}} \mathbf{F}(\mathbf{r}') \cdot d\mathbf{r}' \quad (2.68)$$

irrespective of the pathway chosen from the infinite, that is, $\mathbf{r}' = \infty$, to the actual position $\mathbf{r}' = \mathbf{r}$. In other terms, this feature can be expressed by

$$\oint \mathbf{F}(\mathbf{r}') \cdot d\mathbf{r}' = 0 \quad (2.69)$$

In this case, the integral refers to a closed contour. The attribute “conservative” thus refers to the energy of the bodies in the system under consideration. There is no *dissipation* of energy to a heat bath defined by innumerable disordered and therefore uncontrollable degrees of freedom.

Motions of particles that are exclusively subject to conservative forces are *reversible*. Reversing the sign of time in Newton’s equation of motion, Eq. (2.140), leads to solutions describing the same trajectories with the only difference that the particles now move in reversed direction. It is clear that this reversibility works in microsystems where only very few degrees of motional freedom are involved. In larger systems with innumerable degrees of freedom, the situation is totally different. In this case, the concept of *friction* must be introduced. This is a *nonconservative* force. Another example is *radiation damping* relevant for motions of charged particles. The rationale of friction is the impossibility to describe *all* degrees of motional freedom of *all* particles that are involved in a process at a time. Mathematically, an exact treatment of many-particle dynamics is impossible, not to speak of the say 10^{23} particles relevant in a practical system.⁵ Rather, this is the realm of *statistical physics*.

Take the motions of a polymer chain in solution, for example. As will be outlined in Chap. 5, equations of motion can formally be established for the segments of a polymer chain. However, since the segments interact also with the surrounding solvent molecules, there will be a permanent exchange of energy with innumerable non-polymeric degrees of motional freedom. That is, only *coarse-grained* descriptions are possible. The coarse-grained equations of motions for the segments of the polymer must therefore imply a friction term as a *nonconservative* force. Segment motions are consequently *irreversible*.

The quantity referring to friction in fluids is *viscosity*. It will be discussed in more detail in the following section. The definition will be based on the quantity *stress*.

2.3 Stress, Strain, and Shear Flow

The mechanical response of soft-matter objects to external forces or pressure is usually considered in the continuum limit referring to length scales much larger than atomistic or molecular dimensions. Treatments of this sort are subsumed as *continuum mechanics*.

⁵ Apart from this, the tiniest fluctuation of the initial conditions of the involved particles tends to cause *deterministic chaos* making the resulting trajectories unpredictable. Expressed in a more flowery language, this is also known as the “effect of the stroke of a butterfly” on a macroscopic system (see, e.g., Ref. [19]).

2.3.1 Stress and the Stress Tensor

The first of the quantities to be discussed in more detail, *stress*, is defined as the force per unit surface area of a virtual or real interface in a body. The orientation of a surface is specified by the unit normal vector $\mathbf{n}$ on it as illustrated in Fig. 2.14. Primarily, the stress vector $\boldsymbol{\sigma}$ is defined by

$$\boldsymbol{\sigma} = \frac{\partial \mathbf{F}}{\partial A} \quad (2.70)$$

that is, by the infinitesimal force $\partial \mathbf{F}$ acting on an infinitesimal surface element $\partial A = \mathbf{n} \partial A$. If $\partial \mathbf{F} \perp \mathbf{n}$, one speaks of *shear stress*. The alignment $\partial \mathbf{F} \parallel \mathbf{n}$ characterizes *normal stress*.

More precisely, we can specify the stress vector by its components along the normal $\mathbf{n}$ and in the two orthogonal directions perpendicular to $\mathbf{n}$. Assuming for the moment that $\mathbf{n}$ points along the x -axis of the reference frame, that is,

$$\mathbf{n} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad (2.71)$$

the stress vector component along this axis can be referred to as σ_{xx} , while the two in-plane components along the y and z directions are σ_{yx} and σ_{zx} , respectively. In terms of this nomenclature, the stress vector is represented by

$$\boldsymbol{\sigma} = \begin{pmatrix} \sigma_{xx} \\ \sigma_{yx} \\ \sigma_{zx} \end{pmatrix} \quad (2.72)$$

Likewise, if $\mathbf{n}$ were aligned along the y - or z -axes, the stress vectors would be

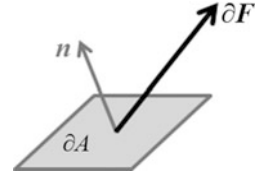
$$\boldsymbol{\sigma} = \begin{pmatrix} \sigma_{xy} \\ \sigma_{yy} \\ \sigma_{zy} \end{pmatrix} \quad \text{and} \quad \boldsymbol{\sigma} = \begin{pmatrix} \sigma_{xz} \\ \sigma_{yz} \\ \sigma_{zz} \end{pmatrix} \quad (2.73)$$

respectively.

More generally, the normal vector $\mathbf{n}$ of the relevant interface can be aligned along any direction relative to the reference frame so that it is better represented by components according to

$$\mathbf{n} = \begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} \quad (2.74)$$

Fig. 2.14 Force ∂F acting on a surface element ∂A with the normal vector $\mathbf{n}$



For this general interface orientation, the stress vector is then given as the sum of the vectors given in Eqs. (2.72) and (2.73):

$$\boldsymbol{\sigma} = n_x \begin{pmatrix} \sigma_{xx} \\ \sigma_{yx} \\ \sigma_{zx} \end{pmatrix} + n_y \begin{pmatrix} \sigma_{xy} \\ \sigma_{yy} \\ \sigma_{zy} \end{pmatrix} + n_z \begin{pmatrix} \sigma_{xz} \\ \sigma_{yz} \\ \sigma_{zz} \end{pmatrix} \quad (2.75)$$

weighted by the components of the normal vector. We are thus dealing with the tensor relation

$$\boldsymbol{\sigma} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} = \boldsymbol{\mathcal{G}} \mathbf{n} \quad (2.76)$$

where

$$\boldsymbol{\mathcal{G}} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \quad (2.77)$$

is the second-rank *stress tensor* in Cartesian representation.

Here, the “in-on” subscript notation is used for the tensor elements: The stress tensor elements refer to forces acting *in* the direction denoted by the first subscript *on* the surface denoted by the second subscript. Instead of the unspecific expression in Eq. (2.70), we thus prefer a definition of stress by the tensor elements σ_{ij} with $i, j = x, y, z$ according to

$$\sigma_{ij} = \frac{\partial F_i}{\partial A_j} \quad (2.78)$$

σ_{ij} relates the force component ∂F_i to the surface component $\partial A_j \equiv n_j \partial A$. The diagonal elements σ_{xx} , σ_{yy} , σ_{zz} consequently represent *normal stresses*, whereas the off-diagonal elements σ_{xy} , σ_{xz} , σ_{yz} , etc., symbolize *shear stresses*.

Based on Eq. (2.76), the stress vector can straightforwardly be calculated for any well-defined interface. Consider, for example, the “ x surface” of the volume element with the normal vector along the x -axis (see Fig. 2.15):

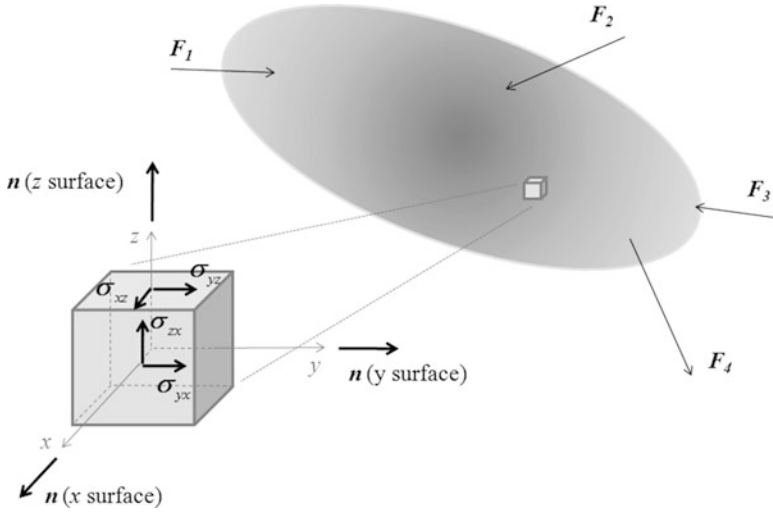


Fig. 2.15 Schematic representation of stress vectors acting on a volume element of a body subjected to external forces. The situation is assumed to be static so that the equilibrium conditions $\sum_i \mathbf{F}_i = 0$ and $\sum_i \mathbf{T}_i = 0$ apply. The sums of all external forces and torques on the body vanish. Likewise, the sums of all internal forces and torques acting on the volume element arising from elastic deformations of the body vanish as well

$$\mathbf{n} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad (2.79)$$

In this case, the stress vector results as⁶

$$\boldsymbol{\sigma} = \underline{\sigma} \mathbf{n} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} \sigma_{xx} \\ \sigma_{yx} \\ \sigma_{zx} \end{pmatrix} \quad (2.80)$$

The three components of the stress vector acting on the x surface, σ_{xx} , σ_{yx} , and σ_{zx} , are given as the respective forces along the x -, y -, and z -axes per unit area. Likewise, the stress vector acting on the y surface defined by a normal vector along the y direction,

⁶ Applying a second-rank (Cartesian) tensor $\underline{A} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$ to a (column) vector $\mathbf{B} = \begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix}$ gives a new (column) vector $\mathbf{C} = \underline{A} \cdot \mathbf{B}$ with elements $c_i = \sum_{j=1}^3 a_{ij} b_j$, $i = 1, 2, 3$ (rule of thumb: “row elements times column elements”).

$$\mathbf{n} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad (2.81)$$

is given by

$$\boldsymbol{\sigma} = \underline{\sigma} \mathbf{n} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \sigma_{xy} \\ \sigma_{yy} \\ \sigma_{zy} \end{pmatrix} \quad (2.82)$$

Finally, the stress vector acting on the z surface with normal vector along the z -axis,

$$\mathbf{n} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad (2.83)$$

reads

$$\boldsymbol{\sigma} = \underline{\sigma} \mathbf{n} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} \sigma_{xz} \\ \sigma_{yz} \\ \sigma_{zz} \end{pmatrix} \quad (2.84)$$

If all off-diagonal elements of the stress tensor vanish, that is, $\sigma_{ij} = 0$ for $i \neq j$, the stress vectors in Eqs. (2.80), (2.82), and (2.84) will be oriented parallel to the respective normal vectors. That is, the diagonal elements represent *normal stresses*. An obvious example where this scenario matters is a fluid without structural elasticity in equilibrium and at rest:

$$\underline{\sigma} = \begin{pmatrix} \sigma_{xx} = -p & 0 & 0 \\ 0 & \sigma_{yy} = -p & 0 \\ 0 & 0 & \sigma_{zz} = -p \end{pmatrix} \quad (2.85)$$

p is the hydrostatic pressure which is a positive quantity. The minus signs indicate that the forces on the surfaces are inward in this case, while the normal vectors point outward (see Fig. 2.15). The normal stresses are consequently the same on all faces of the volume element provided that gravitational effects are negligible. Only in materials with some structural elasticity, the diagonal elements will no longer be equal, and diagonal elements can be finite.

If on the other hand all diagonal elements are zero, the resulting stress vectors will be perpendicular to the respective normal vectors. We are then dealing with *shear stresses*. A simple example is

$$\underline{\sigma} = \begin{pmatrix} 0 & 0 & \sigma_{xz} \\ 0 & 0 & 0 \\ \sigma_{zx} & 0 & 0 \end{pmatrix} \quad \text{and} \quad \mathbf{n} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad (2.86)$$

In this case, the (shear) stress vector is

$$\boldsymbol{\sigma} = \underline{\sigma} \mathbf{n} = \begin{pmatrix} 0 & 0 & \sigma_{xz} \\ 0 & 0 & 0 \\ \sigma_{zx} & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \sigma_{zx} \end{pmatrix} \equiv \boldsymbol{\sigma}_{zx} \quad (2.87)$$

It points along the z -axis, acts on the x plane, and has the magnitude σ_{zx} . The same stress tensor combined with a normal vector for the z surface results in the stress vector:

$$\boldsymbol{\sigma} = \underline{\sigma} \mathbf{n} = \begin{pmatrix} 0 & 0 & \sigma_{xz} \\ 0 & 0 & 0 \\ \sigma_{zx} & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} \sigma_{xz} \\ 0 \\ 0 \end{pmatrix} \equiv \boldsymbol{\sigma}_{xz} \quad (2.88)$$

which is aligned along the x -axis and acts on the z surface. The normal and stress vectors of the latter two examples are illustrated in Fig. 2.15. As suggested by Eq. (2.70), the total force acting on a volume element of a body such as the one depicted in Fig. 2.15 is given by the integral over the whole surface of the element:

$$\mathbf{F} = \int \underline{\sigma} \mathbf{n} dA \quad (2.89)$$

The definition of the stress tensor anticipates equilibrium so that inertial forces are absent. The body is assumed to be at rest, and no translational or rotational accelerations take place. That is, the sum of all forces and the sum of all torques externally acting on the body under consideration must be zero, $\sum_i \mathbf{F}_i = 0$ and $\sum_i \mathbf{T}_i = 0$. As a consequence, the volume element under consideration must be in equilibrium as well. This in particular means that there is no torque tending to rotate the volume element. In the example shown in Fig. 2.15, the magnitudes of the two shear stresses must therefore be equal, $\sigma_{xz} = \sigma_{zx}$, so that the respective torques acting on the volume element compensate each other. Otherwise, the object would tend to rotate about the y -axis. The stress tensor in Eq. (2.86) is therefore *symmetric*. This property is required in general for all equilibrium stress tensors. Equation (2.77) can thus be simplified by the symmetry condition:

$$\sigma_{ij} = \sigma_{ji} \quad \text{for} \quad j, i = x, y, z \quad (2.90)$$

As a consequence, there are only six independent tensor elements.

The stress tensor elements depend on the coordinate system used for the description of the stress vector. However, as with all other physical quantities, the formal

choice of a frame of reference must not affect the intrinsic physical properties inherent to the stress tensor. That is, there must be invariants independent of the orientation of a stressed body relative to a coordinate system. As a second-rank tensor, these invariants are the three *principal stresses* to be calculated as the eigenvalues of the tensor. Formally, they are expected to be *real* quantities as a consequence of the symmetry property of the stress tensor. From the physical point of view, this is not astonishing since imaginary stress forces are not defined.

A stress tensor valid for an arbitrarily oriented coordinate system can always be transformed to the *principal-axes system* relative to which the stress tensor is *diagonal* with the eigenvalues $\sigma_1, \sigma_2, \sigma_3$ as diagonal elements:

$$\underline{\sigma}_{\text{p.a.}} = \begin{pmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_2 & 0 \\ 0 & 0 & \sigma_3 \end{pmatrix} \quad (2.91)$$

According to the above definition of stress vectors, the principal-stress vectors act *orthogonal* to each other along the normal vectors of the planes spanned by the principal-axes system.

The transformation from an arbitrary orthogonal Cartesian coordinate system x, y, z to the principal-axes system $x_{\text{p.a.}}, y_{\text{p.a.}}, z_{\text{p.a.}}$ can be performed in the following way. Let

$$\mathbf{n} = \begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} \quad (2.92)$$

be a normal vector on a plane across the body. The components are expressed relative to the original frame of reference. If $\mathbf{n}$ coincides with the normal vector on one of the orthogonal planes spanned by the principal-axes system, it is called an eigenvector obeying the *eigenvalue equation*:

$$\underline{\sigma} \mathbf{n} = \lambda \mathbf{n} \quad (2.93)$$

where λ represents an eigenvalue. Written in components, this equation reads

$$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} = \lambda \begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} \quad (2.94)$$

or in modified form

$$\begin{pmatrix} \sigma_{xx} - \lambda & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} - \lambda & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} - \lambda \end{pmatrix} \begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} = 0 \quad (2.95)$$

Mathematically, Eq. (2.95) is equivalent to a set of three linear homogeneous equations which possess nontrivial solutions only if the *secular determinant* vanishes:

$$\begin{vmatrix} \sigma_{xx} - \lambda & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} - \lambda & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} - \lambda \end{vmatrix} = 0 \quad (2.96)$$

This is the so-called *characteristic equation*. It is of third order in λ and has consequently three solutions. The three solutions provide the eigenvalues (or the *principal values*) of the stress tensor σ :

$$\lambda = \sigma_1, \quad \lambda = \sigma_2, \quad \lambda = \sigma_3 \quad (2.97)$$

Inserting these values into Eq. (2.91) gives the *stress tensor relative to the principal-axes system*. The three eigenvectors in terms of components relative to the original coordinate system are obtained by inserting the corresponding eigenvalues into Eq. (2.94) leading in each case to a coupled set of three linear equations for the three Cartesian components of the eigenvector. The three solutions of each of these sets of equations are the components of the respective eigenvectors $\mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3$. In this way, the problem is completely solved: The principal-axes values $\sigma_1, \sigma_2, \sigma_3$ of the stress tensor Eq. (2.91) are quantified, and the principal-axes frame spanned by the three orthogonal eigenvectors $\mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3$ is defined.

2.3.2 Strain and the Strain Tensor

Exerting stress on a body causes deformations. In solids and solid-like materials, stationary stress will lead to static deformations composed of translations, rotations, and strain of material elements. For a formal treatment, we consider two closely spaced points $O(0,0,0)$ and $P(x,y,z)$ in a continuous medium as illustrated in Fig. 2.16. After deformation of the body by stress, the points will be displaced to $O'(a_0, b_0, c_0)$ and $P'(x+a, y+b, z+c)$, respectively. Inhomogeneous deformations of the medium lead to inhomogeneous displacements. That is, the displacements vary from position to position. The displacement components a, b, c of point $P(x, y, z)$ along the three coordinate axes will therefore deviate from the displacement components a_0, b_0, c_0 of point $O(0,0,0)$. Actually, the displacement components of point P are functions $a = a(x, y, z)$, $b = b(x, y, z)$, and $c = c(x, y, z)$, where the variables x, y, z are the components of the distance vector from point O to point P .

The differences of the displacement components can be expanded in Taylor series according to

$$\begin{aligned}
a - a_0 &= \frac{\partial a}{\partial x}x + \frac{\partial a}{\partial y}y + \frac{\partial a}{\partial z}z + \cdots \\
b - b_0 &= \frac{\partial b}{\partial x}x + \frac{\partial b}{\partial y}y + \frac{\partial b}{\partial z}z + \cdots \\
c - c_0 &= \frac{\partial c}{\partial x}x + \frac{\partial c}{\partial y}y + \frac{\partial c}{\partial z}z + \cdots
\end{aligned} \tag{2.98}$$

For sufficiently close positions of the two points, the series can be truncated after the linear terms as an approximation. On this basis, the displacement vector $\mathbf{s}$ of point P can be expressed by the components

$$\begin{aligned}
a &= a_0 + (\text{odd terms}) + (\text{even terms}) \\
&= a_0 + \left(0 + \frac{a_{12} - a_{21}}{2}y + \frac{a_{13} - a_{31}}{2}z\right) + \left(a_{11}x + \frac{a_{12} + a_{21}}{2}y + \frac{a_{13} + a_{31}}{2}z\right) \\
b &= b_0 + \left(\frac{a_{21} - a_{12}}{2}x + 0 + \frac{a_{23} - a_{32}}{2}z\right) + \left(\frac{a_{21} + a_{12}}{2}x + a_{22}y + \frac{a_{23} + a_{32}}{2}z\right) \\
c &= c_0 + \left(\frac{a_{31} - a_{13}}{2}x + \frac{a_{32} - a_{23}}{2}y + 0\right) + \left(\frac{a_{31} + a_{13}}{2}x + \frac{a_{32} + a_{23}}{2}y + a_{33}z\right)
\end{aligned} \tag{2.99}$$

with the definitions $a_{11} \equiv \partial a / \partial x$, $a_{12} \equiv \partial a / \partial y$, $a_{13} \equiv \partial a / \partial z$, $a_{21} \equiv \partial b / \partial x$, $a_{31} \equiv \partial c / \partial x$, etc. The terms in Eq. (2.99) have been decomposed into sums of “odd” and “even” expressions with respect to subscript exchange, where we have used the identity

$$a_{ik} \equiv \underbrace{\frac{a_{ik} - a_{ki}}{2}}_{\text{odd}} + \underbrace{\frac{a_{ik} + a_{ki}}{2}}_{\text{even}} \tag{2.100}$$

Having a closer look at Eqs. (2.99), we see that the displacement vector $\mathbf{s}$ can be analyzed into three terms:

$$\mathbf{s} \equiv \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \mathbf{s}_0 + \mathbf{s}_1 + \mathbf{s}_2 \tag{2.101}$$

representing translations, rotations, and strain.

Translations, that is, homogeneous parallel displacements of all points, are described by the vector

$$\mathbf{s}_0 \equiv \begin{pmatrix} a_0 \\ b_0 \\ c_0 \end{pmatrix} \tag{2.102}$$

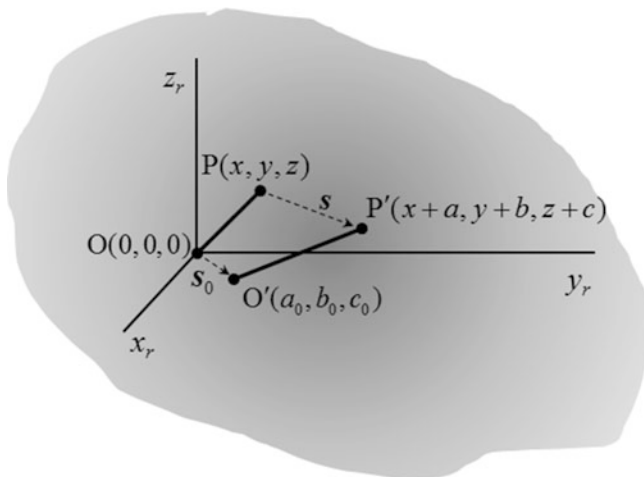


Fig. 2.16 Inhomogeneous deformation of a medium: The displacements of the two points O and P to the points O' and P' are different

Rotations of the vector $\mathbf{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$ connecting points O and P are the result of the operation

$$\mathbf{s}_1 = \begin{pmatrix} 0 & \frac{a_{12} - a_{21}}{2} & \frac{a_{13} - a_{31}}{2} \\ \frac{a_{21} - a_{12}}{2} & 0 & \frac{a_{23} - a_{32}}{2} \\ \frac{a_{31} - a_{13}}{2} & \frac{a_{32} - a_{23}}{2} & 0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (2.103)$$

The second-rank tensor in Eq. (2.103) is the (antisymmetric) *rotation* tensor. *Deformations* in the proper sense are finally described by the vector

$$\mathbf{s}_2 = \begin{pmatrix} a_{11} & \frac{a_{12} + a_{21}}{2} & \frac{a_{13} + a_{31}}{2} \\ \frac{a_{21} + a_{12}}{2} & a_{22} & \frac{a_{23} + a_{32}}{2} \\ \frac{a_{31} + a_{13}}{2} & \frac{a_{32} + a_{23}}{2} & a_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (2.104)$$

or shortly

$$\mathbf{s}_2 = \boldsymbol{\xi} \mathbf{r} \quad (2.105)$$

$\boldsymbol{\xi}$ is the (symmetric) second-rank *strain* tensor. More specifically, the strain tensor can be expressed by

$$\mathcal{E} = \begin{pmatrix} \frac{\partial a}{\partial x} & \frac{1}{2} \left(\frac{\partial a}{\partial y} + \frac{\partial b}{\partial x} \right) & \frac{1}{2} \left(\frac{\partial a}{\partial z} + \frac{\partial c}{\partial x} \right) \\ \frac{1}{2} \left(\frac{\partial a}{\partial y} + \frac{\partial b}{\partial x} \right) & \frac{\partial b}{\partial y} & \frac{1}{2} \left(\frac{\partial b}{\partial z} + \frac{\partial c}{\partial y} \right) \\ \frac{1}{2} \left(\frac{\partial a}{\partial z} + \frac{\partial c}{\partial x} \right) & \frac{1}{2} \left(\frac{\partial b}{\partial z} + \frac{\partial c}{\partial y} \right) & \frac{\partial c}{\partial z} \end{pmatrix} \quad (2.106)$$

after inserting the definitions of the terms a_{ik} defined in the context of Eq. (2.99).

Practically, it may be preferable to diagonalize the strain tensor. This transformation to its principal-axes system is performed in analogy to the derivation of the principal-axes representation of the stress tensor Eq. (2.91). The diagonal elements represent the three principal or eigenvalues of the strain tensor:

$$\mathcal{E}_{\text{p.a.}} = \begin{pmatrix} \varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_2 & 0 \\ 0 & 0 & \varepsilon_3 \end{pmatrix} \quad (2.107)$$

2.3.3 Elastic Moduli (Hookean Limit)

Stress and strain are intimately related with each other. The elements of the stress tensor depend in particular on the (local) interaction potentials of the material outlined in Sect. 2.1. If deformations are small relative to the extension of the object under stress, the elastic potential W can be approximated in lowest (“harmonic”) order as a function of the *squares* of the strain-tensor elements. The elements of the stress tensor can be expressed as first derivatives of the elastic potential W by the strain-tensor components. They will therefore be *linearly* related to the strain-tensor elements. This linear relation between the elements σ_{ij} of the stress tensor and the elements ε_{kl} of the strain tensor valid under such circumstances is called *Hooke’s law*. In its most general form, it reads

$$\sigma_{ij} = \sum_{k,l} E_{ijkl} \varepsilon_{kl} \quad (2.108)$$

where the subscripts i, j, k, l stand for the Cartesian coordinates x, y, z . The coefficients E_{ijkl} , that is, the *elastic moduli*, represent elements of the *elasticity tensor* $\underline{E}$. They are defined by

$$E_{ijkl} = \frac{\partial^2 W}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \quad (2.109)$$

that is, by the second derivatives of the elastic potential.

The relation inverse to Eq. (2.108) is

$$\varepsilon_{ij} = \sum_{k,l} J_{ijkl} \sigma_{kl} \quad (2.110)$$

with the *elastic compliances* J_{ijkl} , the components of the *compliance tensor* $\mathcal{J}$. The respective tensorial forms of Eqs. (2.108) and (2.110) are

$$\underline{\sigma} = \underline{\mathcal{E}} \cdot \underline{\varepsilon} \quad \text{and} \quad \underline{\varepsilon} = \underline{\mathcal{J}} \cdot \underline{\sigma} \quad (2.111)$$

In the validity range of Hooke's law, that is, for sufficiently small deformations, the elastic moduli and compliances are *independent* of strain and stress, respectively. As fourth-rank tensors, $\underline{\mathcal{E}}$ and $\underline{\mathcal{J}}$ have $3^4 = 81$ elements each. Fortunately, these elements are not completely independent of each other. Let us shortly demonstrate this for the case of the elasticity tensor.

The stress and strain tensors are symmetric, that is, $\sigma_{ij} = \sigma_{ji}$ and $\varepsilon_{kl} = \varepsilon_{lk}$, respectively. Consequently, $E_{ijkl} = E_{jikl} = E_{ijlk}$. Furthermore, the commutability of the second derivatives of the interaction potential, Eq. (2.109), suggests $E_{ijkl} = E_{klij}$. In summary, only 21 of the 81 tensor elements are independent and different in the most general case. They determine the values of the remaining 60 elements. Further reductions are possible on the basis of symmetries inherent to crystalline or liquid crystalline materials.

The situation is particularly simple in isotropic media such as in a piece of ordinary rubber, for example. In this case, only two independent elastic moduli remain, one for deformations parallel to stress and one for deformations perpendicular to stress. In the principal-axes coordinate system, relative to which both the stress and strain tensors are of a diagonal form with the principal values $\sigma_1, \sigma_2, \sigma_3$ (see Eq. 2.91) and $\varepsilon_1, \varepsilon_2, \varepsilon_3$ (see Eq. 2.107), respectively, we have

$$\begin{aligned} \sigma_1 &= 2\mu\varepsilon_1 + \lambda(\varepsilon_1 + \varepsilon_2 + \varepsilon_3) \\ \sigma_2 &= 2\mu\varepsilon_2 + \lambda(\varepsilon_1 + \varepsilon_2 + \varepsilon_3) \\ \sigma_3 &= 2\mu\varepsilon_3 + \lambda(\varepsilon_1 + \varepsilon_2 + \varepsilon_3) \end{aligned} \quad (2.112)$$

The two elastic constants 2μ and λ in these relations are called *Lamé moduli*. Transforming Eq. (2.112) to an arbitrarily rotated frame of reference leads to the strain–stress relation between the strain and the stress tensor elements:

$$\sigma_{ij} = 2\mu\varepsilon_{ij} + \lambda\delta_{ij}(\varepsilon_1 + \varepsilon_2 + \varepsilon_3) \quad (2.113)$$

δ_{ij} is the Kronecker symbol.⁷ Note that the trace $\text{Tr}\{\underline{\varepsilon}\} = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}$ (as a general property of second-rank tensors) is invariant under rotation and therefore independent of the frame of reference. The sum of the diagonal elements

⁷The Kronecker symbol is defined by $\delta_{ij} = 1$ for $i = j$ and $\delta_{ij} = 0$ otherwise.

in the principal-axes system, $\varepsilon_1 + \varepsilon_2 + \varepsilon_3$, is equal to the sum of the diagonal elements in any other reference frame, $\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}$. The inverse expression, the stress–strain relation, reads

$$\varepsilon_{ij} = \frac{1}{2\mu} \sigma_{ij} + \frac{\lambda}{2\mu(2\mu + 3\lambda)} \delta_{ij} \text{Tr}\{\boldsymbol{\sigma}\} \quad (2.114)$$

with the trace of the stress tensor $\text{Tr}\{\boldsymbol{\sigma}\} = \sigma_1 + \sigma_2 + \sigma_3 = \sigma_{xx} + \sigma_{yy} + \sigma_{zz}$ which is again independent of the reference frame.

Instead of the two elastic Lamé moduli, *Young's modulus* E , the *shear modulus* G , and the *compression (or bulk) modulus* K_c are more common in practice. They are related to the Lamé moduli by the expressions

$$\begin{aligned} E &= \frac{\mu(2\mu + 3\lambda)}{\mu + \lambda} \\ G &= \mu \\ K_c &= \frac{2\mu + 3\lambda}{3} \end{aligned} \quad (2.115)$$

As a further quantity of practical interest, the *lateral contraction number* or *Poisson's ratio*,

$$\nu = \frac{\lambda}{2(\mu + \lambda)} \quad (2.116)$$

is in use.

The redefinitions given in Eqs. (2.115) are closely related to practically relevant deformation scenarios. An example is a rod of length l and cross-sectional area A . The material is assumed to be homogeneous and isotropic. The rod be aligned along the x -axis and fixed at one end as illustrated in Fig. 2.17. Let it be stretched by an amount Δl by a force F acting uniformly on the surface at the other end in $+x$ direction. In this case, the strain and the effective stress can be expressed by $\varepsilon = \varepsilon_{xx} = \varepsilon_1 = \Delta l/l$ and $\sigma = \sigma_{xx} = \sigma_1 = F/A$, respectively. Under Hookean conditions, these two quantities are related by

$$\sigma = E\varepsilon \quad (2.117)$$

with *Young's modulus* E as the proportionality constant.

Stretching the rod causes lateral contraction. The relative variation of the rod diameter, $\Delta d/d$, which is a negative quantity, is related to the (positive) elongation according to

$$\frac{\Delta d}{d} = -\nu\varepsilon \quad (2.118)$$

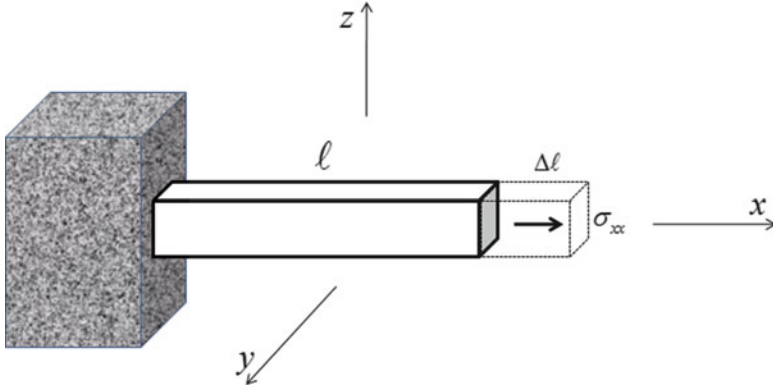


Fig. 2.17 Uniaxial deformation of a rod anchored on the *left side*

with the *lateral contraction number* ν as the proportionality constant (apart from the sign).

Another example of practical interest is a cube under shear stress. The material is again assumed to be homogeneous and isotropic. A tangential force acting on the top face along the $+y$ direction (see Fig. 2.18 for an illustration) while the bottom face is fixed causes a shear stress σ_{yz} which deforms the cube by a small angle $\gamma \approx \tan \gamma$. Under Hookean conditions, the shear stress and the deformation angle are related by

$$\sigma_{yz} = G\gamma \quad (2.119)$$

with the *shear modulus* G as the proportionality constant. The work to be expended for the elastic shear deformation of a volume element by a shear angle γ (see Fig. 2.18) is in the Hookean limit:

$$\delta W = \int_0^{\delta y} \sigma_{yz} A dy' = \int_0^{\delta y} \sigma_{yz} A \ell \frac{dy'}{\ell} = A \ell \int_0^{\gamma} \sigma_{yz} d\gamma' = VG \int_0^{\gamma} \gamma' d\gamma' = \frac{1}{2} VG \gamma^2 \quad (2.120)$$

The corresponding elastic energy density is consequently

$$\rho_W = \frac{1}{2} G \gamma^2 \quad (2.121)$$

Another scenario is hydrostatic pressure exerted isotropically on all sides of the cube. If this pressure is increased by an amount Δp , the relative reduction of the volume, $\Delta V/V$, obeys the Hookean relation

$$\Delta p = -K_c \frac{\Delta V}{V} \quad (2.122)$$

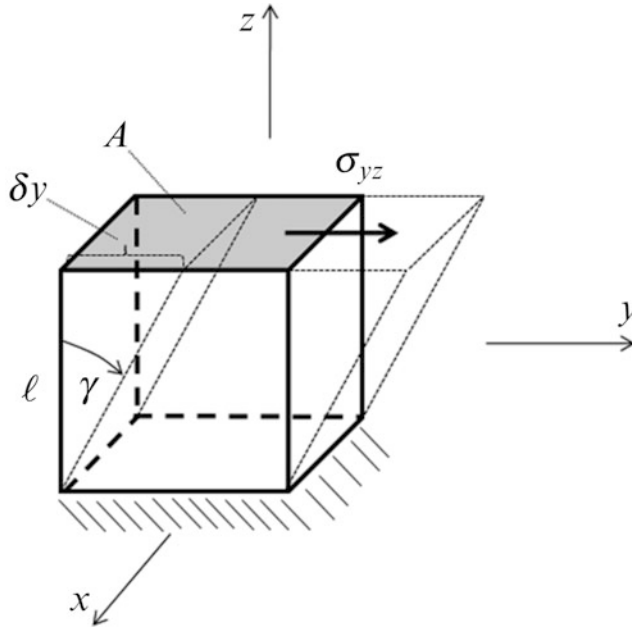


Fig. 2.18 Shear deformation of a volume element anchored at the *bottom* (A top surface, ℓ edge length, δy shear length, $\gamma \approx \delta y/\ell$ shear angle, σ_{yz} stress component along the y direction)

with the *compression (or bulk) modulus* K_c as the proportionality constant. Note that the relative volume variation $\Delta V/V$ is a negative quantity since the volume is reduced upon exertion of pressure.

The elastic quantities E, ν, G, K_c are not independent of each other as follows from the fact that they depend on only two Lamé moduli according to Eqs. (2.115) and (2.116). On this basis, two more equations relating the elastic quantities with each other can be established, namely,

$$E = 3K_c(1 - 2\nu) \quad (2.123)$$

and

$$E = 2G(1 + \nu) \quad (2.124)$$

Under Hookean conditions, the elastic properties of bodies consisting of homogeneous isotropic materials can completely be described by any pair of elastic constants. Each of the four parameters E, G, K_c , and ν can be expressed by any choice of two of the other constants. For example, a relation of particular interest can be derived by eliminating ν from Eqs. (2.123) and (2.124):

$$K_c = \frac{EG}{3(3G - E)} \quad (2.125)$$

Thus, relative to the up to 21 constants that may be necessary for a complete description of crystalline materials, the situation is much simpler in the isotropic case where just two elastic constants are sufficient.

In solids, the elastic moduli are of similar orders of magnitude. This is in contrast to viscous and viscoelastic materials, where Young's modulus and the shear modulus are strongly reduced relative to the bulk modulus. Soft matter and in particular liquids can therefore be considered to be "incompressible." That is, the bulk modulus is much larger than all other moduli, so that the limit $K_c \rightarrow \infty$ appears to be adequate. From Eq. (2.125), we thus obtain the approximate relation

$$E \approx 3G \quad (2.126)$$

to which we will refer later several times.

2.3.4 Viscosity and Shear Stress Tensor

The previous sections referred to the elastic behavior of bodies. Solids in particular are *structure elastic*. If stress of any sort is released, the original structure will be recovered. This property applies as long as there is no *plastic*, that is, permanent, deformation which occurs if the strain exceeds certain limits far beyond the Hookean range. The counterpart of structure elastic behavior is *viscous* flow as it applies to fluids (gases and liquids) under stress. The crossover from structure elastic to viscous responses to stress is smooth and depends on the time scale of the applied stress load. A solid may be perfectly structure elastic on a short enough time scale not yet permitting molecular or atomistic rearrangements by thermal motion. However, when stress is applied over long enough periods, viscous flow becomes detectable.⁸

Expressed the other way round, viscous liquids show elastic responses if stress is applied transiently on a time scale short relative to thermal motions. This in particular becomes obvious with polymeric materials where molecular processes are particularly slow. One then speaks of *viscoelasticity*. So, whether a condensed-matter body of any sort shows elastic or viscous response to stress is primarily a matter of time scale.

⁸ Provided that the time scale is long enough, any material subjected to thermal molecular motions will flow indeed. However, it is a widespread misbelief that medieval glass windows in churches are thicker at the bottom due to viscous flow over the centuries. It is true that window glass flows under gravitational stress in principle. But this can perceptibly occur only on time scales much longer than the age of the oldest churches.

Let us now turn to purely viscous flow as expected on sufficiently long time scales of stress exertion. Instead of the strain tensor $\underline{\varepsilon}$, the quantity of interest is now the *strain rate tensor* $\dot{\underline{\varepsilon}}$, that is, the strain variation per unit time. The origin of flow is stress acting on volume elements of the fluid. The problem is therefore to relate the stress tensor with the strain rate tensor.

The stress tensor can be analyzed in terms of *isotropic* and *anisotropic* contributions:

$$\underline{\sigma} = \underline{\sigma}_0 + \underline{\tau} \quad (2.127)$$

The first term on the right-hand side,

$$\underline{\sigma}_0 = \begin{pmatrix} \sigma_0^{xx} & 0 & 0 \\ 0 & \sigma_0^{yy} & 0 \\ 0 & 0 & \sigma_0^{zz} \end{pmatrix} \quad (2.128)$$

with the elements $\sigma_0^{i,k} = -p\delta_{ik}$ is analogous to the isotropic contribution of hydrostatic pressure in a fluid at rest. The parameter p can formally be taken as the pressure effective under flow conditions.⁹ Note, however, that its value can deviate from the static pressure referred to in Eq. (2.85). The minus sign indicates that forces on this basis act inward on the fluid element under consideration.

The anisotropic contribution,

$$\underline{\tau} = \begin{pmatrix} \tau_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & \tau_{yy} & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & \tau_{zz} \end{pmatrix} \quad (2.129)$$

is often called *deviatoric stress tensor*. It vanishes in the absence of fluid motion and is therefore of primary interest in the present context as a quantity sensitive to flow. In the case of incompressible fluids, the elements of the deviatoric stress tensor are proportional to the corresponding elements of the strain rate tensor with the proportionality factor $2\eta_0$:

$$\tau_{ik} = 2\eta_0 \dot{\varepsilon}_{ik} \quad (2.130)$$

⁹For a discussion of the thermodynamically somewhat delicate term “pressure” under flow conditions, see Ref. [20], for example.

The material parameter η_0 is termed the (dynamic) *viscosity* of the fluid.¹⁰ If not specified otherwise, one usually assumes *Newtonian liquids*, where the viscosity is independent of the shear strain rate. That is, the proportionality factor $2\eta_0$ is a constant and Eq. (2.130) is truly linear in this case. This is in contrast to the so-called *shear thinning* and *shear thickening* cases where the respective viscosity decreases and increases with the (shear) strain rate. This sort of anomalies may occur in very viscous liquids and in colloid suspensions and emulsions.

The off-diagonal elements of τ represent *shear stresses*, whereas the diagonal elements refer to *normal stresses*. The trace, that is, the sum of the diagonal elements, vanishes. As illustrated in Fig. 2.19, the origin of shear stress acting on a volume element of the fluid is the so-called *viscous drag* in a gradient of the flow velocity. Let us examine this in more detail by specifying the relation between the strain rate and the velocity gradient.

In Cartesian coordinates, the flow velocity vector can be expressed by

$$\mathbf{v} = \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix} = \begin{pmatrix} \frac{\partial a}{\partial t} \\ \frac{\partial b}{\partial t} \\ \frac{\partial c}{\partial t} \end{pmatrix} \quad (2.131)$$

where a, b, c are the respective displacements of fluid particles along the x, y, z -axes. The time derivative of Eq. (2.106) gives the *rate-of-strain tensor*

$$\begin{aligned} \dot{\epsilon} &= \frac{\partial}{\partial t} \begin{pmatrix} \frac{\partial a}{\partial x} & \frac{1}{2} \left(\frac{\partial a}{\partial y} + \frac{\partial b}{\partial x} \right) & \frac{1}{2} \left(\frac{\partial a}{\partial z} + \frac{\partial c}{\partial x} \right) \\ \frac{1}{2} \left(\frac{\partial a}{\partial y} + \frac{\partial b}{\partial x} \right) & \frac{\partial b}{\partial y} & \frac{1}{2} \left(\frac{\partial b}{\partial z} + \frac{\partial c}{\partial y} \right) \\ \frac{1}{2} \left(\frac{\partial a}{\partial z} + \frac{\partial c}{\partial x} \right) & \frac{1}{2} \left(\frac{\partial b}{\partial z} + \frac{\partial c}{\partial y} \right) & \frac{\partial c}{\partial z} \end{pmatrix} \\ &= \begin{pmatrix} \frac{\partial v_x}{\partial x} & \frac{1}{2} \left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x} \right) & \frac{1}{2} \left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x} \right) \\ \frac{1}{2} \left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x} \right) & \frac{\partial v_y}{\partial y} & \frac{1}{2} \left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y} \right) \\ \frac{1}{2} \left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x} \right) & \frac{1}{2} \left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y} \right) & \frac{\partial v_z}{\partial z} \end{pmatrix} \end{aligned} \quad (2.132)$$

This is obviously a symmetric tensor, that is, $\dot{\epsilon}_{ij} = \dot{\epsilon}_{ji}$. According to the definition of the tensor elements given in Eq. (2.130), the deviatoric stress tensor is therefore symmetric as well:

¹⁰ To make clear that *viscoelasticity* is not under consideration here, one better speaks of the *zero-shear viscosity*, where “zero shear” means that the strain rate is slow relative to any molecular dynamic processes. Sometimes, the viscosity per se introduced above is called the *dynamic* or *absolute* viscosity. It is distinguished from the *kinematic* viscosity defined as the dynamic viscosity divided by the density. Further terms in use are the *volume* viscosity (or *bulk* viscosity) which however matters only with sound phenomena in compressible fluids.

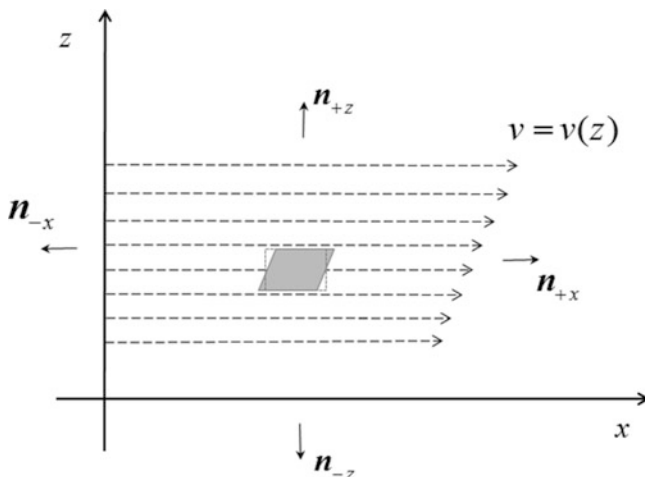


Fig. 2.19 Cross section of a fluid element flowing along the x -axis in a velocity gradient in $+z$ direction. The initially cubic fluid element is subjected to shear deformation by viscous drag as schematically indicated for two time moments. The normal unit vectors refer to the surfaces of the fluid element prior to the deformation

$$\begin{aligned}
 \boldsymbol{\tau} &= 2\eta_0 \begin{pmatrix} 0 & \dot{\epsilon}_{xy} & \dot{\epsilon}_{xz} \\ \dot{\epsilon}_{yx} & 0 & \dot{\epsilon}_{yz} \\ \dot{\epsilon}_{zx} & \dot{\epsilon}_{zy} & 0 \end{pmatrix} + 2\eta_0 \begin{pmatrix} \dot{\epsilon}_{xx} & 0 & 0 \\ 0 & \dot{\epsilon}_{yy} & 0 \\ 0 & 0 & \dot{\epsilon}_{zz} \end{pmatrix} \\
 &= \eta_0 \begin{pmatrix} 0 & \left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right) & \left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x}\right) \\ \left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right) & 0 & \left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y}\right) \\ \left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x}\right) & \left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y}\right) & 0 \end{pmatrix} + \eta_0 \begin{pmatrix} 2\frac{\partial v_x}{\partial x} & 0 & 0 \\ 0 & 2\frac{\partial v_y}{\partial y} & 0 \\ 0 & 0 & 2\frac{\partial v_z}{\partial z} \end{pmatrix} \quad (2.133)
 \end{aligned}$$

The first term on the right-hand side will be called *shear stress tensor* $\boldsymbol{\tau}_{\text{shear}}$; the second term is the (deviatoric) *normal stress tensor*¹¹ $\boldsymbol{\tau}_n$.

It may be instructive to analyze the relations between stress and strain rate in more detail for the particular scenario depicted in Fig. 2.19. The sample is thought to be subdivided into a stack of layers of infinitesimal thickness. Each layer is characterized by a certain flow velocity in x direction increasing along the z -axis. Because of this gradient, the layers are sheared by friction forces arising from the difference of the velocities of adjacent layers.

The friction forces acting between layers can be understood on a molecular basis not unlike the explanation of pressure in kinetic gas theory. In a fluid, there is

¹¹ In the case of *compressible* fluids, the so-called *second viscosity coefficient* λ must be taken into account in addition. The diagonal elements are then extended to $\tau_{ii} = \lambda \nabla \cdot \mathbf{v} + 2\eta_0 \partial v_i / \partial i$, where $i = x, y, z$ [21].

permanent exchange of molecules between the layers. Owing to the different flow velocities, the momentum component along the flow direction will vary as well. Exchange therefore means momentum transfer. The force acting on the layers is then the momentum transfer per time unit.

For example, a molecule entering a slower layer from above will feed some extra momentum into that slice. As a consequence, there will be a drag force in $+x$ direction on the fluid element under consideration. Likewise, a molecule transferred to the fluid element from below will be accelerated so that the drag force on the element will be in $-x$ direction. As a result, the fluid element will be sheared by the force pair established in this way as illustrated in Fig. 2.19.

The flow field assumed in Fig. 2.19 is characterized by the components $v_x = v_x(z)$, $v_y = 0$, and $v_z = 0$. According to Eq. (2.132), the shear strain rate tensor consequently takes the form

$$\dot{\hat{\epsilon}} = \begin{pmatrix} 0 & 0 & \frac{1}{2} \frac{\partial v_x}{\partial z} \\ 0 & 0 & 0 \\ \frac{1}{2} \frac{\partial v_x}{\partial z} & 0 & 0 \end{pmatrix} \quad (2.134)$$

The only nonvanishing elements are due to derivatives by ∂z : $\dot{\epsilon}_{xz} = \dot{\epsilon}_{zx} = \frac{1}{2} \frac{\partial v_x}{\partial z}$. The upper surface of the volume element is defined by the normal vector $\mathbf{n}_{+z}$ along the $+z$ -axis. The *shear rate vector* of that surface is thus

$$\dot{\hat{\epsilon}}(\mathbf{n}_{+z}) = \dot{\hat{\epsilon}} \mathbf{n}_{+z} = \begin{pmatrix} 0 & 0 & \frac{1}{2} \frac{\partial v_x}{\partial z} \\ 0 & 0 & 0 \\ \frac{1}{2} \frac{\partial v_x}{\partial z} & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} \frac{1}{2} \frac{\partial v_x}{\partial z} \\ 0 \\ 0 \end{pmatrix} \quad (2.135)$$

It points to the right along the $+x$ -axis if the velocity gradient along the z -axis is positive (as assumed in Fig. 2.19).

Likewise, for the particular scenario depicted in Fig. 2.19, the nonvanishing shear stress tensor elements defined by the first term on the right-hand side of Eq. (2.133) are

$$\tau_{xz} = \tau_{zx} = \eta_0 \frac{\partial v_x}{\partial z} \quad (2.136)$$

so that the *shear stress tensor* τ_{shear} reads in matrix form

$$\tau_{\text{shear}} = \begin{pmatrix} 0 & 0 & \eta_0 \frac{\partial v_x}{\partial z} \\ 0 & 0 & 0 \\ \eta_0 \frac{\partial v_x}{\partial z} & 0 & 0 \end{pmatrix} \quad (2.137)$$

The *shear stress vector* $\boldsymbol{\tau}_{\text{shear}}(\mathbf{n}_{+z})$,

$$\boldsymbol{\tau}_{\text{shear}}(\mathbf{n}_{+z}) = \tau_{\text{shear}} \mathbf{n}_{+z} = \begin{pmatrix} 0 & 0 & \eta_0 \frac{\partial v_x}{\partial z} \\ 0 & 0 & 0 \\ \eta_0 \frac{\partial v_x}{\partial z} & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} \eta_0 \frac{\partial v_x}{\partial z} \\ 0 \\ 0 \end{pmatrix} \quad (2.138)$$

thus points in $+x$ direction.

The lower interface of the fluid element is analogously defined by a normal vector $\mathbf{n}_{-z}$ aligned in $-z$ direction. The shear stress vector thus acts in $-x$ direction:

$$\boldsymbol{\tau}_{\text{shear}}(\mathbf{n}_{-z}) = \tau_{\text{shear}} \mathbf{n}_{-z} = \begin{pmatrix} 0 & 0 & \eta_0 \frac{\partial v_x}{\partial z} \\ 0 & 0 & 0 \\ \eta_0 \frac{\partial v_x}{\partial z} & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ -1 \end{pmatrix} = \begin{pmatrix} -\eta_0 \frac{\partial v_x}{\partial z} \\ 0 \\ 0 \end{pmatrix} \quad (2.139)$$

The volume element in Fig. 2.19 is thus sheared by a pair of counteracting shear stress vectors.

The careful reader may observe a little problem at this point: The combined action of the shear stress pair $\boldsymbol{\tau}_{\text{shear}}(\mathbf{n}_{+z})$ and $\boldsymbol{\tau}_{\text{shear}}(\mathbf{n}_{-z})$ simultaneously gives rise to a torque acting on the fluid element. That is, a compensatory torque of the same magnitude but acting in the opposite direction must exist for the scenario depicted in Fig. 2.19. This counteracting torque can be produced by a pair of shear stress vectors $\boldsymbol{\tau}_{\text{shear}}(\mathbf{n}_{+x})$ and $\boldsymbol{\tau}_{\text{shear}}(\mathbf{n}_{-x})$ acting along the $-z$ and $+z$ directions on the interfaces with the normal vectors $\mathbf{n}_{+x}$ and $\mathbf{n}_{-x}$. Actually, the calculation analogous to Eqs (2.138) and (2.139) but with the normal vectors replaced by $\mathbf{n}_{+x}$ and $\mathbf{n}_{-x}$, respectively, predicts such a torque. Where does it come from? From the physicist's point of view, it will be established in the last resort by the countermoving cover plates at the top and bottom of a corresponding experimental setup. These cover plates confine the fluid and *force* it to follow the straight streamlines anticipated in Fig. 2.19.

The third set of interface planes orthogonal to the previous two is defined by the normal vectors $\mathbf{n}_{+y}$ and $\mathbf{n}_{-y}$. It can readily be seen that the shear stress vectors $\boldsymbol{\tau}_{\text{shear}}(\mathbf{n}_{+y})$ and $\boldsymbol{\tau}_{\text{shear}}(\mathbf{n}_{-y})$ vanish under the conditions assumed here: There is neither a flow component nor a velocity gradient along the y -axis.

This section provided a first introduction to issues of flow properties. Dynamics of incompressible fluids will be described and demonstrated in Chap. 4 in more detail.

2.4 From Newton's Equation of Motion to the Langevin Equation

Soft matter is usually composed of molecules or molecular complexes with numerous internal degrees of motional freedom. Apart from the three rotational degrees of freedom about the axes of the laboratory frame of reference and the three

translational degrees of freedom of the center of mass along the axes of this frame, there may be a manifold isomerism of molecular conformations. The attempt to describe molecular dynamics in all details would therefore be unduly complicated. However, as will be shown in the following, there are simplifying concepts permitting the derivation of manageable laws as far as relevant for typical measurands in experiments.

Let us start at the most fundamental level of dynamics, that is, Newton's equation of motion of a "tagged" atom labeled by number i . The mass be m_i and the position vector $\mathbf{r}_i = \mathbf{r}_i(t)$. The general equation of motion reads then

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \sum_{j \neq i} \mathbf{F}_{i,j}(t) \quad (2.140)$$

The *inertial* (or *d' Alembert*) force on the left side is an apparent force and is equal to the sum of all real forces acting on the particle. The interactions with other atoms are numbered by the subscript j . Supplemented by initial conditions for the positions and velocities of all interacting particles, it defines the trajectory of the tagged atom as a function of time as far as mathematically tractable (with the reservation mentioned in footnote 5 and discussed below).

The tagged atom may be part of a molecule, and the molecule will be part of an ensemble of other molecules within the soft-matter system. The forces acting on an atom can therefore be subdivided into intra- and intermolecular forces, so that the right-hand side of the equation of motion can be detailed according to

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \sum_{k \neq i} \mathbf{F}_{i,k}^{\text{intra}}(t) + \sum_l \mathbf{F}_{i,l}^{\text{inter}}(t) \quad (2.141)$$

The subscript k refers to atoms interacting with atom i within the same molecule, and the subscript l to all interaction partners on other molecules. Interactions with external fields such as gravitation or electrodynamic radiation are normally of negligible importance and are therefore not considered here.

The effective potential an atom "sees" is a function of the constellation of all interacting atoms and molecules. If there are N interacting particles, the potential acting on atom i can be approximated by a sum of pair interactions $W_i \approx \sum_{j \neq i} W_{i,j}(\mathbf{r}_i, \mathbf{r}_j)$ in the simplest case (compare footnote 1). In an ensemble of say 10^{23} molecules, that is, the order of magnitude of Avogadro's constant, N will be such an enormous number that any attempt to establish the function W_i appears to be hopeless. That is, the set of Newton's equation of motion, Eq. (2.140), cannot be written down explicitly not to mention be solved unless we restrict ourselves to intramolecular forces in molecules consisting of only a few atoms. However, even then, there would be no exact algebraic solution of Eq. (2.140) for $N \geq 3$. Apart from the fact that three- or more-body problems are analytically unsolvable, there is a tendency to deterministic-chaotic dynamics [19]. The slightest fluctuation of the

initial conditions will result in entirely diverging solutions even if approached numerically. There is no operational way to reach analytical results based on such an atomistic perspective.

2.4.1 Strategy for a Better Tractability

To avoid the many-particle dilemma, the strategy is (a) to employ *effective* quantities which are the global result of innumerable molecular interactions and collisions, (b) to use a *coarse-grained* picture by replacing the potential energy W by thermodynamic potentials implying entropy effects, and (c) to postulate *randomness* of molecular collisions. One may suspect that one catches a tartar by such incisive measures. This is not really the case. In the contrary, the objective is to derive concepts for the macroscopic dynamic behavior of matter. This stipulates global views on all molecular processes that do not directly and individually affect macroscopic dynamics.

The consequence of simplification (a) is that forces formulated on this basis are no longer conservative. The nonconservative approximation implies dissipation of energy to countless background degrees of freedom. Energy is “lost” (dissipated) to a “bath” formed by all degrees of freedom not under specific consideration. Here, the bath can be assumed to be large enough to permit the neglect of any temperature changes. The introduction of a thermodynamic bath means that the principle of microscopic reversibility is abandoned: Processes must then be considered to be *irreversible* in the thermodynamic sense. The processes can only be reversed at the expense of work compensating the increase of entropy of the bath. The effective forces resulting in this way depend on temperature, concentration, and parameters specific for the material such as viscosity and friction coefficient.

The second point, (b), means that instead of single particles, ensembles of atoms or molecules are considered throughout. With the aid of probabilistic treatments, statistical physics provides concepts to treat *average* system properties. Examples are equilibrium distributions of macromolecular conformations based on the configurational entropy of the macromolecule itself and the mixing entropy with a solvent if present. This is the basis of our understanding of the so-called rubber elasticity or the cooperativity of the helix–coil transition of polypeptides, for instance [7].

Finally, the third point, (c), leads directly back to an equation of motion: It is not necessary to know any time dependence of intermolecular forces in the sense of the actual and chronological sequence of molecular impacts. It suffices to know that it is almost perfectly stochastic in the Markov sense. A *Markov process* is characterized by a vanishing correlation to its prehistory [22]. Practically, this property can be taken for granted in the case of intermolecular forces. Furthermore, intermolecular forces acting on different molecules can be assumed to be uncorrelated. Therefore, the actual time dependence of intermolecular forces cannot and need not be predicted in applications.

Consider now the following scenario: Brownian particles, this can be colloid particles, macromolecules, or simply larger solute molecules, are dissolved in a solvent of small molecules and are permanently bombarded by the surrounding solvent molecules. The result is Brownian motion. The particles will be displaced entirely randomly. For this process, two time scales can be distinguished. Firstly, the time how long an impact between a solvent molecule and a solute molecule takes is in the range $\tau_{\text{imp}} = 10^{-13} \dots 10^{-12}\text{s}$ for typical low-viscosity liquids. Let us call it the *impact time*. Actually it is not much longer than a typical vibration period of a small molecule. It is so-to-speak the elementary time unit of molecular processes.

The second time scale characterizes the effective momentum transfer between a Brownian particle and the many solvent molecules surrounding it. As a consequence, the Brownian particle moves with a randomly varying velocity both with respect to magnitude and direction. Since any perceptible change of the momentum requires numerous molecular impacts, the time scale on which the velocity of the Brownian particle fluctuates is much longer than the impact time. The autocorrelation function of an entirely random process of the Markov type is known to decay exponentially.¹² For the velocity autocorrelation function of the Brownian particle, we may thus write

$$\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle = \langle v^2 \rangle \exp\left(-\frac{|t|}{\tau_v}\right) \quad (2.142)$$

where $\tau_v \gg \tau_{\text{imp}}$ is the velocity correlation time defined by

$$\tau_v = \frac{1}{\langle v^2 \rangle} \int_0^\infty \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle dt \quad (2.143)$$

(see Eq. 1.7).

2.4.2 Fluctuations of Intermolecular Forces

Before the background outlined above, both the velocity of a Brownian particle and the sum of all intermolecular forces acting on it can be decomposed in slowly and fast-varying contributions according to

¹² For an explanation of exponential correlation functions, see Sect. 1.1.3. A well-known example for this sort of statistics is radioactive decay with the mean lifetime as the time constant. Note that Eq. (2.142) follows from the Langevin equation as well if supplemented by an inertial term as will be shown below in the context of Eq. (2.161) and the explicit expression for the time constant τ_v given in Eq. (2.162).

$$\mathbf{v}(t) = \bar{\mathbf{v}}(t) + \mathbf{v}'(t) \quad (2.144)$$

and

$$\sum_j \mathbf{F}_j^{\text{inter}}(t) = \overline{\mathbf{F}^{\text{inter}}}(t) + \mathbf{f}(t) \quad (2.145)$$

respectively. The fast-fluctuating terms, $\mathbf{v}'(t)$ and $\mathbf{f}(t)$, are the consequence of the stochastic impacts of the surrounding molecules on the tagged particle. On the other hand, the terms with slow time dependence,

$$\begin{aligned} \bar{\mathbf{v}}(t) &\equiv \langle \mathbf{v} \rangle_{\tau_{\text{imp}} \ll t_{\text{av}} \ll \tau_v} \\ \overline{\mathbf{F}^{\text{inter}}}(t) &\equiv \left\langle \sum_j \mathbf{F}_j^{\text{inter}} \right\rangle_{\tau_{\text{imp}} \ll t_{\text{av}} \ll \tau_v} \end{aligned} \quad (2.146)$$

are the global result from numerous molecular impacts on the tagged particle on a time scale much longer than the molecular collision time, $t \gg \tau_{\text{imp}} = 10^{-13} \dots 10^{-12}$ s. The slowly varying terms are therefore given as averages over an interval t_{av} chosen somewhere between the molecular collision time and the velocity correlation time, that is, $\tau_{\text{imp}} \ll t_{\text{av}} \ll \tau_v$.

2.4.2.1 Stochastic Force

The fast-fluctuating force $\mathbf{f}(t)$ on the tagged particle, the so-called *stochastic force*, results from a high collision rate with other molecules. The directions of these impacts are random, and many momentum transfer events are superimposed at a time. According to the *central-limit theorem*,¹³ the distribution of the resultant net force will therefore be a *Gaussian* function. Gaussian distributions are completely determined by the first two moments.¹⁴ The first moment vanishes due to the stochastic character of the force:

¹³ The *central-limit theorem* [22] states that sums of the form $\sigma_N = \sum_{j=1}^N \xi_j$ which are repeatedly formed of N random and statistically independent variables ξ_j are distributed according to a Gaussian function in the limit $N \rightarrow \infty$. An important characteristic of this theorem is that the random distribution, with which the variables vary, may be arbitrary provided that it is the same for each variable and that its second moment is finite.

¹⁴ The ν -th moment of a distribution function $g(\Omega)$ of a variable Ω is defined by $M_\nu = \int_{-\infty}^{\infty} g(\Omega) \Omega^\nu d\Omega$. If the distribution is even, all odd moments vanish and vice versa. The second moment is the mean-square fluctuation of the variable. In the case of a Gaussian distribution (which is an even function), the second moment determines all higher moments according to $M_4 = 3M_2^2$, $M_6 = 15M_2^3$, $\dots$ or generally $M_{2j} = 1 \cdot 3 \cdot 5 \dots (2j-1)M_2^j$ where j is a natural number.

$$\langle \mathbf{f} \rangle = 0 \quad (2.147)$$

The angle brackets indicate an average over the ensemble of particles or, equivalently, over the time evolution of a single particle. The second moment is represented in the form of a correlation function linking the stochastic forces on two particles labeled by the numbers i and j at the respective times t' and t'' :

$$\langle \mathbf{f}_i(t') \cdot \mathbf{f}_j(t'') \rangle = 6\zeta_0 k_B T \delta_{ij} \delta(t' - t'') \quad (2.148)$$

In terms of Cartesian components represented by the respective subscripts $\alpha = x, y, z$ and $\beta = x, y, z$, Eq. (2.148) can be expressed in the form

$$\langle f_{i,\alpha}(t') f_{j,\beta}(t'') \rangle = 2\zeta_0 k_B T \delta_{ij} \delta_{\alpha\beta} \delta(t' - t'') \quad (2.149)$$

The Kronecker symbol δ_{ij} is defined by $\delta_{ij} = 0$ for $i \neq j$ and $\delta_{ii} = 1$ for $i = j$. It indicates that there is no correlation between forces acting on different particles. Likewise, the symbol $\delta_{\alpha\beta}$ is specified by $\delta_{\alpha\beta} = 0$ for $\alpha \neq \beta$ and $\delta_{\alpha\alpha} = 1$ for $\alpha = \beta$. It expresses the absence of any correlation between different Cartesian components of the stochastic force. This in particular refers to the orientation of the forces at different times.

Finally, Dirac's delta function with the properties $\delta(t' - t'') = 0$ for $t' \neq t''$, $\delta(t' - t'') \rightarrow \infty$ for $t' = t''$, and $\int_{-\infty}^{\infty} \delta(t) dt = 1$ implies that stochastic forces acting at different times on a particle are uncorrelated. In other words, the correlation time which is expected to be of the order of the molecular collision time $\tau_{\text{imp}} \approx 10^{-13} \dots 10^{-12}$ s is set zero relative to the time scale of interest, that is, $t \gg \tau_{\text{imp}}$.

The prefactors $2\zeta_0 k_B T$ and $6\zeta_0 k_B T$ in Eqs. (2.149) and (2.148), respectively, have been chosen in such a way that the second moment is compatible with the Einstein relation for the mean-square displacement of Brownian particles. To demonstrate this, we refer to the Langevin equation to be formulated in the subsequent Sect. 2.4.3: In the absence of internal degrees of freedom, this equation of motion is of the simple form:

$$\zeta_0 \mathbf{v} = \zeta_0 \frac{\partial \mathbf{r}}{\partial t} = \mathbf{f} \quad (2.150)$$

where ζ_0 is the *friction coefficient* of the particle in the surrounding medium (for a detailed expression for the friction coefficient, see Eq. 2.156).

Assuming that the particle is initially located at the origin, $\mathbf{r}(0) = 0$, the integral of Eq. (2.150) reads

$$\mathbf{r}(t) = \frac{1}{\zeta_0} \int_0^t \mathbf{f}(t') dt' \quad (2.151)$$

The mean-square displacement is then

$$\langle \mathbf{r}^2(t) \rangle = \frac{1}{\zeta_0^2} \left\langle \int_0^t \mathbf{f}(t') dt' \cdot \int_0^t \mathbf{f}(t'') dt'' \right\rangle = \frac{1}{\zeta_0^2} \int_0^t dt' \int_0^t dt'' \langle \mathbf{f}(t') \cdot \mathbf{f}(t'') \rangle \quad (2.152)$$

Substituting Eqs. (2.148) into (2.152) gives

$$\langle \mathbf{r}^2(t) \rangle = \frac{6k_B T}{\zeta_0} t = 6Dt \quad (2.153)$$

This and the relation between the translational diffusion coefficient D and the friction coefficient ζ_0 ,

$$D = \frac{k_B T}{\zeta_0} \quad (2.154)$$

are known as *Einstein relations*. They will be discussed in more detail in Sect. 2.5.4.1.

2.4.2.2 Viscous Drag

The slowly fluctuating intermolecular force $\overline{\mathbf{F}^{\text{inter}}}$ on a Brownian particle assumed in Eq. (2.145) always counteracts the instantaneous velocity of the particle: When the particle is in motion, the momentum change by molecular impacts is greater on the advancing forefront than on the reverse side. In the average, there is consequently a net force tending to slow up the Brownian particle. This is the friction force or viscous drag always acting in a direction opposite to that of the velocity. It will vanish only if the velocity is zero. Therefore, the friction force must be a homogeneous function of $\bar{\mathbf{v}}$. Expanding the friction force around $\bar{\mathbf{v}} = 0$ by a Taylor series leads in linear approximation to

$$\overline{\mathbf{F}^{\text{inter}}} \approx -\zeta_0 \bar{\mathbf{v}} \quad (2.155)$$

A functional relationship well known from *Stokes' law* according to which the friction coefficient is given as

$$\zeta_0 = 6\pi\eta_0 a_h \quad (2.156)$$

η_0 is the (dynamic) viscosity of the solvent, and a_h is the hydrodynamic (or Stokes) radius of the particle. The hydrodynamic radius is defined as the radius of a sphere that would diffuse with the same rate as the Brownian particle the shape of which does not need to be necessarily spherical. For a derivation of Stokes' law, see Sect. 4.7.

2.4.3 Langevin Equation

Let us resume the discussion of the equation of motion in Eq. (2.141). The left side represents the inertial term. Due to viscous drag, the motion of a Brownian particle will be “overdamped” as one says. There is no free translation of the particle on the time scale of interest. The inertial term can therefore be set zero on average, $\langle d^2\mathbf{r}/dt^2 \rangle \approx 0$, where the average refers to a time scale $t \gg \tau_{\text{imp}} \approx 10^{-13}$ s. Combining this with Eqs. (2.141), (2.145), and (2.155) leads to the *Langevin equation* for atom i of a Brownian particle:

$$\sum_{k \neq i} \mathbf{F}_{i,k}^{\text{intra}} - \zeta_0 \bar{\mathbf{v}}_i + \mathbf{f}_i = 0 \quad \text{for } t \gg \tau_{\text{imp}} \quad (2.157)$$

In the absence of external fields, the Langevin equation consists of three terms, the sum of the *intramolecular elastic forces* $\mathbf{F}_{i,k}^{\text{intra}}$, the *friction force* $-\zeta_0 \bar{\mathbf{v}}_i$, and the *stochastic force* $\mathbf{f}_i$. The vanishing inertial term is the reason why solutions of this equation of motion are steadily decaying with time in contrast to those adequate for oscillatory systems.

2.4.4 Velocity Correlation Function

The exponential velocity correlation function assumed in Eq. (2.142) directly follows from the Langevin equation if the inertial term is reintroduced in order to extend the relevant time scale down to $t \approx \tau_{\text{imp}}$. Since this consideration refers to the translational motion of a Brownian particle in general and not to intramolecular dynamics, we may omit the elastic term and the subscript i . Modified in this way, the Langevin equation including the inertial term reads

$$m \frac{\partial \bar{\mathbf{v}}}{\partial t} = -\zeta_0 \bar{\mathbf{v}} + \mathbf{f} \quad \text{for } t > \tau_{\text{imp}} \quad (2.158)$$

We multiply this equation by the velocity of the tagged Brownian particle at time 0, $\bar{\mathbf{v}}(0)$, and perform an ensemble average. The vectors $\bar{\mathbf{v}}(0)$ and $\mathbf{f}(t)$ are independent of each other and are therefore uncorrelated:

$$\langle \bar{\mathbf{v}}(0) \cdot \mathbf{f}(t) \rangle = \langle \bar{\mathbf{v}}(0) \rangle \cdot \langle \mathbf{f}(t) \rangle = 0 \quad (2.159)$$

Taking this into account, the result is the linear differential equation

$$\frac{d}{dt} \langle \bar{\mathbf{v}}(0) \cdot \bar{\mathbf{v}}(t) \rangle = -\frac{\zeta_0}{m} \langle \bar{\mathbf{v}}(0) \cdot \bar{\mathbf{v}}(t) \rangle \quad (2.160)$$

with the exponential solution

$$\langle \bar{\mathbf{v}}(0) \cdot \bar{\mathbf{v}}(t) \rangle = \langle \bar{\mathbf{v}}^2 \rangle \exp(-t/\tau_v) \quad (2.161)$$

for times $t \geq 0$. The time constant is given as the quotient of the particle mass and the friction coefficient:

$$\tau_v = \frac{m}{\zeta_0} \quad (2.162)$$

Velocity correlation functions are also of interest in the context of transport coefficients. In the long-time limit, the *self-diffusion coefficient* to which we will refer in the following section is related to the velocity correlation function by

$$D = \frac{1}{3} \int_0^\infty \langle \bar{\mathbf{v}}(0) \cdot \bar{\mathbf{v}}(t) \rangle dt \quad (2.163)$$

This is an example of a *Green/Kubo relation* linking *transport coefficients* to time-correlation functions of the relevant fluctuating quantities as already mentioned in Sect. 1.2. Inserting Eqs. (2.161) and (2.162) and evaluating the mean-square velocity $\langle \bar{\mathbf{v}}^2 \rangle$ from the expression for the mean kinetic energy of a particle in thermal equilibrium,

$$W_{\text{kin}} = \frac{3}{2} k_B T = \frac{1}{2} m \langle \bar{\mathbf{v}}^2 \rangle \quad (2.164)$$

lead to the *Einstein relation*

$$D = \frac{k_B T}{\zeta_0} \quad (2.165)$$

A detailed discussion will follow in Sect. 2.5.4.1.

2.5 Brownian Motion, Self-Diffusion, Interdiffusion, and Rotational Diffusion

The term *diffusion* in general addresses transport of particles self-propelled by thermal energy. The random character of diffusion arises from the multiparticle nature of thermal motions. The particles can be molecules or larger objects subjected to frequent molecular collisions with molecules in the environment. If the particles are large enough to be visible directly or in a microscope, one

speaks of classical *Brownian motion*. However, this term is usually generalized to any sort of thermally induced molecular dynamics irrespective of the particle size.

Diffusion can strongly be affected by *gradients of the chemical potential* as it will be the case for solutes in solution with an inhomogeneous concentration distribution [23]. The consequence of such gradients will be that the transport of the solute molecules is expedited. On these grounds, the diffusion coefficient characterizing the spread of the solute molecules in space toward a homogeneous distribution will depend on the local concentration (see below).

For vanishing gradients of the chemical potential, one speaks of *self-diffusion*. Somewhat imprecisely, the same situation is often referred to as plainly *diffusion* if not specified otherwise. Uniform distributions of the chemical potential are not only expected for neat systems. Isotopically or otherwise labeled tracer molecules *interdiffusing* unlabeled molecules of the same species belong to this category as well, since their presence will not or only negligibly affect the chemical potential.

Diffusion is normally adverted to *translational* displacements. Since thermal energy likewise mediates molecular *reorientations*, a respective analogue exists and is termed *rotational diffusion*.

As a further transport mechanism with random features, we will occasionally refer to *hydrodynamic dispersion*. This is a superposition of diffusion in the Brownian sense and laminar shear flow also known as *Taylor/Aris dispersion*. As an additional randomization element, the potentially tortuous nature of the geometry of the confining medium may play a role. In this case, one speaks of *mechanical dispersion* [24].

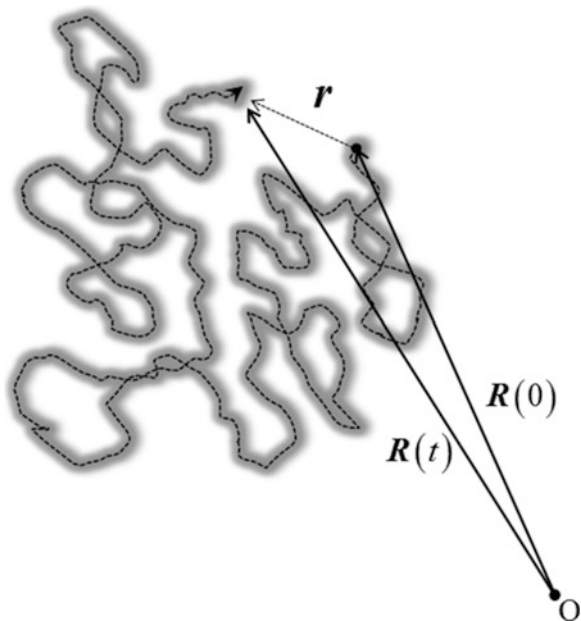
2.5.1 Diffusion Equations and Propagators

Figure 2.20 schematically shows a random walk leading to a particle displacement $\mathbf{r} = \mathbf{R}(t) - \mathbf{R}(0)$. As a matter of course, the displacements reached in a given time interval t vary from random walk to random walk. One therefore often uses the *mean-square displacement* $\langle r^2 \rangle$ as an average quantity for the characterization of the extension of random walks. The angle brackets indicate an ensemble average. Despite the random, that is, unpredictable element intrinsic to all trajectories of this sort, the statistics of random walks can be very different depending on the mutual interaction of molecules, the interaction with confining pore walls, and the topology of the pore space. So the question arises, how to characterize the distribution of trajectories analytically [25].

The crucial function usually employed for this purpose is the *propagator*¹⁵ $P(\mathbf{r}, t)$, that is, the probability density for a displacement $\mathbf{r}$ in a time interval t . The probability that a particle is displaced into the volume element d^3r in a distance $\mathbf{r}$ in a time interval

¹⁵ Synonymous expressions in use are *probability distribution* and *probability density function*.

Fig. 2.20 Schematic representation of the trajectory and the displacement of a random walker



t is consequently given by $P(\mathbf{r}, t)d^3r$. The trajectory is thought to start at the origin and to end in the volume element d^3r around the position in a distance $\mathbf{r}$.

The stochastic processes of interest are normally *stationary*, that is, the time t can represent any interval of this length irrespective of the absolute time. Other conditions often assumed for stochastic mechanisms, namely, *homogeneity* and *isotropy* of the medium in which the random walk takes place are more critical. In complex materials such as porous systems, the propagator $P(\mathbf{r}, t)$ must in principle be specified for a certain starting position relative to the pore space geometry.

Since such detailed considerations are of little tractability, one refers often to the *mean propagator* which is the average over all possible starting positions in a complex medium [26]. The mean propagator can be indicated by a *scalar* representation of the displacement, that is, by the position- and orientation-independent magnitude instead of the vector $\mathbf{r}$.

The full propagator given as an analytical function may contain more information than needed for the characterization and classification of random walk trajectories. In this case, it may be convenient to consider the *mean-square displacement* defined by

$$\langle r^2 \rangle = \int r^2 P(\mathbf{r}, t) d^3r \quad (2.166)$$

where the integral covers the whole space. Synonymous expressions for the mean-square displacement are *variance* or *second moment* of the propagator $P(\mathbf{r}, t)$.

2.5.1.1 Self-Diffusion

The analytical forms of self-diffusion propagators can be obtained as solutions of differential equations with the initial condition $P(\mathbf{r}, 0) \propto \delta(\mathbf{r})$, where $\delta(\mathbf{r})$ is Dirac's delta function. *Fick's second law* for self-diffusion, also called the ordinary diffusion equation,

$$\frac{\partial P(\mathbf{r}, t)}{\partial t} = D \nabla^2 P(\mathbf{r}, t) \quad (2.167)$$

in combination with boundary conditions depending on the system under consideration is valid for *isotropic* and *homogeneous* fluid media. The quantity D is the (translational) diffusion coefficient which is assumed to be constant in space (but not necessarily with respect to time). Assuming an infinitely extended medium of Euclidian dimension $d (= 1, 2, 3)$, the solution of Eq. (2.167) for the above initial condition is the Gaussian propagator:

$$P(r, t) = \frac{1}{(4\pi Dt)^{d/2}} \exp\left\{-\frac{r^2}{4Dt}\right\} \equiv \frac{1}{(4\pi Dt)^{d/2}} \exp\left\{-\frac{x^2 + y^2 + z^2}{4Dt}\right\} \quad (2.168)$$

The second moment is then

$$\langle r^2 \rangle = 2dDt \quad (2.169)$$

Inserting the Einstein relation Eq. (2.165) gives the d -dimensional *mean-square displacement of Brownian particles* with the friction coefficient ζ_0 as a function of time:

$$\langle r^2 \rangle = 2d \frac{k_B T}{\zeta_0} t \quad (2.170)$$

Figure 2.21 shows a plot of this propagator for the x component of the displacements. The mean-square displacement is a linear function of time provided that D is a constant in time. The linear time dependence of Eq. (2.169) represents *normal diffusion* as will be discussed below in more detail.

2.5.1.2 Solute Diffusion

Diffusion of solute molecules in solutions with an inhomogeneous concentration distribution $c = c(\mathbf{R}, t)$ can be described with the aid of *Fick's second law* in the version

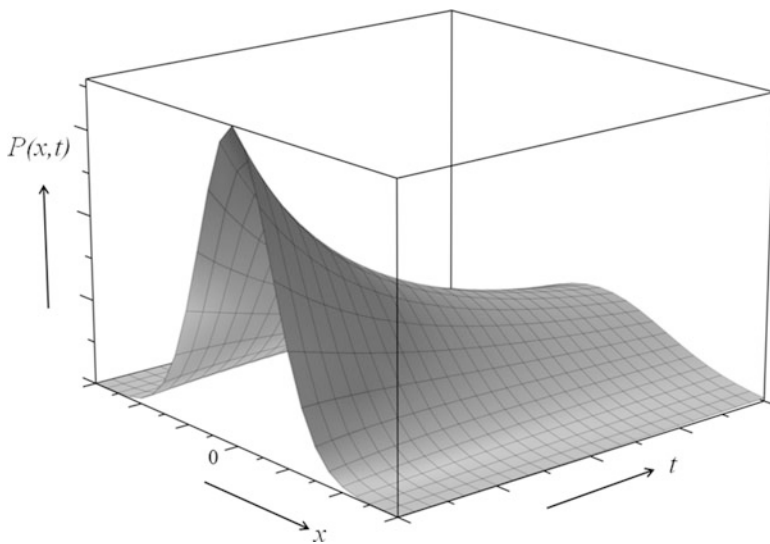


Fig. 2.21 Schematic plot of the Gaussian propagator given in Eq. (2.168) as a function of the x coordinate and time t (all variables in arbitrary units)

$$\frac{\partial c}{\partial t} - \nabla \cdot (D \nabla c) = 0 \quad (2.171)$$

Here, we have replaced the probability density $P(\mathbf{r}, t)$ depending on the *displacement* $\mathbf{r}$ by the solute concentration $c(\mathbf{R}, t)$ which is a function of the *location* $\mathbf{R}$. This is justified since the propagator can be interpreted formally as a concentration of the tagged diffusing particles. As mentioned above, $P(\mathbf{r}, t)$ evolves starting from a delta function distribution about the origin at time 0 so that the displacement $\mathbf{r}$ is equivalent to the location $\mathbf{R}$.

More generally, in nonequilibrium situations, the solute concentration and consequently the chemical potential will be a function of the position $\mathbf{R}$ and, as a consequence of diffusive equilibration, of time t . The local diffusion coefficient D will therefore depend on the concentration as well. This is the reason of the special analytical form of the second term in Eq. (2.171), where ∇c is the local gradient of the concentration. The initial condition $c = c(\mathbf{R}, 0)$ can be any well-defined distribution of the solute concentration [23]. As an example, a steplike initial distribution will be considered in Sect. 3.3.1.2.

2.5.1.3 Anomalous Propagators

A generalization of the self-diffusion propagator Eq. (2.168) for versions with second moments depending on time according to nonlinear power laws is the *fractional diffusion equation* for one dimension [25]:

$$\frac{\partial P(x, t)}{\partial t} = {}_0R_t^{1-\kappa} D_\kappa \frac{\partial^2}{\partial x^2} P(x, t) \quad (2.172)$$

where ${}_0R_t^{1-\kappa}$ is the *Riemann/Liouville operator* and D_κ is the generalized diffusion coefficient which is of dimension $\text{m}^2/\text{s}^\kappa$. κ is an exponent the meaning of which will become obvious below. In the displacement limit $|x| \gg \sqrt{D_\kappa t^\kappa}$, the solution can be expressed by the *stretched Gaussian*

$$P(x, t) \propto \frac{1}{\sqrt{4\pi D_\kappa t^\kappa}} \sqrt{\frac{1}{2-\kappa}} \left(\frac{2}{\kappa}\right)^{\left(\frac{1-\kappa}{2-\kappa}\right)} \left(\frac{|x|}{\sqrt{D_\kappa t^\kappa}}\right)^{-\left(\frac{1-\kappa}{2-\kappa}\right)} \exp\left[-\frac{2-\kappa}{2} \left(\frac{\kappa}{2}\right)^{\frac{\kappa}{2-\kappa}} \left(\frac{|x|}{\sqrt{D_\kappa t^\kappa}}\right)^{\frac{1}{1-\kappa/2}}\right] \quad (2.173)$$

With this propagator, the mean-square displacement obeys

$$\langle x^2 \rangle \propto D_\kappa t^\kappa \quad (2.174)$$

That is, anticipating a given value for the so-called diffusion exponent κ permits one to extend the propagator representation to *anomalous diffusion* as classified in the following section. Note however that a certain species of propagators exists for which the second moment does no longer converge. Examples are *Lévy flights* [27]. In Sect. 7.5.3, we will get back to this sort of problem in the context of *Lévy walks* along surfaces of porous media.

2.5.2 Classification of Normal and Anomalous Diffusion

Displacements of molecules are called *normal* if the propagator is of a Gaussian form (Eq. 2.168) and if the mean-square displacement is a linear function of time (Eq. 2.170). The conditions under which normal diffusion can be expected are (1) the particle trajectories correspond to purely random walks. There are no correlations or memory effects between elementary steps with respect to step rate (no waiting time distribution) and direction (the system is isotropic in the frame of its dimensionality). (2) The particle displacements are unrestricted on the experimental time scale. There are no walls, geometrical confinements, obstacles, or heterogeneities of the medium affecting random walks. The medium in which the molecules are diffusing is homogeneous and “infinite” in principle. Any possible particle trajectory in space is permitted. (3) There is no mutual obstruction of the diffusing particles. (4) There is no superimposed flow of the medium. A typical example of normal displacement behavior is self-diffusion of small molecules in

homogeneous liquids in bulk provided that the root mean-square displacement in the measuring time is much shorter than the sample dimensions.

Systems of interest in nature and technology tend however to be more complex. If any of the above conditions is violated, the consequence will be *anomalous particle transport*. If the time dependence of the mean-square displacement can be represented by a power law,

$$\langle r^2 \rangle \sim t^\kappa. \quad (2.175)$$

the following distinction of cases can be based on the values of the exponent: $\kappa = 0$, *localized*; $0 < \kappa < 1$, *subdiffusive*; $\kappa = 1$, *normal*; $\kappa > 1$, *superdiffusive*; $\kappa = 2$, *ballistic*; and $\kappa = 3$, *turbulent*. Note that the term “diffusion” is used here in a more generalized sense including particle transport phenomena other than displacements by Brownian molecular motions. Rather, transport by flow, hydrodynamic dispersion, and thermal convection in more or less random porous media or even in bulk can be relevant in this context as well.

2.5.2.1 Obstruction Effect

Apart from the above classification based on power law exponents, two principally different categories of anomalous particle transport must be distinguished with respect to the origin of the anomalies. Let us first consider *Gaussian propagators* as they result for homogeneous media from Fick’s diffusion equation. Instead of a constant diffusion coefficient D , we now assume that this parameter is modified by a certain time dependence. The mean-square displacement

$$\langle r^2(t) \rangle = 6D_{\text{mod}}(t)t \quad (2.176)$$

thus becomes anomalous in the sense defined above. Notabene, this sort of anomaly does not conflict with the fact that the propagator is still of a Gaussian shape for a given time. Replacing the diffusion coefficient in the Gaussian propagator given in Eq. (2.168) by a coefficient with a certain time dependence $D_{\text{mod}} = D_{\text{mod}}(t)$ and inserting this propagator into Eq. (2.167) readily demonstrates that this generalization is inherent to Fick’s diffusion equation indeed.

As an example of this sort of diffusive anomaly, Rouse modes of polymers will be discussed in Sect. 5.4.3.6. The point is that the segments of polymer chains obstruct each other as a consequence of chain connectivity and excluded volume. Another example is the so-called *single-file diffusion* process of molecules in straight and tight pores not permitting molecules to pass each other. An illustration can be found in Fig. 2.22. On a short enough length scale relative to the extension of the pores, such systems can be considered to be homogeneous. The sole source of anomalies is then the mutual obstruction of molecules. The mutual hindrance

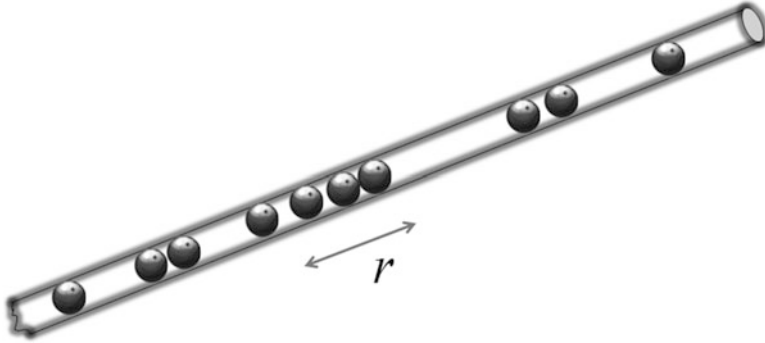


Fig. 2.22 Illustration of the single-file constraint giving rise to anomalous diffusion of particles in *thin pore channels* as an example for the obstruction effect

increases with time and displacement so that the modified diffusion coefficient *decreases*. The consequence is a square root, that is, subdiffusive behavior

$$\langle r^2 \rangle \propto D_{\text{mod}}(t)t \propto t^{1/2} \quad (2.177)$$

resulting from the proportionality $D_{\text{mod}} \propto t^{-1/2}$. The different dimensions on the left- and right-hand sides of the proportionality are compensated by the proportionality factors. Corresponding computer simulations demonstrating this law on a certain time scale and its crossover to ordinary Fickian diffusion for wider channels can be found in Refs. [28, 29]. From the point of view of the elementary back-and-forth diffusion steps particles are subjected to, a diffusion *constant* D can be defined which applies *in the absence* of obstruction by other particles. On this basis, Eq. (2.177) can be rewritten as

$$\langle r^2 \rangle \propto (Dt)^{1/2} \quad (2.178)$$

2.5.2.2 Trapping Effect

The second origin of displacement anomalies arises if geometrical restrictions matter in the dimensions in which displacements are considered. This scenario is often circumscribed by *waiting time distributions* due to “traps” where the particles are temporarily kept back or slowed down. The source of diffusion anomalies on this basis will be called *trapping effect*. The consequence is a *non-Gaussian propagator* and a nonlinear time dependence of the mean-square displacement. From the theoretical point of view, the example par excellence is a random walk on a percolation cluster with a potentially fractal structure [30]. Diffusing particles

getting lost in a dead end of the cluster will take a long time until they can escape to the main transport channels as illustrated in Fig. 2.23.

This sort of trapping is expected to be relevant in fluids confined in random porous media and channel networks. Displacements of fluid molecules are then subjected to the tortuosity of the available free space. This and other parameters characterizing random pore spaces will be defined and discussed in Sect. 4.9.1. On a length scale below the *correlation length*¹⁶ but beyond the pore dimension of the available space, mean-square displacements tend to scale in an anomalous way.

In a sense, the trapping effect is also relevant in the reptation mechanism postulated for the snakelike diffusion process of entangled polymers (see Sect. 5.4.6 and Fig. 5.35). If a polymer segment happens to be in a folded or strongly coiled section of the confining tube, it will take a long time until it can escape from that region and proceed to diffuse along the space direction probed by the measuring technique. Temporarily, it will be trapped locally, so that displacements along the measuring direction will be retarded to some degree.

2.5.3 Rotational Diffusion

Rotational diffusion refers to random and continuous reorientations of molecules or particles in an interval τ as a consequence of random thermal collisions. Notabene, in the present context, “rotational diffusion” is to be distinguished from the excitation of steady rotational energy states of molecules. Such excited quantum states are of minor importance in liquids and with larger particles and will therefore not be considered here.

Depending on the investigation method, the particle orientation relative to an external field can be defined by a molecular symmetry axis, an electric dipole moment, or an intramolecular internuclear vector. The initial and final orientations are given by the unit vectors $\mathbf{u}_i$ and $\mathbf{u}_f$, respectively, as illustrated in Fig. 2.24. In the following, these vectors will be expressed by the polar coordinates φ (azimuth angle), ϑ (polar angle), and $r = 1$ length unit relative to the laboratory frame of reference (see Fig. 2.24a).

The rotational counterpart to Fick’s second law for translational diffusion, Eq. (2.167), is

$$\frac{\partial P(\mathbf{u}_i, \mathbf{u}_f, \tau)}{\partial \tau} = D_r \nabla^2 P(\mathbf{u}_i, \mathbf{u}_f, \tau) \quad (2.179)$$

¹⁶ In macroscopically isotropic media, the *correlation length* is defined analogous to the correlation time (see Eq. (1.7), for instance): If $G(r) = \langle \mathbf{A}(r) \cdot \mathbf{B}^*(0) \rangle$ is the spatial correlation function linking two spatial functions $\mathbf{A}(\mathbf{R}_1), \mathbf{B}(\mathbf{R}_2)$ in a distance $\mathbf{r} = \mathbf{R}_2 - \mathbf{R}_1$, the correlation length is given by $\xi = [G(0) - G(\infty)]^{-1} \int_0^\infty [G(x) - G(\infty)] dx$, where x is an arbitrary coordinate of $\mathbf{r}$.



Fig. 2.23 Schematic illustration of the trapping effect on a random walker in a ramified pore space (white). The dotted lines represent two possible trajectories of the random walker across the pore space cluster. If the random walker gets temporarily “trapped” in a dead end or in a side area badly interconnected to the main cluster, it will take a long time until the main transport pathways across the cluster will be rejoined

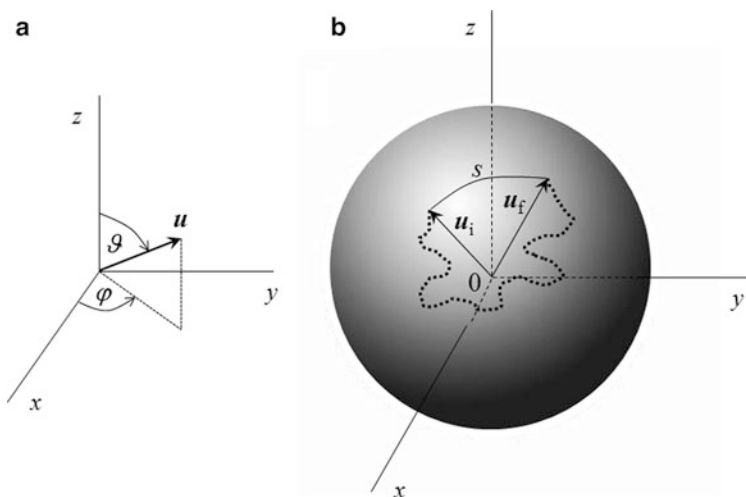


Fig. 2.24 Illustration of rotational diffusion: (a) Definition of the orientation of a molecular axis $\mathbf{u}$ in terms of the polar and azimuthal angles ϑ and φ , respectively, relative to the laboratory frame x , y , z (b) The initial and final orientations of a diffusing particle are represented by the initial and final unit vectors $\mathbf{u}_i$ and $\mathbf{u}_f$, respectively. The “displacement” after a number random reorientation steps is represented by the arc s on the unit sphere around the center 0 (compare the translational counterpart depicted in Fig. 2.20)

where D_r is the *rotational diffusion coefficient* which has the dimension of inverse time. The operator ∇^2 is the Laplace differential operator in terms of the azimuthal and polar angles φ_f and ϑ_f , respectively, of the final particle orientation $\mathbf{u}_f$ (see Eq. 2.182). The rotational propagator $P(\mathbf{u}_i, \mathbf{u}_f, \tau)$ describes the distribution of the final orientations $\mathbf{u}_f$ after the time τ for a given initial orientation $\mathbf{u}_i$.

The initial condition can be expressed by Dirac's delta function as

$$P(\mathbf{u}_i, \mathbf{u}_f, 0) = \delta(\mathbf{u}_f - \mathbf{u}_i) \quad (2.180)$$

As usual with rotation problems, the propagator is best expanded in terms of spherical harmonics $Y_{l,m} = Y_{l,m}(\varphi, \vartheta)$ of degree l and order m :

$$P(\mathbf{u}_i, \mathbf{u}_f, \tau) = \sum_{l,m} c_{l,m}(\tau) Y_{l,m}(\mathbf{u}_f) \quad (2.181)$$

In this way, time and orientation dependences are separated. The Laplace operator in Eq. (2.179) acts selectively on the polar coordinates of the spherical harmonics according to

$$\nabla^2 Y_{l,m}(\varphi_f, \vartheta_f) = \frac{1}{\sin \vartheta_f} \frac{\partial}{\partial \vartheta_f} \left(\sin \vartheta_f \frac{\partial Y_{l,m}(\varphi_f, \vartheta_f)}{\partial \vartheta_f} \right) + \frac{1}{\sin^2 \vartheta_f} \frac{\partial^2 Y_{l,m}(\varphi_f, \vartheta_f)}{\partial \varphi_f^2} \quad (2.182)$$

Note that this is the usual version of the Laplace operator in polar coordinates (see, e.g., [18]) reduced by all terms vanishing for $r = \text{const}$ ($= 1$ unit length). On the other hand, spherical harmonics obey the eigenvalue equation

$$\nabla^2 Y_{l,m}(\varphi_f, \vartheta_f) = -l(l+1) Y_{l,m}(\varphi_f, \vartheta_f) \quad (2.183)$$

with the degree numbers $l = 0, 1, 2, \dots$

Combining Eqs. (2.179), (2.180), (2.181), (2.182), and (2.183), multiplying both sides of the resulting equation by $Y_{l',m'}^*(\varphi_f, \vartheta_f)$, and integrating over the full solid angle lead to

$$\frac{dc_{l',m'}}{d\tau} = -D_r l'(l'+1) c_{l',m'} \quad (2.184)$$

Here, we have made use of the orthonormal property of spherical harmonics,

$$\int_0^{2\pi} d\varphi \int_0^\pi d\vartheta \sin \vartheta Y_{l',m'}^*(\vartheta, \varphi) Y_{l,m}(\vartheta, \varphi) = \delta_{ll'} \delta_{mm'} \quad (2.185)$$

with the Kronecker symbols $\delta_{ll'}$ and $\delta_{mm'}$.

The rotational diffusion equation is thus converted to a linear differential equation for the time-dependent coefficients $c_{l',m'}$. The solution of Eq. (2.184) is

$$c_{l',m'}(\tau) = c_{l',m'}(0) \exp\{-D_r l'(l' + 1) \tau\} \quad (2.186)$$

The initial condition $c_{l,m}(0)$ is derived by (1) multiplying the ansatz Eq. (2.181) on both sides by $Y_{l',m'}^*(\mathbf{u}_f)$, (2) integrating both sides over the full solid angle with respect to $\mathbf{u}_f$, (3) again employing the orthonormal property of spherical harmonics, Eq. (2.185), and (4) inserting the initial condition for $P_c(\mathbf{u}_i, \mathbf{u}_f, 0)$, Eq. (2.180). The result is

$$c_{l',m'}(0) = Y_{l',-m'}(\mathbf{u}_i) \quad (2.187)$$

The primes of the subscripts in Eqs. (2.186) and (2.187) can now be omitted, so that Eqs. (2.181), (2.186), and (2.187) can be combined. The result is the rotational diffusion propagator

$$P(\mathbf{u}_i, \mathbf{u}_f, \tau) = \sum_{l,m} Y_{l,-m}(\mathbf{u}_i) Y_{l,m}(\mathbf{u}_f) \exp\left\{-\frac{\tau}{\tau_l}\right\} \quad (2.188)$$

which is a linear combination of exponential functions with time constants

$$\tau_l = \frac{1}{D_r l(l+1)} \quad (2.189)$$

Applications of this formalism can be found in Sects. 3.1.7 and 3.9.3 where autocorrelation functions for spin–lattice and dielectric relaxation are derived on this basis. The respective degrees of the relevant spherical harmonics are $l = 2$ and $l = 1$ in these cases (see Eq. 1.8).

2.5.4 The Stokes/Einstein Relations

2.5.4.1 Stokes/Einstein Relation for Translations of Neutral Particles

The Stokes/Einstein relations relate diffusion coefficients of spherical particles with friction coefficients. The topic was already touched in Sect. 2.4.2.1. Let us return to this issue from a somewhat different perspective now including rotational diffusion. For this purpose, we link the Langevin equation Eq. (2.158) (containing the friction coefficient), Einstein's relation for the mean-square displacement, Eq. (2.169) (implying the diffusion coefficient), and Stokes' friction law Eq. (2.156). The Langevin equation for the position $\mathbf{r}$ of a single rigid and electrically neutral particle of mass m reads

$$m \frac{\partial^2 \mathbf{r}}{\partial t^2} = -\zeta \frac{\partial \mathbf{r}}{\partial t} + \mathbf{f}(t) \quad (2.190)$$

where ζ is the friction coefficient and $\mathbf{f}(t)$ is the stochastic force acting on the particle. The problem is now to evaluate the mean-square displacement on this basis.

Multiplying each term of Eq. (2.190) by the vector $\mathbf{r}$ and modifying the derivations correspondingly lead to

$$\frac{m}{2} \frac{\partial^2 \langle \mathbf{r}^2 \rangle}{\partial t^2} - m \left\langle \left(\frac{\partial \mathbf{r}}{\partial t} \right)^2 \right\rangle = -\frac{\zeta}{2} \frac{\partial \langle \mathbf{r}^2 \rangle}{\partial t} + \langle \mathbf{r} \cdot \mathbf{f} \rangle. \quad (2.191)$$

The result can readily be verified by carrying out the derivations of $\langle \mathbf{r}^2 \rangle$ in part. Forming the ensemble average $\langle \dots \rangle$ gives

$$\frac{m}{2} \frac{\partial^2 \langle \mathbf{r}^2 \rangle}{\partial t^2} - m \left\langle \left(\frac{\partial \mathbf{r}}{\partial t} \right)^2 \right\rangle = -\frac{\zeta}{2} \frac{\partial \langle \mathbf{r}^2 \rangle}{\partial t} + \langle \mathbf{r} \cdot \mathbf{f} \rangle \quad (2.192)$$

The term $\langle \mathbf{r} \cdot \mathbf{f} \rangle \approx 0$ can be neglected because of the stochastic nature of molecular collisions. Furthermore, we can replace $m \left\langle \left(\frac{\partial \mathbf{r}}{\partial t} \right)^2 \right\rangle = m \langle v^2 \rangle = 3k_B T$ according to the equipartition theorem of thermal energy. We thus arrive at the linear differential equation for the mean-square particle displacement $\langle \mathbf{r}^2 \rangle = \langle [\mathbf{r}(t)]^2 \rangle$:

$$\frac{\partial^2 \langle \mathbf{r}^2 \rangle}{\partial t^2} + \frac{\zeta}{m} \frac{\partial \langle \mathbf{r}^2 \rangle}{\partial t} = 6 \frac{k_B T}{m} \quad (2.193)$$

Integrating once over the time interval t gives

$$\frac{\partial \langle \mathbf{r}^2 \rangle}{\partial t} = 6 \frac{k_B T}{\zeta} \left(1 - \exp \left\{ -\frac{t}{\tau_f} \right\} \right) \quad (2.194)$$

where the time constant $\tau_f = m/\zeta$ is the *viscous relaxation time*. In the limit $t \gg \tau_f$, the exponential function can be neglected relative to 1 so that

$$\frac{\partial \langle \mathbf{r}^2 \rangle}{\partial t} \Big|_{t \gg \tau_f} \approx 6 \frac{k_B T}{\zeta} \quad (2.195)$$

or

$$\langle \mathbf{r}^2 \rangle \Big|_{t \gg \tau_f} \approx 6 \frac{k_B T}{\zeta} t \quad (2.196)$$

The comparison with the three-dimensional version of the mean-square displacement expression in Eq. (2.169) and Stokes' friction law Eq. (2.156) finally leads to the *Stokes/Einstein relation*

$$D = \frac{k_B T}{\zeta} = \frac{k_B T}{6\pi\eta a_h} \quad (2.197)$$

for translational motions, where η is the dynamic viscosity of the (Newtonian) medium and a_h is the hydrodynamic radius of the particle.

The proportionality $D \propto \eta^{-1}$ has frequently been tested in literature. Deviations from this relation have been observed in particular in glass-forming and supercooled liquids [31] as well as in the nonfreezing surface layers of solvents confined in porous media [32] referred to in Sect. 7.4.2.

2.5.4.2 Einstein Relation for Charged Particles

Equation (2.197) is valid for electrically neutral particles. In the charged case, the Langevin equation for particles with the velocity $\mathbf{v}$ must be supplemented by an electrostatic term according to

$$m \frac{\partial \mathbf{v}}{\partial t} = q\mathbf{E} - \zeta \mathbf{v} + \mathbf{f}(t) \quad (2.198)$$

where $\mathbf{E}$ is the strength of a homogeneous electric field to which the particle of charge q is subjected. Forming the ensemble average on both sides gives

$$m \frac{\partial \langle \mathbf{v} \rangle}{\partial t} = q\mathbf{E} - \zeta \langle \mathbf{v} \rangle + \langle \mathbf{f}(t) \rangle \quad (2.199)$$

with the drift velocity $\langle \mathbf{v} \rangle$. The ensemble average of the stochastic force vanishes, that is, $\langle \mathbf{f}(t) \rangle = 0$. In the steady state, we have moreover $\partial \langle \mathbf{v} \rangle / \partial t = 0$. Equation (2.199) thus reduces to

$$q\mathbf{E} - \zeta \langle \mathbf{v} \rangle = 0 \quad (2.200)$$

The drift velocity is proportional to the electric field strength, $\langle \mathbf{v} \rangle = \mu \mathbf{E}$, with the *electrical mobility* μ as a – in the case of isotropic fluids – scalar proportionality factor. The vectors can be replaced by their magnitudes so that Eq. (2.200) can be rewritten as

$$\frac{\zeta}{q} = \frac{E}{\langle v \rangle} = \frac{1}{\mu} \quad (2.201)$$

This leads to the following expression for the friction coefficient:

$$\zeta = \frac{q}{\mu} \quad (2.202)$$

Inserting Eqs. (2.202) into (2.197) finally results in the *Einstein relation for charged particles*:

$$D = \frac{\mu k_B T}{q} \quad (2.203)$$

2.5.4.3 Stokes/Einstein/Debye Relation for Rotational Diffusion

In Sect. 2.5.3, we have seen that there is a certain analogy of rotational and translational diffusion of spherical particles. The counterpart of the translational displacement $\mathbf{r}$ (Fig. 2.20) is the reorientation arc s on the unit sphere (measured in radians) due to rotational diffusion (Fig. 2.24). The mean-square translational displacement along a single space direction is given by $\langle x^2 \rangle = 2Dt$ with the translational diffusion coefficient D (dimension $[\text{length}]^2[\text{time}]^{-1}$; see Eq. 2.169). Likewise, the mean-square angular deviation about a single axis obeys $\langle s^2 \rangle = 2D_r t$ with the rotational diffusion coefficient D_r (dimension $[\text{radian}]^2[\text{time}]^{-1}$).

In this sense, the expression analogous to the Stokes/Einstein relation Eq. (2.197) for translational diffusion of a neutral particle is the *Stokes/Einstein/Debye relation* for rotational diffusion [33]:

$$D_r = \frac{k_B T}{\zeta_r} = \frac{k_B T}{8\pi\eta a_h^3} \quad (2.204)$$

The rotational friction coefficient ζ_r of a sphere of hydrodynamic radius a_h in a medium with dynamic viscosity η is given by Stokes' law modified accordingly as $\zeta_r = 8\pi\eta a_h^3$.

If the full dimensionality is considered, the mean-square translational displacement in *three*-dimensional space obeys $\langle r^2 \rangle = 6Dt$, whereas the space relevant for rotational diffusion is topologically *two*-dimensional, so that the mean-square angular deviation is $\langle s^2 \rangle = 4D_r t$ implying variations of the polar angle ϑ and the azimuthal angle φ .

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Chapter 3

Noninvasive Methods

Abstract The global classifications relevant for soft-matter dynamics are coherent and incoherent particle motions and translational and rotational molecular dynamics. The methodology permitting the exploration of these phenomena is of paramount importance for the whole field. In this chapter, the most common techniques suitable for soft-matter studies will be outlined. “Noninvasive” means that the sample materials can be examined in their native form without modifications such as labeling with probe molecules. The same samples can in principle be subjected to different investigations employing complementary techniques. That is, the microstructure remains undistorted by label compounds. Unavoidably, this chapter is relatively long due to the fact that no adequate compendium comprising this particular methodology exists in the literature. Paying tribute to the conceptual philosophy of this book, the specific features of the methods will be presented with particular reference to correlation functions and with a consistent symbolism throughout. The methodological categories under consideration will be diverse NMR-based techniques, quasi-elastic neutron scattering, dynamic light scattering, mechanical relaxation, and dielectric relaxation spectroscopy.

This chapter is to represent the methodological part of this book. Countless techniques are in use for probing dynamic features of matter. A selection is therefore unavoidable. The criterion will be the general degree of applicability to problems that are typically of interest in soft-matter research. We will restrict ourselves to noninvasive, that is, non-labeling, methods that can be applied more or less universally to any material to be studied without further treatment or modification. The most prominent and versatile examples of this class of techniques are *magnetic resonance-based methods, quasi-elastic neutron or light scattering experiments, broadband dielectric spectroscopy, and rheological and dynamic mechanical examinations*. Other methods such as those employing compounds labeled by fluorescent dye groups, radionuclides, and electron-paramagnetic species as probes for the examination of molecular dynamics may be powerful as well but are considered to be of subordinate interest in the present context.

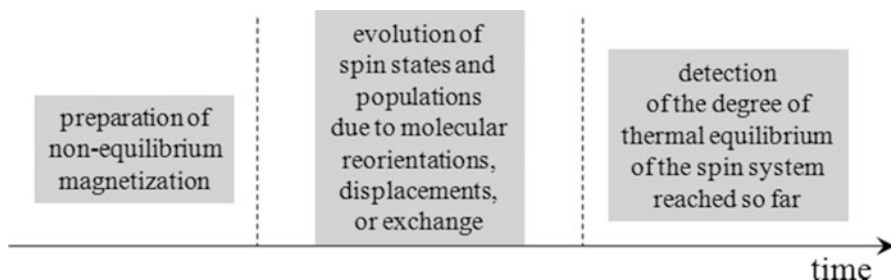


Fig. 3.1 Schematic representation of the three principal intervals which one can distinguish in magnetic resonance experiments probing incoherent molecular motions

The diverse methods and experiments for the analysis of molecular dynamics are usually represented by different communities of experimenters possessing the expert knowledge specific for their own fields. The unavoidable consequence is that results are presented in peculiar technical terms making comparisons between different techniques difficult even though the experiments refer to the same system. Following the strategy mentioned in the introductory section, we will therefore prefer to express the final evaluation formalisms on the basis of correlation functions as a universally conceivable terminology.

A large variety of techniques suitable for studies of molecular dynamics are deduced from the *nuclear magnetic resonance* (NMR) phenomenon.¹ This is the basis of the most versatile but also the most demanding methodological category to be treated in the following. Correspondingly ample space will be devoted to this class of techniques in Sects. 3.1, 3.2, 3.3, 3.4, and 3.5.

NMR experiments of particular interest probe *spin relaxation*, *self-diffusion*, and – in case sites with different resonance and mobility parameters exist – *chemical exchange*. Despite the different nature of these dynamic processes, the respective experimental protocols can commonly be analyzed by the scheme shown in Fig. 3.1. It consists of three intervals describing the crucial steps of the experiments to be outlined in the following.

A further set of NMR techniques includes spatial resolution. Such *microscopy-based experiments* are particularly powerful for studies of fluid dynamics as will be demonstrated in Chap. 4.

The second big class of dynamic methods implies *neutron and light scattering* in their quasi-elastic variants. These techniques are sensitive to translational displacements of molecules. An incident beam of particles or photons is irradiated on the sample. The particles scattered under a certain scattering angle are analyzed with respect to energy and wave-number shifts. If the energy shifts are much less than any excitation energy of the scattering center, one speaks of *quasi-elastic*

¹ The electron version, *electron spin resonance* (ESR), can also be the basis of interesting applications provided that the system contains unpaired electrons (free radicals or electron-paramagnetic atoms or molecules). ESR techniques are however beyond the scope of this book. The principles of the experiments are anyway the same.

scattering. As already mentioned in Sect. 1.1.2, scattering techniques are further methods probing dynamic structure factors for translational self-diffusion of particles and for diffusion of particles relative to each other. The corresponding methodological formalisms will be outlined in Sects. 3.6 and 3.7.

A wide application field and a large methodological arsenal for studies of dynamic properties are based on *rheological and mechanical relaxation*, the third class of techniques to be delineated here. Samples are subjected to shear, torsion, or strain relax via molecular rearrangements or displacements. The time or frequency dependences probed in this sort of experiments are indicative for the underlying dynamic processes. The principles of this vast field will be detailed in Sect. 3.8.

Finally, *broadband dielectric spectroscopy* will shortly be reviewed in Sect. 3.9. Techniques on this basis can favorably be applied to *polar* systems.

3.1 Spin Relaxation

3.1.1 General Remarks and Definitions

As the name implies, the general term “relaxation” refers in this case to spins, that is, to an immaterial system. The dynamics of molecules can therefore be probed on this basis only in a principally indirect way. Equilibration of spin populations is induced by orientational or translational fluctuations of molecules in thermal equilibrium. In other words, the spin systems under consideration start from a nonequilibrium state, while all mechanical, that is, molecular and atomistic degrees of freedom in the sample, are and remain in equilibrium. Before outlining the theory linking spin relaxation with molecular-dynamics characteristics, let us specify a number of definitions and typical experimental setups. Introductory reading can be found in Refs. [1–4].

In typical spin-relaxation experiments, the sample is placed in a laboratory magnet producing the external magnetic flux density $\mathbf{B}_0$, which is usually assumed to be aligned along the z direction of a Cartesian laboratory frame of reference (see Fig. 3.2). The eigenvalues of the Zeeman Hamiltonian

$$\mathcal{H}_0 = -\boldsymbol{\mu} \cdot \mathbf{B}_0 = -\gamma \hbar \mathbf{I} \cdot \mathbf{B}_0 = -\gamma \hbar I_z B_0 \quad (3.1)$$

for a magnetic dipole with the dipole-moment vector operator $\boldsymbol{\mu}$ in a magnetic field with the flux density $\mathbf{B}_0$ are given by

$$E_m = -\gamma \hbar m_I B_0 \quad (3.2)$$

m_I is the magnetic quantum number, γ is the gyromagnetic ratio of the particle, $\hbar$ is Planck’s constant divided by 2π , $\mathbf{I}$ is the (dimensionless) spin vector operator, and I_z

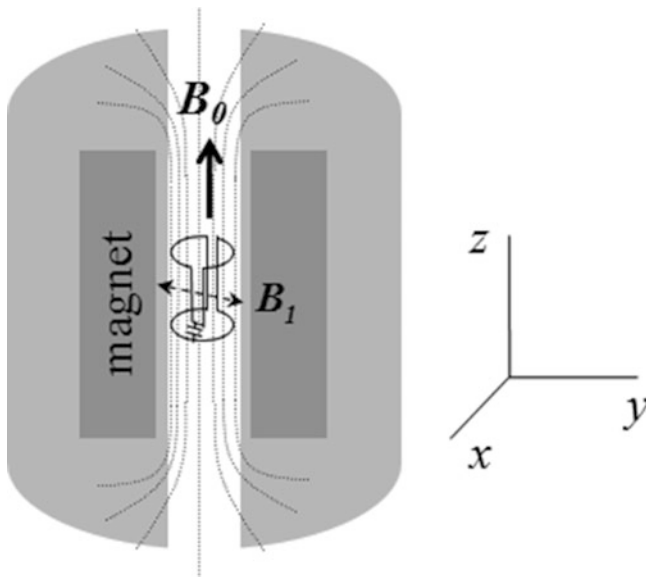


Fig. 3.2 Typical setup of an NMR experiment. The cryomagnet represented by a cross-sectional view produces the main magnet field with the flux density B_0 aligned along the z -axis of the laboratory frame of reference. The sample (not shown) is placed in the saddle coil in the middle of the magnet. The saddle coil is tuned with the aid of capacitors to the carrier radio frequency (RF) of the system and matched to the transmitter and the (phase-sensitive) receiver. The RF coil serves both the application of RF pulses to the sample and the reception of NMR signals. The RF flux density B_1 produced by the saddle coil oscillates perpendicular to B_0

is the z component of the spin vector operator (with the eigenvalues $m_I = \pm 1/2$ in the case of spins $1/2$ (see Fig. 3.3)). The *Zeeman energy splitting* is

$$\Delta E = \hbar \gamma B_0 \quad (3.3)$$

corresponding to the angular *magnetic resonance frequency*

$$\omega_0 = \gamma B_0 \quad (3.4)$$

This is identical to the magnitude of the *Larmor frequency*,

$$\omega_L = -\gamma B_0 \quad (3.5)$$

with which the spins precess about the magnetic flux density B_0 .

Under stationary magnetic-field conditions, an equilibrium magnetization

$$\mathbf{M}_0 = V^{-1} \sum_j \langle \boldsymbol{\mu}_j \rangle \quad (3.6)$$

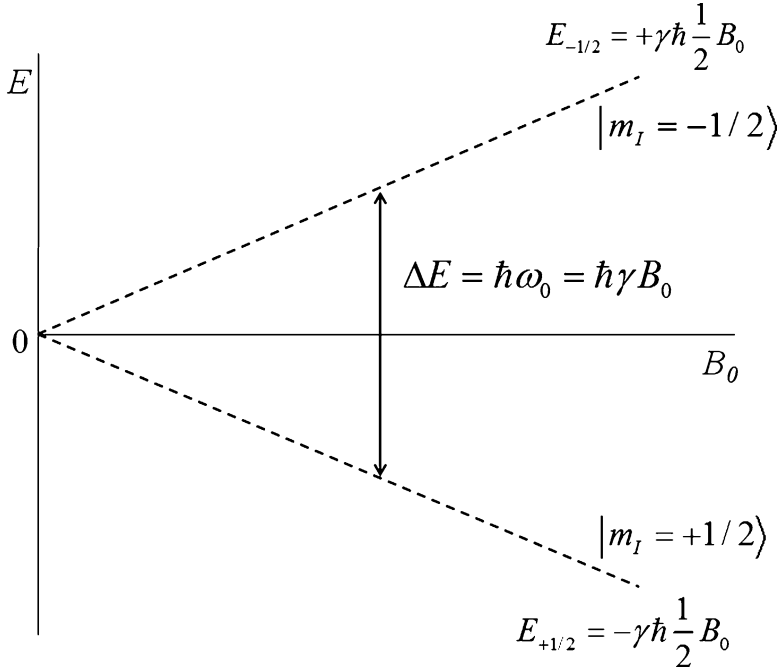


Fig. 3.3 Zeeman energy levels of spins $1/2$. The eigen-values of the spin operator I_z are given by the magnetic quantum numbers $m_I = \pm 1/2$ corresponding to “spin-up” and “spin-down” states. The Zeeman splitting is $\Delta E = \hbar\gamma B_0$ so that the angular resonance frequency results in $\omega_0 = \gamma B_0$. The signs in this scheme are chosen for *positive* values of the gyromagnetic ratio γ

builds up, where V is the sample volume. The sum runs over the quantum-mechanical expectation value vectors $\langle \boldsymbol{\mu}_i \rangle$ of the magnetic dipole operators $\boldsymbol{\mu}_j$ in the sample. In the limit of high temperatures where the mean thermal energy per particle ($\sim k_B T$) is much larger than the Zeeman splitting energy,

$$k_B T \gg \Delta E = |\gamma| \hbar B_0 \quad (3.7)$$

the equilibrium magnetization obeys Curie’s law

$$\mathbf{M}_0 = \frac{n\gamma^2 \hbar^2 I(I+1)}{3k_B T} \mathbf{B}_0 \quad (3.8)$$

The quantity I is the spin quantum number, and n is the number density of the spin-bearing particles. The nuclear paramagnetic species most important in soft-matter applications is light hydrogen, the nuclei of which are usually addressed as “protons” according to the only nucleon these nuclei consist of. Therefore, whenever the term *proton* appears in the present context, the nuclei of light hydrogen will be meant. The proton spin quantum number is $I = 1/2$. Nuclei of heavy hydrogen (shortly referred to as “deuterons”) are also often studied in NMR investigations of soft matter. In this case, the spin quantum number is $I = 1$.

Since the quantizing magnetic-field $\mathbf{B}_0$ is usually assumed to be aligned along the z -axis of the reference frame, we distinguish the longitudinal magnetization M_z and the transverse magnetization M_{trans} which is usually expressed in the form of a complex quantity

$$m = M_x + iM_y \quad (3.9)$$

The real part is M_x and M_y is the imaginary part. In this context, the term *spin coherence* is in use. This expression addresses an *ensemble* of spin systems. The observation of a finite transverse magnetization means that the spins precess *coherently*. A spin “system” can be composed of a single (i.e., isolated) spin or several (i.e., coupled) spins. Coupling among different spins can be mediated by *dipolar* or *scalar* spin interactions as specified in Eqs. (3.58) and (3.59), respectively.

Quantum mechanically, homonuclear transverse magnetization is defined as the *mean* expectation value of the complex transverse components $\mu_{j,x} + i\mu_{j,y}$ of the dipole operators subject to *single-quantum* coherences:

$$\begin{aligned} m &= M_x + iM_y \\ &= V^{-1} \sum_j \langle \mu_{j,x} + i\mu_{j,y} \rangle \\ &= n \overline{\langle \mu_x + i\mu_y \rangle} \\ &= n\gamma\hbar \text{Tr}\{ (I_x + iI_y) \rho \} \end{aligned} \quad (3.10)$$

The angle brackets indicate the quantum-mechanical expectation value of the operators included, whereas the bar stands for the average over the distribution of states in the ensemble of spin systems. Such an ensemble average of expectation values of operators can be calculated with the aid of the density operator ρ by evaluating the trace $\text{Tr}\{\dots\}$ of the product of the spin operators with the density operator. A very readable introduction into the density operator formalism can be found in Ref. [5] (see also footnote 8).

In the definition of the complex transverse magnetization, Eq. (3.10), the term “single quantum” means that the relevant transition of the spin system is characterized by a change of the total magnetic quantum number by $|\Delta m_I| = 1$. This restriction accounts for the fact that multiple- or zero-quantum coherences defined by $|\Delta m_I| \neq 1$ do not contribute directly to observable magnetization.

If the spins are exposed to an inhomogeneous magnetic field, the local spin coherences will be subject to a distribution of different Larmor frequencies according to Eq. (3.5). The consequence will be that the transverse magnetization of the sample fades soon due to destructive superposition of the more and more dephased spin coherences. Provided that irreversible relaxation or diffusion processes are not yet effective, the coherences may still exist *locally*, but cannot be detected in the form of *global* transverse magnetization of the sample unless being refocused. This phenomenon will be subject of the spin-echo experiment to be discussed in Sect. 3.1.4.6, for example. The interested reader who would like to learn more about spin coherences and their evolution properties is referred to Refs. [1–4].

According to the scheme shown in Fig. 3.1, a *spin-relaxation experiment* begins in general with the preparation of a nonequilibrium state of the sample. In particular, this refers to magnetization vector components deviating from the Curie's values $M_x = 0$, $M_y = 0$, $M_z = M_0$. Such nonequilibrium scenarios are typically prepared by a short intense radio frequency (RF) pulse applied to the transmitter coil in the probehead (see Fig. 3.2). It excites the spin systems in the sense that the magnetization vector is “flipped” into a direction different from the positive z -axis. Another measure producing nonequilibrium magnetizations is an abrupt variation of the external magnetic flux density as described in Sect. 3.1.4.4 in the context of field-cycling NMR relaxometry.

After establishing a nonequilibrium magnetization, a certain time interval is allowed for changes of the spin state populations by molecular fluctuations. As such, reorientations, translational displacements, and exchange processes between sites deviating in their NMR properties come into question. Finally, the transverse magnetization still present or generated at the end of the evolution interval is detected in the form of an RF voltage induced in the receiver pickup coil (which is normally identical with the transmitter coil; see Fig. 3.2).

Spin relaxation in general can be traced back to fluctuations of the spin interactions as a consequence of molecular or lattice dynamics. For instance, rotational diffusion of a molecule gives rise to stochastic modulations of all anisotropic spin couplings within that molecule. There are a number of different sorts of couplings that can be relevant for spin relaxation. However, depending on the nuclear species and the molecular system in which the spin-bearing particles reside, there is normally just a single sort of interaction that dominates spin relaxation.

Spin interactions of particular interest and relevance in soft-matter systems are magnetic *dipole–dipole coupling* and the *interaction of electric nuclear quadrupole moments with electric-field gradients* produced by the charge distribution in molecules. Temporal fluctuations of the former type of interactions normally dominate the relaxation of protons (which do not possess a finite electric quadrupole moment). On the other hand, fluctuations of quadrupole interaction tend to govern deuteron relaxation (the dipole moment of deuterons is comparatively inefficient). Detailed treatments will follow in Sect. 3.1.5. If present, electron-paramagnetic species are also very effective and often prevailing coupling partners via dipolar or scalar interaction between the nuclear and unpaired-electron spins (see Eqs. (3.58) and (3.59), respectively). Spin–lattice relaxation based on this sort of coupling will be discussed in Sects. 3.1.5.8 and 3.1.5.9.

3.1.2 Bloch Equations

The Bloch equations are differential equations providing the time dependence of the magnetization vector, that is, the spin-relaxation functions, in the course of magnetic resonance experiments. Historically, these equations of motion have been

established from a phenomenological starting point. However, as will be shown in Sect. 3.1.5, they can also be derived in an equivalent form for many important paradigm situations on a quantum-mechanical basis. This in particular refers to an ensemble of pairs of coupled spins $1/2$.

In the laboratory frame, the *Bloch equation* for the magnetization $\mathbf{M}$ reads

$$\begin{aligned} \frac{d\mathbf{M}}{dt} &= \underbrace{\gamma \mathbf{M} \times \mathbf{B}_0}_{\text{precession}} - \underbrace{\frac{M_x}{T_2} \mathbf{u}_x - \frac{M_y}{T_2} \mathbf{u}_y - \frac{M_z - M_0}{T_1} \mathbf{u}_z}_{\text{relaxation}} \\ &= \gamma \begin{pmatrix} M_y B_{0z} - M_z B_{0y} \\ M_z B_{0x} - M_x B_{0z} \\ M_x B_{0y} - M_y B_{0x} \end{pmatrix} - \frac{1}{T_2} \begin{pmatrix} M_x \\ M_y \\ 0 \end{pmatrix} - \frac{1}{T_1} \begin{pmatrix} 0 \\ 0 \\ M_z - M_0 \end{pmatrix} \quad (3.11) \end{aligned}$$

where $\mathbf{u}_x$, $\mathbf{u}_y$ and $\mathbf{u}_z$ are unit vectors along the axes of the Cartesian laboratory frame of reference. The Bloch equation contains two parameters, namely, the *spin–lattice (or longitudinal) relaxation time* T_1 and the *transverse relaxation time* T_2 . These are the time constants with which the longitudinal and transverse magnetization components, respectively, relax toward thermal equilibrium. T_1 thus refers to the z component of the magnetization which relaxes toward the Curie's value M_0 given in Eq. (3.8), while the magnetization transverse to the quantization magnetic-field $\mathbf{B}_0$ relaxes with T_2 toward its equilibrium value 0.

The relaxation times can also be defined as the mean lifetimes of the initial nonequilibrium populations of the respective spin states. The reason why longitudinal and transverse relaxation must be distinguished and why the two species of relaxation times tend to be different will be given in Sect. 3.1.5: Transitions conserving the Zeeman energy of the coupled spin system contribute to transverse but not to longitudinal relaxation. This has to do with the different spin transitions relevant for equilibration of longitudinal and transverse magnetization components.

As concerns transverse relaxation, it must be emphasized that the Bloch equation is only valid under *motional-averaging conditions*. That is, the time-scale limit in which the transverse relaxation term in Eq. (3.11) applies is defined by $t \gg \tau_c$, where τ_c is the correlation time of the fluctuating spin interactions. The fluctuations are the consequence of molecular motions, that is, molecular reorientations and distance variations.

A further remark is deemed appropriate in this context: The Bloch equation in the form of Eq. (3.11) is the simplest version taking merely relaxation into account. It does not imply effects by translational diffusion in the presence of field gradients and/or molecular exchange phenomena between sites of different resonance and/or relaxation conditions. In these cases, additional terms will be needed [1]. Corresponding formalisms will be provided in later sections.

In magnetic-resonance experiments, RF fields are applied perpendicular to the main magnetic-field $\mathbf{B}_0$ with the aid of RF coil configurations such as the one shown in Fig. 3.2. The flux density of resonant RF can be represented by

$$\mathbf{B}_{\text{RF}} = 2\mathbf{B}_1 \cos \omega_c t \quad (3.12)$$

where ω_c is the angular carrier frequency of the spectrometer. It is normally adjusted to match to the magnitude of the Larmor or resonance frequency of the spins under investigation:

$$\omega_c = \omega_L = \omega_0 = \gamma B_0 \quad (3.13)$$

The factor of two on the right-hand side of Eq. (3.12) is introduced for formal reasons as will be explained below. The total magnetic flux density acting during an RF pulse on the sample is given by the sum

$$\mathbf{B}(t) = \mathbf{B}_0 + \mathbf{B}_{\text{RF}}(t) \quad (3.14)$$

Assuming that $\mathbf{B}_{\text{RF}}$ oscillates along the x -axis of the laboratory frame and that it was initially aligned along the positive x -axis, the vector $\mathbf{B}(t)$ can be rewritten and analyzed in component form as

$$\mathbf{B}(t) = \underbrace{\begin{pmatrix} 2B_1 \cos(\omega_0 t) \\ 0 \\ B_0 \end{pmatrix}}_{\text{linear oscillation}} \equiv \underbrace{\begin{pmatrix} B_1 \cos(\omega_0 t) \\ B_1 \sin(\omega_0 t) \\ B_0/2 \end{pmatrix}}_{\substack{\text{counter-clockwise} \\ \text{rotation in the } x/y \text{ plane} \\ \text{as seen from above}}} + \underbrace{\begin{pmatrix} B_1 \cos(\omega_0 t) \\ -B_1 \sin(\omega_0 t) \\ B_0/2 \end{pmatrix}}_{\substack{\text{clockwise} \\ \text{rotation in the } x/y \text{ plane} \\ \text{as seen from above}}} \quad (3.15)$$

According to this expression, the linearly polarized RF field is composed of two counter-rotating circularly polarized RF fields as manifested by the two terms on the right-hand side of the identity in Eq. (3.15). Obviously, these field components *rotate* in the x/y plane of the laboratory frame, that is, around the static magnetic flux density $\mathbf{B}_0$ (compare Fig. 3.2).

Equation (3.15) is valid for laboratory-frame components. Practically, it is however more convenient to treat equations of motion in a reference frame x', y', z' , rotating with the same frequency and in the same sense as Larmor precession about the z -axis. This frame is shortly called the *rotating frame*. In axial-vector form, the angular Larmor frequency is given by

$$\boldsymbol{\omega}_L = -\gamma \mathbf{B}_0 \quad (3.16)$$

For positive gyromagnetic ratio γ as it is the case for most nuclei and in particular for protons, the vector $\boldsymbol{\omega}_L$ points in the direction opposite to the magnetic flux density $\mathbf{B}_0$. That is, Larmor precession in this case rotates in clockwise direction when looking on the transverse plane from above.

The consequence is that the clockwise component of the RF field (second term on the right-hand side of Eq. (3.15)) will be stationary relative to the rotating frame, whereas the counterclockwise component (first term on the right-hand side of Eq. (3.15)) rotates with *twice* the Larmor frequency. After transformation to the rotating frame, the total magnetic flux density given in Eq. (3.15) for the laboratory frame thus takes the rotating-frame form

$$\mathbf{B}'(t) = \begin{pmatrix} B_1 \cos(2\omega_L t) \\ B_1 \sin(2\omega_L t) \\ 0 \end{pmatrix} + \begin{pmatrix} B_1 \\ 0 \\ 0 \end{pmatrix} \quad (3.17)$$

Note that the main magnetic field, $\mathbf{B}_0$, disappears upon this transformation since no Larmor precession about this field is expected relative to the rotating frame. Spins subjected to a field with the flux density given by Eq. (3.17) “see” a stationary or *secular* part (second term on the right-hand side) and a rapidly oscillating or *non-secular* component (first term on the right-hand side). In the average, the effect of the non-secular component cancels since spins cannot be deviated perceptibly from their original orientation by such fast oscillations. The magnetic flux density effective in the resonantly rotating frame can therefore be approximated by the then stationary vector

$$\mathbf{B}'(t) \approx \begin{pmatrix} B_1 \\ 0 \\ 0 \end{pmatrix} \quad (3.18)$$

By the way, this simple form of the resulting flux density is the justification for the introduction of the factor of two in Eq. (3.12).

More generally, the *effective magnetic flux density* in the frame rotating with an arbitrary angular-frequency ω_c about $\mathbf{B}_0$ is given by [1]

$$\mathbf{B}' = \mathbf{B}_1 + \mathbf{B}_0 + \frac{\omega_c}{\gamma} \quad (3.19)$$

where $\mathbf{B}_1$ is the RF flux density component synchronously rotating with the rotating frame.

If ω_c is aligned opposite to $\mathbf{B}_0$, the magnitude is

$$B' = \sqrt{\left(B_0 - \frac{\omega_c}{\gamma}\right)^2 + B_1^2} \quad (3.20)$$

Under resonant conditions, that is, if $\boldsymbol{\omega}_c = \boldsymbol{\omega}_L = -\gamma\mathbf{B}_0$, Eqs. (3.19) and (3.20) reduce to Eq. (3.18).

On this basis, the *resonantly rotating-frame version of the Bloch equation*² results in matrix representation as

$$\begin{pmatrix} \frac{dM_{x'}}{dt} \\ \frac{dM_{y'}}{dt} \\ \frac{dM_{z'}}{dt} \end{pmatrix} = \underbrace{\gamma \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & B_1 \\ 0 & -B_1 & 0 \end{pmatrix} \begin{pmatrix} M_{x'} \\ M_{y'} \\ M_{z'} \end{pmatrix}}_{\text{precession about } \mathbf{B}'_1} + \underbrace{\begin{pmatrix} -\frac{1}{T_2} & 0 & 0 \\ 0 & -\frac{1}{T_2} & 0 \\ 0 & 0 & -\frac{1}{T_1} \end{pmatrix} \begin{pmatrix} M_{x'} \\ M_{y'} \\ M_{z'} - M_0 \end{pmatrix}}_{\text{relaxation}} \quad (3.21)$$

In this expression, the rotating-frame direction of the RF field, that is $\mathbf{B}_1$, is (arbitrarily) assumed along the x' -axis. The individual magnetization components consequently obey the rotating-frame equations of motion

$$\begin{aligned} \frac{dM_{x'}}{dt} &= -\frac{M_{x'}}{T_2} \\ \frac{dM_{y'}}{dt} &= \gamma B_1 M_{z'} - \frac{M_{y'}}{T_2} \\ \frac{dM_{z'}}{dt} &= -\gamma B_1 M_{y'} - \frac{M_{z'} - M_0}{T_1} \end{aligned} \quad (3.22)$$

which merely anticipate motional averaging as concerns transverse relaxation (see above). In Sects. 3.2 and 3.4, these equations of motion will be supplemented by terms accounting for translational diffusion and molecular exchange, respectively. In free-evolution intervals where no RF is irradiated, this set of equations can be rewritten as the vectorial *rotating-frame Bloch equation*

$$\frac{d\mathbf{M}'}{dt} = -\tilde{R} \cdot (\mathbf{M}' - \mathbf{M}_0) \quad (3.23)$$

with the relaxation rate matrix

$$\tilde{R} = \begin{pmatrix} T_2^{-1} & 0 & 0 \\ 0 & T_2^{-1} & 0 \\ 0 & 0 & T_1^{-1} \end{pmatrix} \quad (3.24)$$

²The analytical form of this expression is self-explanatory. It can also be derived straightforwardly by applying the transformation laws between frames rotating relative to each other. For details, the reader is referred to Ref. [1], for instance. Note that the z -axes of both frames of reference are assumed to coincide, that is, $z = z'$. Note furthermore that coordinates and quantities referring to the rotating frame are represented here and in the following by primed quantities, whereas symbols expressed relative to the laboratory frame are written without primes.

Solutions of the above equations can be used for the treatment of the various RF pulse sequences to be described in the following. This in particular means that partial solutions are established for each pulse interval with the result of the preceding interval as initial condition. For example, B_1 takes a finite value during RF pulses, while relaxation rates are normally negligible in these short periods. On the other hand, in the more extended free-evolution intervals, no RF is irradiated, whereas relaxation matters. The sequel of interval solutions thus leads to the final result predicting the signal to be expected after a given RF pulse sequence. A number of examples will be analyzed in detail in the following sections.

3.1.3 RF Pulses, Flip Angle, and Free-Induction Decay³

NMR experiments usually consist of sequences of short, resonant RF pulses. A typical and simple example is shown in Fig. 3.4. Before explaining the sequence of RF pulses, we need to derive the general effect an RF pulse produces when applied to a magnetization vector.

Assume that the initial magnetization is in equilibrium, that is, its laboratory frame components are $M_x = 0$; $M_y = 0$; $M_z = M_0$, and the duration of the RF pulse be τ_α . Usually the pulse width is very short relative to the relaxation times, $\tau_\alpha \ll T_1, T_2$. Relaxation during the RF pulse can therefore be neglected. Let us now turn to the resonantly rotating frame. The flux density $\mathbf{B}_1$ is assumed to be aligned along the x' -axis of the rotating frame. On this basis, the y' and z' rotating-frame components of the magnetization approximately obey the reduced differential equations (see Eq. 3.22)

$$\begin{aligned}\frac{dM_{x'}}{dt} &= 0 \\ \frac{dM_{y'}}{dt} &\approx \gamma B_1 M_{z'} \\ \frac{dM_{z'}}{dt} &\approx -\gamma B_1 M_{y'}\end{aligned}\tag{3.25}$$

With the initial conditions $M_{x'}(0) = 0$, $M_{y'}(0) = 0$ and $M_{z'}(0) = M_0$, the solutions are

³ In presentations, the RF pulse sequences to be considered in the following are often explained with the aid of “hand-waving arguments.” To the author’s teaching experience, this sort of illustrations tend to be a bit elusive for beginners contrary to the intention. A clear analytical representation of the effect of RF pulses and evolution intervals is considered to be more instructive. Compilations of practical details of NMR experiments can be found in Refs. [6–8].

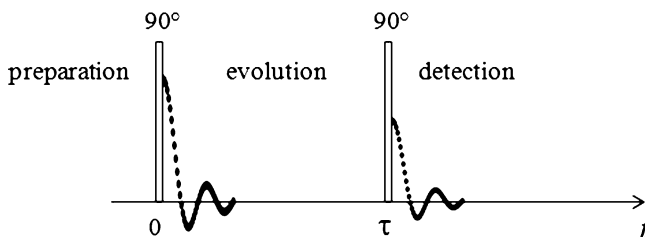


Fig. 3.4 Saturation/recovery RF pulse scheme for measuring the spin–lattice relaxation time T_1 . The sequence starts with the spin systems in thermal equilibrium. The first 90° RF pulse flips the magnetization in the transverse plane. After this “preparation,” the z' component will be zero. The free-induction signal generated by the transverse components is represented by the *undulatory dotted line*. It decays shortly because of field inhomogeneities and transverse relaxation. In the “evolution” interval, z' magnetization builds up again and relaxes toward the equilibrium value M_0 . The instantaneous z' magnetization after an interval τ is measured with the aid of a second 90° RF pulse generating another free-induction signal in the “detection” interval. The amplitude of this FID is proportional to $M_{z'}(\tau_-)$

$$\begin{aligned} M_{x'}(t) &= 0 \\ M_{y'}(t) &= M_0 \sin(\gamma B_1 t) \\ M_{z'}(t) &= M_0 \cos(\gamma B_1 t) \end{aligned} \quad (3.26)$$

At the end of the RF pulse, that is, at $t = \tau_\alpha$, the argument of the sine and cosine functions takes the particular value $\gamma B_1 \tau_\alpha = \alpha$. That is, the rotating-frame magnetization components are converted by the RF pulse to⁴

$$M_{x'}(\tau_\alpha) = 0, \quad M_{y'}(\tau_\alpha) = M_0 \sin \alpha, \quad M_{z'}(\tau_\alpha) = M_0 \cos \alpha \quad (3.27)$$

The magnetization vector is “flipped” in a direction tilted by a flip angle α relative to the z' -axis or the direction of the flux density $\mathbf{B}_0$ of the external magnetic field. Evidently, the spin system has been excited by the RF pulse to a nonequilibrium state.

The transverse magnetization component precesses about $\mathbf{B}_0$ when transformed back from the rotating to the laboratory frame. A precessing magnetization causes an oscillating magnetic flux in the RF coil, which in turn induces a signal voltage that can be picked up and amplified in the receiver of the system. This signal, which tends to decay to zero with time, is called the *free-induction decay* or shortly FID (see the schematic representation in Fig. 3.4). The attribute “free” means that no RF is irradiated on the sample during the signal decay period.

RF pulses of particular relevance in NMR experiments are 90° (or $\pi/2$) and 180° (or π) pulses producing flip angles $\alpha = \gamma B_1 \tau_\alpha = 90^\circ$ and 180° , respectively. The adjusted phase direction of the $\mathbf{B}_1$ field in the rotating frame is often specified in the form of a subscript, for example, $(90^\circ)_{x'}$ or $(\pi/2)_{x'}$ in the case treated above.

⁴ Here and in the following, we assume a *positive* value of the gyromagnetic ratio γ as it is the case for protons, the most important nucleus in the present context.

3.1.4 Experiments for Measuring Spin Relaxation Times

RF pulse sequences such as the one depicted in Fig. 3.4 are suitable for the determination of NMR relaxation times. The relaxation curves from which these parameters can be evaluated are solutions of the Bloch equation. The RF pulses are usually of negligible duration relative to the pulse spacings. We will therefore indicate times just before an RF pulse and immediately thereafter by minus and plus signs, respectively. According to this symbolical nomenclature, the two RF pulses in Fig. 3.4 begin at $t = 0 -$ and $t = \tau -$ and end at $t = 0 +$ and $t = \tau +$, respectively.

3.1.4.1 Saturation/Recovery Pulse Sequence for Measuring T_1

Figure 3.4 shows one of the standard RF pulse sequences for the measurement of the spin–lattice (or longitudinal) relaxation time T_1 . It consists of two RF pulses spaced at an interval τ . After ensuring equilibration, that is, allowing for a long precursor interval $\tau_{\text{eq}} \gg T_1$, the measurement is prepared by a 90° RF pulse as treated in the previous section. The flux density B_1 of this pulse is assumed to be aligned along the x' -axis of the rotating frame. At the end of the 90° RF pulse, the argument of the sine and cosine functions in Eq. (3.27) takes the particular value $\gamma B_1 \tau_{90} = \pi/2$. That is, the rotating-frame magnetization components are converted by the 90° pulse to

$$M_{x'}(0+) = 0, \quad M_{y'}(0+) = M_0, \quad M_{z'}(0+) = 0 \quad (3.28)$$

This is the result of the *preparation* interval.

In the subsequent *evolution* interval, the RF is switched off so that $B_1 = 0$. The precession of the transverse laboratory-frame components gives rise to an FID which soon relaxes toward 0 and is of no further interest in the present context. On the other hand, the longitudinal component $M_{z'}$ will be subject to spin–lattice relaxation and obeys

$$\frac{dM_{z'}}{dt} = -\frac{M_{z'} - M_0}{T_1} \quad (3.29)$$

according to Eq. (3.22). Taking Eq. (3.28) as initial condition for the evolution interval τ defined in Fig. 3.4, the solution just before the second RF pulse, that is, at the time $t = \tau -$, is

$$M_{z'}(\tau-) = M_0 \left(1 - \exp \left\{ -\frac{\tau}{T_1} \right\} \right) \quad (3.30)$$

Since the longitudinal axes z and z' of the laboratory and rotating frames, respectively, coincide by definition, this solution and the equation of motion in Eq. (3.29) could equivalently be written without primed symbols. To be consistent, we will however refer to the rotating frame throughout if not stated otherwise.

In the course of the evolution interval, the z' magnetization component builds up again and relaxes in the long-time limit toward its equilibrium value M_0 . In order to obtain a detectable induction signal that can be picked up by the RF coil, the instantaneous z' magnetization must be flipped into the transverse plane. This is done by the second 90° pulse at the end of the evolution interval. Assuming that the RF flux density B_1 is aligned along the x' -axis of the rotating frame as before, Eq. (3.25) is again valid. The initial condition is given by Eq. (3.30). The effect of the second RF pulse thus is the conversion of the z' magnetization to the transverse magnetization components

$$\begin{aligned} M_{y'}(t) &= M_{z'}(\tau_-) \sin(\gamma B_1 t) \\ M_{z'}(t) &= M_{z'}(\tau_-) \cos(\gamma B_1 t) \end{aligned} \quad (3.31)$$

The flip angle of the second RF pulse is usually chosen to be $\gamma B_1 \tau_{90} = \pi/2$ again so that it produces the transverse magnetization

$$M_{y'}(\tau_+) = M_{z'}(\tau_-) = M_0 \left(1 - \exp\left\{ -\frac{\tau}{T_1} \right\} \right) \quad (3.32)$$

This is proportional to the amplitude of the induction voltage finally detected by the transmitter/receiver RF coil.

Varying the evolution interval τ thus permits one to acquire the relaxation curve point by point. The spin–lattice relaxation time T_1 can then directly be evaluated as the time constant of this curve. The recycle delay between repetitive applications of the saturation/recovery pulse sequence must be long enough to ensure thermal equilibrium at the beginning of the next cycle. A recycle delay in the range $5 \dots 10 \times T_1$ is normally sufficient.

Solutions of the Bloch equation such as Eq. (3.32) are normally based on mono-exponential functions. Deviations that may arise in multi-spin systems in principle are minor, scarcely detectable, and therefore safely negligible. This statement should however not be confused with heterogeneity effects in *multicomponent* or *multiphase* samples which are characterized by strongly non-exponential relaxation curves unless averaged by fast exchange. The respective conditions will be outlined in Sect. 3.4.

As suggested by the general scheme of relaxation experiments in Fig. 3.1, *perturbation–evolution–detection*, there is an infinite variety of pulse sequences that could serve the same purpose in principle. In the following sections, we will therefore restrict ourselves to the description of relaxation experiments that are of particular interest in practical applications.

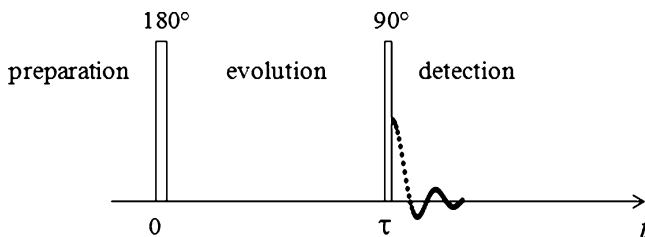


Fig. 3.5 Inversion/recovery RF pulse scheme for measuring the spin–lattice relaxation time T_1 . The sequence starts with the spin system in thermal equilibrium. The 180° RF pulse flips the magnetization in the $-z'$ direction. In the evolution interval, z' magnetization relaxes toward the equilibrium value M_0 . The z' magnetization recovered after an interval τ is measured with the aid of a 90° RF pulse generating an FID (*undulatory dotted line*). The amplitude of this FID is proportional to $M_{z'}(\tau_-)$

3.1.4.2 Inversion/Recovery Pulse Sequence for Measuring T_1

The inversion/recovery variant for spin–lattice relaxation studies is very similar to the saturation/recovery technique. The RF pulse sequence is shown in Fig. 3.5. The only difference is the preparation interval where a 180° RF pulse produces $M_{z'}(0+) = -M_0$ as initial condition for the evolution interval instead of $M_{z'}(0+) = 0$. To generate a flip angle of 180° , the excitation RF pulse is adjusted twice as long (or intense) as in the saturation/recovery case. The solution of Eq. (3.29) at the end of this interval consequently reads

$$M_{z'}(\tau_-) = M_0 \left(1 - 2 \exp \left\{ -\frac{\tau}{T_1} \right\} \right) \quad (3.33)$$

As before, this magnetization component is converted by the subsequent 90° RF pulse to transverse magnetization, and is detected in the form of an FID signal voltage.

3.1.4.3 Progressive-Saturation Pulse Sequence for Measuring T_1

This method is of interest for very viscous or even solid-like systems, where the transverse relaxation time T_2 tends to be much shorter than the spin–lattice relaxation time T_1 . Under such circumstances, the progressive-saturation sequence can be employed very favorably because of its simplicity and robustness.

At first sight, the pulse sequence depicted in Fig. 3.6 appears to deviate categorically from the scheme of relaxation experiments in Fig. 3.1. The three intervals, that is, perturbation, evolution, and detection, do no longer appear one after another. They rather act commonly in integrated form: The spin system is *perturbed* by a long comb of identical and equidistant RF pulses as illustrated in the figure.

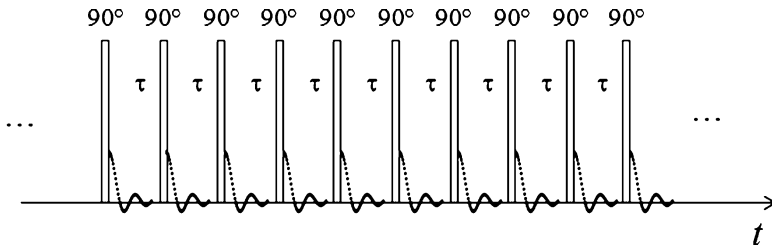


Fig. 3.6 Progressive-saturation RF pulse scheme for measuring the spin–lattice relaxation time T_1 . The sequence consists of a comb of equidistant 90° RF pulses. Each of these pulses flips the z magnetization that was built up in the preceding interval back into the transverse plane where it generates an FID (*undulatory dotted lines*). The amplitude of the FID selected for measurement is acquired as a function of the pulse spacing τ

During the initial part of the pulse comb, the so-called precursor sequence, the magnetization *evolves* toward a steady state in the sense that the amplitudes of the FIDs following the RF pulses are constant. At these instants, the spin system is partially saturated. The FID amplitude is *detected* during the pulse comb after an arbitrary RF pulse in the steady-state part of the sequence. The variation of the pulse spacing τ from small to long values results in increasing FID amplitudes as a consequence of the decreasing saturation degree. In the limit of infinite pulse spacings, the magnetization relaxes toward the Curie's value.

The flip angle of the RF pulses is adjusted to 90° . Imperfections will automatically be compensated by a sufficiently long precursor sequence. In order to avoid restoration of z magnetization by the subsequent 90° RF pulse on the one hand and in order to prevent the generation of undesired spin-echo phenomena leading to superimposed signal artifacts, it must be made sure that the pulse spacing is always much longer than the transverse relaxation time, that is, $\tau \gg T_2$. Apart from the precursor sequel, no recycle delay is required. Arbitrarily assuming that the rotating-frame direction of the RF pulses is aligned along the x' -axis as usual, the amplitude of the FID to be acquired is proportional to the transverse magnetization given by

$$M_{y'}(\tau_+) = M_{z'}(\tau_-) = M_0 \left(1 - \exp\left\{ -\frac{\tau}{T_1} \right\} \right) \quad (3.34)$$

which coincides with Eq. (3.32). The argument is the same: The initial condition at the beginning of the intervals preceding the FID is again $M_{z'} = 0$ as expected for 90° RF pulses applied in the absence of transverse magnetization.

3.1.4.4 Field-Cycling NMR Relaxometry for Measuring T_1 (and T_2) in Low Magnetic Flux Densities

Field-cycling NMR relaxometry is a technique employing an alternative principle for the perturbation of spin systems. Instead of RF pulses, the external magnetic flux

density is switched rapidly to lower or higher values. If this process is performed faster than relaxation, a nonequilibrium magnetization will be established at the end of the switching interval.

The technique is of particular interest if slow molecular motions are to be detected and if the frequency dependence (or “dispersion”) of the spin–lattice relaxation time or spin–lattice relaxation rate is to be examined [9]. Since the frequency is related to the external magnetic flux density by $\nu_0 = \gamma B_0 / (2\pi)$, one actually varies the flux density in this sort of experiment. Figure 3.7a schematically shows a typical field cycle for the determination of the spin–lattice relaxation time T_1 as a function of the external magnetic flux density. Combined with ordinary high-field NMR relaxometry employing the inversion–recovery or saturation–recovery variants, the respective ranges of the resonance frequency for protons (^1H) and deuterons (^2H) are typically

$$10^3 \text{ Hz} < \nu_0(^1\text{H}) < 10^9 \text{ Hz} \quad \text{and} \quad 10^2 \text{ Hz} < \nu_0(^2\text{H}) < 10^8 \text{ Hz} \quad (3.35)$$

The accessibility to such extremely broad frequency scales is the main reason for the unmatched utility of field-cycling NMR relaxometry. There is no other NMR technique offering these particular specifications.

The high-frequency limit of the application range is given by the available high-field magnets. At low frequencies, the technique will be restricted for the following reasons: (1) The so-called *local field* representing the secular part of the spin couplings can possibly approach the mT level if motional averaging is incomplete. The external flux density in the relaxation interval may therefore be outvalued. (2) The same problem can arise if the compensation of the earth field (or other magnetic stray fields in the lab) at the sample position is imperfect. (3) If the field-switching intervals are not short enough, relaxation losses during these intervals may prevail. (4) If the low-field spin–lattice relaxation times become shorter than the correlation time of the longest correlation function component, the Bloch/Wangsness/Redfield (BWR) relaxation theory [10], to be outlined in Sect. 3.1.5, is no longer applicable so that interpretations may become delicate.

As illustrated in Fig. 3.7a, the external magnetic flux density is cycled in a sequence of three different values: the *polarization* field, the *relaxation* or *evolution* field, and the *detection* field. The sample is polarized in the polarization field, B_p , which is chosen as high as compatible with the cooling device of the (usually resistive) magnet coil. This preparation of the initial magnetization takes a couple of spin–lattice relaxation times until the Curie’s equilibrium magnetization $M_0(B_p)$, Eq. (3.8), is reached for the polarization flux density.

The magnetic flux density is then electronically switched down to the preselected relaxation field, B_r , at which spin–lattice relaxation is to be examined. The relevant frequency is consequently given by $\nu_0 = \gamma B_r / (2\pi)$. The field-switching rate must be large enough to avoid excessive relaxation losses of the magnetization during the switching process. As shown in Chapter 15 of Ref. [1], relaxation losses of this sort are largely a matter of the sensitivity but do not lead to artifacts of the measurement as long as the specifications given in Fig. 3.7a for the critical field crossover intervals are granted.

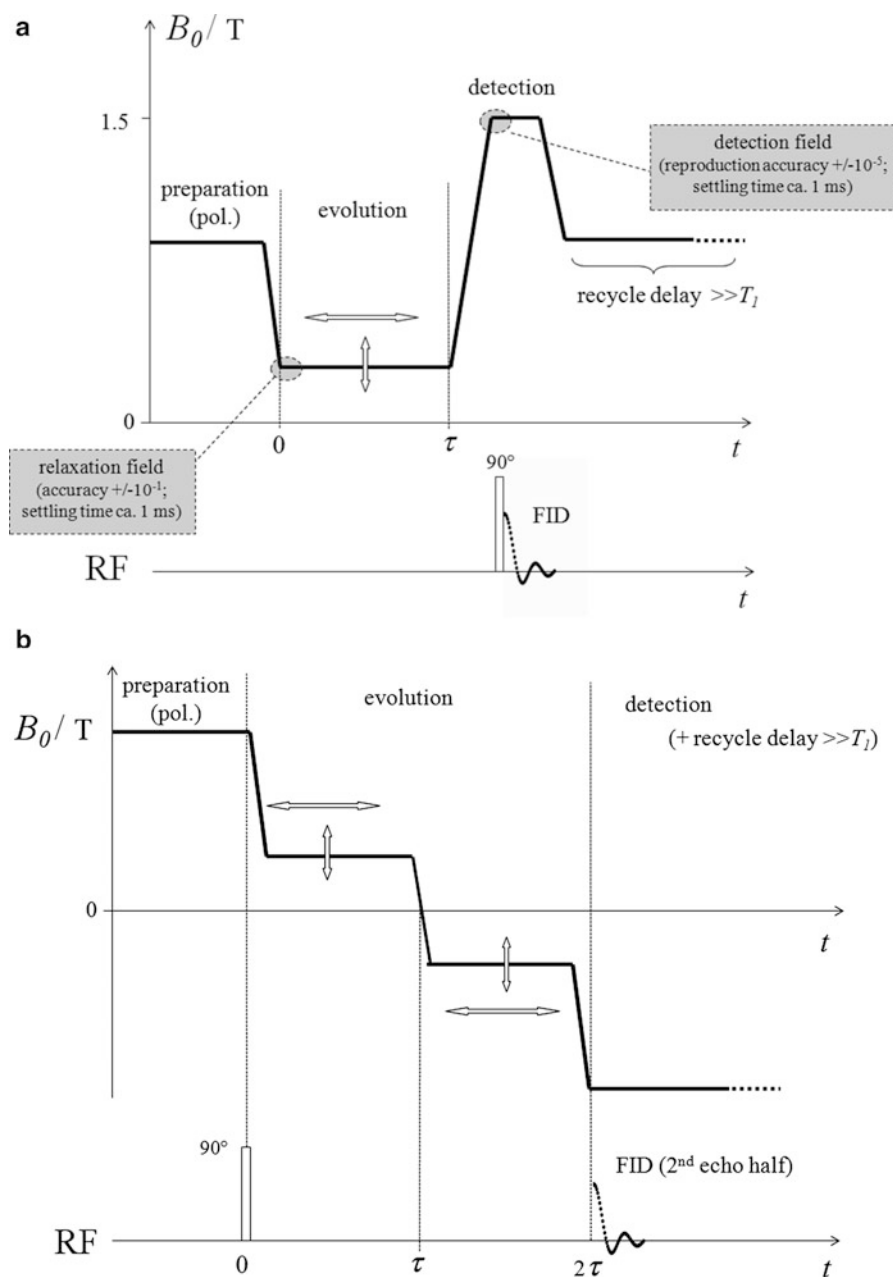


Fig. 3.7 (a) Field-cycling NMR relaxometry technique for measuring the spin–lattice relaxation times T_1 at low fields as a function of the external flux density. A field cycle consists of a *preparation* interval 5–10 times longer than T_1 at the high-flux density of the polarization field. Rapid switching of the flux density to a lower (or higher) relaxation field generates a nonequilibrium magnetization which relaxes in the subsequent *evolution* interval toward the Curie’s

At low fields, proton and especially deuteron spin–lattice relaxation times of viscous systems may easily fall short of a millisecond. That is, coming from the large polarization field of typically 0.5 T, relaxation fields as low as 10^{-5} T must be reached *and* settled *and* stabilized with a desired accuracy of better than 10% within the total passage time (which is in the order of 1 ms). The short settling time is a stringent condition which is technically not easy to fulfill. Likewise, the passage from the relaxation field to the detection field should occur in a transition time of the same order. In particular, the detection flux density needed for magnetic resonance must be matched and reproduced with an accuracy of about 10^{-5} in subsequent transients. It is therefore of paramount importance to check and calibrate the field cycle with the aid of a test device providing the accuracy, the time resolution, and, in particular, the dynamic range required.

In the relaxation field, the magnetization is aligned along the external magnetic-field direction and is initially equal to the Curie's equilibrium magnetization in the polarization field

$$M(0) = M_z(0) \approx M_0(B_p) \quad (3.36)$$

provided that relaxation losses during the switching interval can be neglected. Equation (3.36) is the initial condition for the subsequent relaxation interval. The magnetization relaxes then toward the new Curie's equilibrium magnetization of the relaxation field, $M_0(B_r)$. Based on Bloch's equation for the z component, the magnetization decays according to

$$M_z(\tau) = M_0(B_r) + [M_0(B_p) - M_0(B_r)] \exp\{-\tau/T_1(B_r)\} \quad (3.37)$$

as a function of time.

The magnetization remaining after the relaxation interval τ is finally detected with the aid of a 90° RF pulse after having switched the magnetic flux density to a fixed detection field. Instead of a 90° RF pulse, a Hahn spin-echo sequence can be employed for this purpose as well. Spin-echo signal detection is of interest if contributions from solid-like constituents in the sample are to be suppressed. An example is the heterogeneous composition of biological tissue where signals of the liquid part subjected to motional averaging are of prior interest (see Sect. 7.5.5.5).



Fig. 3.7 (continued) magnetization for the relaxation field. The relaxation curve is probed point by point by varying the length of the evolution interval and switching to a *detection* field as high as possible. The signal is produced with the aid of a 90° RF pulse schematically shown at the *bottom*. The amplitude of the FID (*undulatory dotted line*) generated by this detection pulse is proportional to the magnetization retained at the end of the evolution interval. Typical values of the switching time are in the order of 1 ms. Electronically switched magnets reach flux densities of typically 1–2 T. The values employed for polarization and detection fields are optimized with respect to the duty cycle (Reproduced from Ref. [9] with kind permission of © Elsevier 2004) (b) Proposal for a gradient-echo variant for measuring T_2 . Note that inverting the flux density also inverts the field gradient, so that an echo signal appears after the echo time $t_E = 2\tau$

Since the acquisition of a free-induction signal with the 90° pulse-detection method takes only a few milliseconds, the detection field period can be kept short. As a consequence, the detection flux density can be very strong without thermally overloading the magnet coil in the duty cycle.

After signal acquisition, the flux density is switched back to the polarization field value. Allowing for a delay serving the recovering of the equilibrium magnetization for this field, the field cycle can be resumed with an incremented relaxation interval τ . Repeating this process as often as needed provides the relaxation curve Eq. (3.37) for a given flux density B_r point by point. For rendering the whole spin–lattice relaxation dispersion curve, the relaxation flux density B_r is stepped through a series of discrete values spread over the desired flux density (or frequency) range.

Studies of the field dependence of the transverse relaxation time T_2 are less common since T_2 typically varies in a range of only a factor of 10/3 for like spins as can be concluded from the relaxation formulas given at Eq. (3.208). However, this sort of investigation may be of major interest when dealing with scalar coupling of nuclei to unpaired electrons as a relaxation mechanism (see Sect. 3.1.5.9 and Ref. [11]). Under such circumstances, a strong field dependence of T_2 can arise provided that the correlation time is dominated by spin–lattice relaxation of the coupling partner. This will be the case under the conditions assumed for Eq. (3.215). A corresponding field-cycling method employing gradient echoes for the measurement of T_2 is proposed in Fig. 3.7b. (An explanatory illustration how field-gradient echoes are generated can be found further down in Fig. 3.24.)

3.1.4.5 Pulse Sequence for Measuring the Rotating-Frame Spin–Lattice Relaxation Time $T_{1\rho}$

Field-cycling NMR relaxometry is the best choice for probing the low-frequency regime which is sensitive to particularly slow molecular motions. A certain disadvantage is however that a special switching device for the magnetic field is needed. If this hardware is not available, rotating-frame spin–lattice relaxometry can be employed instead. However, this method can by no means substitute the field-cycling technique. Merely a rather narrow frequency window in the kHz regime can be opened in this way. The only advantage is that the technique can be implemented in ordinary high-field NMR spectrometers without the necessity of special hardware.

Relative to the laboratory frame, the quantization field is the external magnetic flux density B_0 , which determines the Zeeman energies of the spin states. As mentioned before, the resonance frequency is consequently given by

$$\nu_0 = \gamma B_0 / (2\pi) \quad (3.38)$$

This is in contrast to the frequency effective for the rotating-frame method. The principle is to generate a situation where (1) the effective field, Eq. (3.19), is given by the flux density of an RF pulse in the rotating frame and (2) the magnetization is aligned along this effective field. The effective field determines then quantization

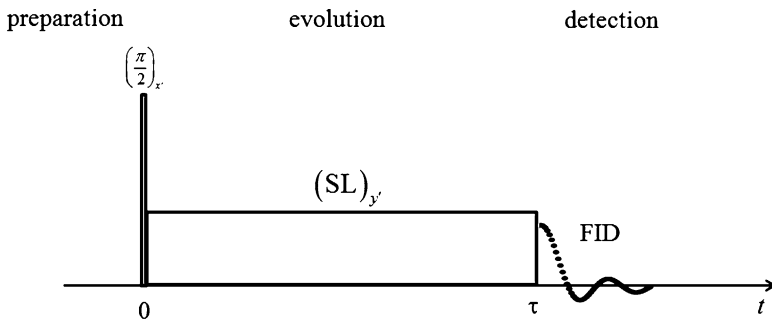


Fig. 3.8 RF pulse scheme for resonant rotating-frame relaxation experiments. The signal to be acquired appears after the spin-lock (SL) pulse in the form of an FID. In the experiment, the duration τ of the spin-lock pulse is incremented in subsequent transients

so that the frequency effective for spin–lattice relaxation in the resonantly rotating frame becomes

$$\nu_1 = \gamma B_1 / (2\pi) \quad (3.39)$$

Depending on the available RF fields, a typical order of magnitude is 1–10 kHz for protons. This is the range for *resonant* rotating-frame relaxometry. A slight extension to larger frequencies can be achieved with *off-resonant* variants (see Refs. [12, 13]).

Figure 3.8 shows the RF pulse scheme for such experiments. Referring to a reference frame resonantly rotating with the (laboratory frame) Larmor frequency, the 90° RF pulse can be treated in the same way as described in Sect. 3.1.3. According to Eq. (3.28), the result is

$$M_{x'}(0+) = 0, \quad M_{y'}(0+) = M_0, \quad M_{z'}(0+) = 0 \quad (3.40)$$

That is, the magnetization is flipped to the y' direction of the rotating frame. Immediately after the initial excitation pulse, the so-called *spin-lock pulse* follows.⁵ It is phase shifted by 90° relative to the excitation pulse. The $\mathbf{B}_1$ field of the spin-lock pulse is consequently aligned along the same direction as the transverse magnetization. It acts therefore as the quantization field relevant in the rotating frame.

The spin-lock magnetization is subject to spin–lattice relaxation (instead of transverse relaxation in the free-evolution case) with the time constant $T_{1\rho}$ (instead of T_2), where the subscript ρ reminds of the rotating frame. The equation of motion of the spin-lock magnetization reads

⁵The term “spin-lock” refers to the fact that transverse magnetization is prevented from getting dephased by field inhomogeneities and spin interactions if the RF amplitude B_1 of the spin-lock field is much larger than any residual fields on these grounds. (It is needless to recall that all fields to be compared in this context are fields *effective in the rotating frame*.)

$$\frac{\partial M_{y'}}{\partial t} = -\frac{M_{y'}}{T_{1\rho}} \quad (3.41)$$

The equilibrium magnetization in the quantization field B_1 is negligible relative to laboratory-frame value M_0 since $B_1 \ll B_0$. The solution of Eq. (3.41) is the exponential relaxation function

$$M_{y'}(\tau) = M_0 e^{-\tau/T_{1\rho}} \quad (3.42)$$

3.1.4.6 Hahn Spin-Echo Pulse Sequence for Measuring T_2

As the name says, transverse relaxation refers to thermal equilibration of transverse magnetization. In contrast to longitudinal relaxation, one is therefore interested in the evolution of this component. As mentioned before, it is generated by an excitation RF pulse. The resulting FID obeys Bloch's equation for the transverse magnetization components. This is the idealized scenario suited best for explaining transverse relaxation curves. The actual measuring technique for practical applications will be discussed afterwards.

For the treatment, we assume that $\mathbf{B}_1$ is aligned along the positive x' -axis. The flip angle of the RF pulse is set equal to 90° as usual. The initial conditions just before the RF are pulse $M_{x'}(0-) = M_{y'}(0-) = 0$ and $M_{z'}(0-) = M_0$. This results in $M_{x'}(0+) = 0$, $M_{y'}(0+) = M_0$, $M_{z'}(0+) = 0$ as already outlined in Sect. 3.1.3 for positive γ . The rotating-frame Bloch equation for this transverse magnetization component reads

$$\frac{dM_{y'}}{dt} = -\frac{M_{y'}}{T_2} \quad (3.43)$$

with the solution

$$M_{y'}(\tau) = M_0 \exp\left\{-\frac{\tau}{T_2}\right\} \quad (3.44)$$

τ is the time period starting at the end of the 90° RF pulse, and T_2 is the transverse relaxation time to be determined. Note that this result is only valid under motional-averaging conditions as will be discussed in more detail in Sect. 3.1.5.11. Actually, this was the presupposition of the Bloch equation in the form of Eq. (3.22) anticipating that all anisotropic secular spin couplings are effectively averaged out.

Under practical conditions, free-induction decays are normally not suitable for the determination of T_2 . More or less strong inhomogeneities of the main magnetic field are unavoidable. The origin of the inhomogeneities can be imperfections of the magnet and/or inhomogeneous magnetic-susceptibility distributions in heterogeneously structured samples. The consequence will be that the evolution of transverse magnetization components will strongly be affected as already discussed

in the introduction Sect. 3.1.1. Dephasing of the coherences on these grounds can even totally conceal the transverse relaxation decay.⁶ The destructive superposition of coherences of different Larmor frequencies results in free-induction decays vanishing faster than expected from transverse relaxation alone.

The fundamental difference of the signal decay by transverse relaxation on the one hand and by field inhomogeneities on the other is that the latter is a *reversible* process not subject to thermal equilibration. Fortunately, this cancellation process can be remedied with the aid of Hahn echoes. The principle is to reverse the evolution of the local transverse magnetizations after some time by one or more additional RF pulses with the consequence that after a certain delay all local magnetizations will be recollected in the same precession phase. The signal reappearing in this way is the so-called *Hahn spin echo*.

Figure 3.9 shows the standard RF pulse sequence used for the generation of a spin echo.⁷ Instead of discussing the spin echo in terms of local transverse magnetizations, that is, the average expectation values of the magnetization operator, it is preferable to use the terminology of *spin coherences* as mentioned before. The standard way of calculating the *reversible* part of the time evolution of expectation values of transverse magnetization operators is the density operator formalism.⁸ The *irreversible* part, that is transverse relaxation or displacements by self-diffusion, can then be introduced thereafter in the form of independent

⁶This is in contrast to spin–lattice relaxation where field inhomogeneities are normally of negligible influence.

⁷This RF pulse sequence is usually called Hahn spin-echo sequence though, strictly speaking, Erwin Hahn [14] originally discovered the spin echo produced by two 90° RF pulses instead of the 90°–180° sequence shown in Fig. 3.9. Apart from a loss of a factor ½ in the echo amplitude, the analytical formalism describing the coherence evolution is however equivalent (see the treatment in Ref. [1]). There can be no doubt that Erwin Hahn is the pioneer of spin echoes!

⁸The time evolution of observables $\mathcal{O}$ in ensembles can be calculated with the aid of density operators $\rho(t)$. The average expectation value of the observable, that is, the measurable quantity, obeys the relation $\overline{\langle \mathcal{O} \rangle} = \text{Tr}\{\rho(t)\mathcal{O}\}$. The bar indicates an average overall states of a state mixture in the ensemble of spin systems. The time dependence of the density operator results from the Liouville/von Neumann equation $\partial\rho(t)/\partial t = i\hbar^{-1}[\rho(t), \mathcal{H}]$ with the initial condition $\rho(0) = \rho_0$, where ρ_0 is the density operator in thermal equilibrium. The solution requires that the Hamiltonian $\mathcal{H}$ under the action of which the evolution takes place must be temporally *constant*. That is, the calculation of a pulse sequence is performed interval by interval with constant Hamiltonians. In the high-temperature approximation, the density operator can be represented by $\rho = a + b\sigma$, where a and b are constants. Since evolution of the observable is not affected by these constants, it suffices to do all calculations with the aid of the *reduced density operator* σ . The solution of the Liouville/von Neumann equation in terms of the reduced density operator is then given for the time interval $0 \rightarrow t$ by the “sandwich” expression $\sigma(t) = \exp\{-(i/\hbar)\mathcal{H}t\}\sigma(0)\exp\{(i/\hbar)\mathcal{H}t\}$. In the present context where we deal with the time evolution of uncoupled spins in a flux density $\mathbf{B}$ (of the external magnetic field or of the RF field), the envisaged operators are $\mathcal{O} = \boldsymbol{\mu} = \gamma\hbar\mathbf{I}$, $\mathcal{H} = -\boldsymbol{\mu} \cdot \mathbf{B}$, and $\sigma(0) = \sigma_0 = I_z$. The vector $\boldsymbol{\mu}$ is the operator of the nuclear magnetic dipole moment, and $\mathbf{I}$ is the dimensionless spin operator. A general introduction to the density operator formalism can be found in Ref. [5]. Selective applications of interest here are elaborated in more detail in Ref. [1].

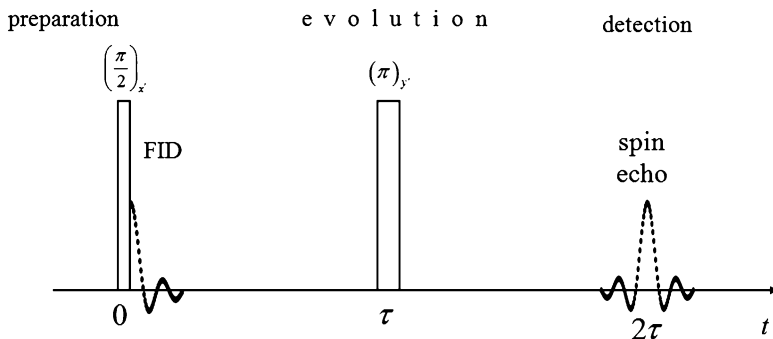


Fig. 3.9 RF pulse scheme for measuring the transverse relaxation time T_2 with the aid of Hahn spin echoes. The respective rotating-frame phase directions of the two RF pulses have arbitrarily been assumed to be x' and y' (the 90° shift of the second RF pulse relative to the first one grants that the spin echo appears with the same precession phase as the initial FID). The pulse sequence starts with the spin system in thermal equilibrium. The first pulse flips the magnetization in the y' direction for positive γ . In the evolution interval, the local transverse magnetizations are dephased by the inhomogeneity of the main magnetic field. The 180° (or π) RF pulse after an interval τ inverts the precession phase shifts so that the local spin coherences are refocused after another interval τ in the form of an echo signal. The echo amplitude relaxes toward 0 with the time constant T_2 provided that anisotropic spin interactions are subject to motional averaging. The FID and the spin echo are represented by *undulatory dotted lines*

attenuation factors. The primary task is thus to calculate the coherence evolution of an ensemble of uncoupled spins $I = 1/2$ during the pulse sequence shown in Fig. 3.9.

The observable to be considered is the nuclear magnetic dipole moment with the vector operator $\boldsymbol{\mu} = \gamma \hbar \mathbf{I}$ where $\mathbf{I}$ is the dimensionless spin vector operator. The density operator in its reduced form where all constant factors and terms are omitted is based on the components of the spin vector operator. Instead of the more common Cartesian representation of spin operators, it is favorable to employ the *spherical product operator* formalism. All definitions and rules needed in the present context can be found in Ref. [1], for instance. According to our convention, time moments just before and immediately after RF and field gradient pulses will be indicated by minus and plus signs, respectively. As a consequence of the field inhomogeneity, there will be a distribution of local Larmor frequencies across the sample. The subsequent formalism therefore refers to a reference frame rotating with the *average* Larmor frequency about the z -axis.

The initial reduced density operator is given by the equilibrium density operator,

$$\sigma(0-) = \sigma_0 = I^{(0)} \quad (3.45)$$

where $I^{(0)} = I_{x'}$ [1]. The sequence begins with a 90° pulse of width τ_{90} and a rotating-frame phase direction arbitrarily assumed along the x' -axis. The rotating-frame Hamiltonian during this RF pulse is defined by $\mathcal{H}_{90} = -\hbar \gamma B_1 I_{x'}$, where B_1 is

the amplitude of the flux density component of the RF field synchronously rotating with the reference frame. The reduced density operator immediately after this pulse reads

$$\sigma(0+) = e^{-\frac{i}{\hbar}\mathcal{H}_{90}\tau_{90}}\sigma(0-)e^{+\frac{i}{\hbar}\mathcal{H}_{90}\tau_{90}} = \frac{i}{\sqrt{2}}\left(I^{(+1)} + I^{(-1)}\right) \quad (3.46)$$

where $I^{(+1)} = 2^{-1/2}(I_{x'} + iI_{y'})$ and $I^{(-1)} = 2^{-1/2}(I_{x'} - iI_{y'})$ [1].

In the first free-evolution interval of length τ , the coherences are subjected to the rotating-frame Hamiltonian $\mathcal{H}_{\text{off}} = -\hbar\gamma B_{\text{off}}I_z$, where B_{off} is the local offset of the magnetic flux density from the mean value in the sample. The result is

$$\sigma(\tau-) = e^{-\frac{i}{\hbar}\mathcal{H}_{\text{off}}\tau}\sigma(0+)e^{+\frac{i}{\hbar}\mathcal{H}_{\text{off}}\tau} = \frac{i}{\sqrt{2}}\left(I^{(+1)}e^{i\varphi_1} + I^{(-1)}e^{-i\varphi_1}\right) \quad (3.47)$$

$\varphi_1 = \gamma B_{\text{off}}\tau$ is the local phase shift produced by the field offset. The subsequent 180° RF pulse of length τ_{180} and a rotating-frame phase direction assumed along the y' direction convert Eq. (3.47) to

$$\sigma(\tau+) = e^{-\frac{i}{\hbar}\mathcal{H}_{180}\tau_{180}}\sigma(\tau-)e^{+\frac{i}{\hbar}\mathcal{H}_{180}\tau_{180}} = \frac{i}{\sqrt{2}}\left(I^{(-1)}e^{i\varphi_1} + I^{(+1)}e^{-i\varphi_1}\right) \quad (3.48)$$

with $\mathcal{H}_{180} = -\hbar\gamma B_1 I_{y'}$.

The second free-evolution interval of the same length τ produces a further phase shift $\varphi_2 = \gamma B_{\text{off}}\tau = \varphi_1$. At the echo time $t_E = 2\tau$, this leads to the reduced density operator

$$\begin{aligned} \sigma(2\tau) &= e^{-\frac{i}{\hbar}\mathcal{H}_{\text{off}}\tau}\sigma(\tau+)e^{+\frac{i}{\hbar}\mathcal{H}_{\text{off}}\tau} = \frac{i}{\sqrt{2}}\left(I^{(-1)}e^{i(\varphi_1-\varphi_2)} + I^{(+1)}e^{-i(\varphi_1-\varphi_2)}\right) \\ &= \frac{i}{\sqrt{2}}\left(I^{(-1)} + I^{(+1)}\right) = iI_{x'} \end{aligned} \quad (3.49)$$

This result is obviously independent of the offset field B_{off} . That is, the precession phase shifts in the two free-evolution intervals cancel irrespective of the position in the inhomogeneous magnetic field. The echo signal is not attenuated by destructive interference. This is the essence of the Hahn spin-echo phenomenon.

The signal voltage to be detected in the experiment is proportional to the transverse magnetization given in complex notation by [5]

$$\begin{aligned} m_{\text{trans}}(2\tau) &= M_{x'}(2\tau) + iM_{y'}(2\tau) \\ &= n\text{Tr}\{\sigma(2\tau)\mu_{x'}\} + i\text{Tr}\{\sigma(2\tau)\mu_{y'}\} \\ &= n\gamma\hbar(\text{Tr}\{\sigma(2\tau)I_{x'}\} + i\text{Tr}\{\sigma(2\tau)I_{y'}\}) \\ &= iM_0 \end{aligned} \quad (3.50)$$

where n is the number density of spins. The transverse magnetization, $M_{y'}(2\tau) = M_0$, is aligned along the positive y' -axis of the rotating frame after the time 2τ just as the transverse magnetization after the excitation pulse has been initially.

This is the reversible part of the spin coherence evolution during the Hahn spin-echo pulse sequence shown in Fig. 3.9. The irreversible echo attenuation by transverse relaxation as a function of the echo time 2τ is the same as the decay of a free-induction signal would be in a perfectly homogeneous field in the absence of residual spin couplings.⁹ The effective relaxation curve is thus established by

$$M_{y'}(2\tau) = M_0 \exp\left\{-\frac{2\tau}{T_2}\right\} \quad (3.51)$$

in analogy to Eq. (3.44). Incrementing the interval τ in subsequent transients of the pulse sequence and measuring the spin-echo amplitude as a function of the echo time permit the evaluation of the transverse relaxation time in inhomogeneous magnetic fields.

From the above derivation of the Hahn echo phenomenon, it becomes evident that distinct spin echoes will only occur if perceptible field inhomogeneities exist. The distribution of Larmor frequencies in the sample must be broad enough for sufficient dephasing of the spin coherences in the RF pulse intervals. Occasionally, it may therefore be difficult to identify distinct Hahn spin echoes in homogeneous samples in the extremely homogeneous fields of high-resolution magnets.

On the other hand, the magnetic field should not be too inhomogeneous in order to avoid conflicts with another condition anticipated in the above analysis: It was assumed that all nuclei remain at the same position during the whole pulse sequence so that the field offset B_{off} “seen” by the spins is stationary. However, if translational diffusion is fast enough, this will no longer be the case, and some additional irreversible attenuation is expected. As will become obvious in the context of field-gradient NMR diffusometry (Sect. 3.2), this effect will only be negligible in the limit $\gamma^2 g^2 \tau^3 \ll D^{-1}$, where D is the self-diffusion coefficient and where the magnetic-field inhomogeneity is characterized by a spatially constant gradient g . If needed, the influence of diffusion can be reduced with the aid of the Carr/Purcell/Meiboom/Gill pulse sequence to be described in the following section.

If secular spin interactions are not or only incompletely averaged out on the NMR time scale (i.e., the reciprocal rigid-lattice linewidth), substantial deviations from the mono-exponential relaxation function predicted by Eq. (3.51) are expected. This scenario will be discussed in the context of the Anderson/Weiss formalism outlined in Sect. 3.1.6. It should also be mentioned that in this case, the so-called *solid echoes* can be generated with the aid of special pulse sequences compensating secular spin interactions rather than field inhomogeneities. Analytical treatments can be found in Refs. [1, 4].

⁹ Losses by other mechanisms such as *radiation damping* may exist but are negligible under normal conditions [15].

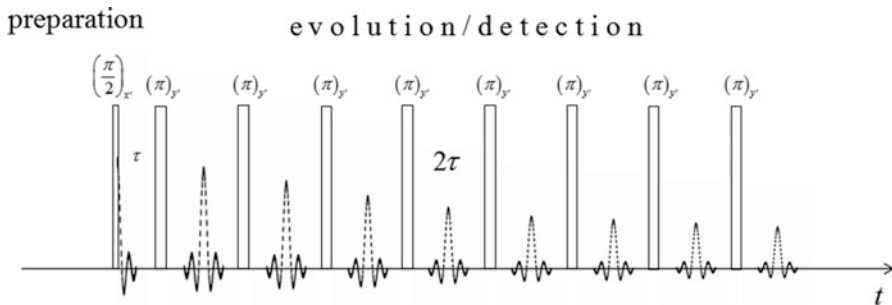


Fig. 3.10 Carr/Purcell/Meiboom/Gill (CPMG) RF pulse sequence for measuring T_2 . The sequence consists of a 90° preparation RF pulse and an equidistant comb of 180° RF pulses with a phase shift of 90° relative to the preparation pulse. The spacing between the 180° pulses is twice as long as the delay of the first 180° pulse from the 90° pulse. The amplitudes of the echoes appearing in the middle between the 180° pulses provide the transverse relaxation curve. The FID and the spin echoes are represented by *undulatory dotted lines*

3.1.4.7 CPMG Pulse Sequence for Measuring T_2

Figure 3.10 shows the RF pulse scheme for the *Carr/Purcell/Meiboom/Gill* (CPMG) technique. Apart from the reduction of the irreversible influence of translational diffusion in inhomogeneous magnetic fields, the advantage of this method is that a series of successive spin echoes is generated in a single transient. This permits the acquisition of the total attenuation curve at one time without the need to increment the pulse intervals in subsequent cycles.

As already demonstrated by Eq. (3.50), the first 180° RF pulse refocuses the spin coherences of the FID initially generated by the preparation pulse. This is the first of a whole series of spin echoes. The next 180° RF pulse reproduces the first spin echo as the second spin echo in the following free-evolution interval, and so on. Since this periodical refocusing process exclusively refers to transverse magnetization, the echoes will be attenuated by transverse relaxation according to

$$M_y(2N\tau) = M_0 \exp\left\{-\frac{2N\tau}{T_2}\right\} \quad (3.52)$$

where N is the number of preceding 180° RF pulses. If the pulse spacing 2τ is chosen short enough so that diffusive displacements in this interval are correspondingly small, attenuation by self-diffusion can be neglected. Assuming a field inhomogeneity in the form of a spatially constant gradient g , one can show that this will be the case in the limit $\gamma^2 g^2 N\tau^3 \ll D^{-1}$ [16].

3.1.5 Bloch/Wangsness/Redfield Theory of Spin Relaxation

3.1.5.1 Outline of the Strategy

Spin relaxation, that is, the evolution of the magnetization components from thermal nonequilibrium to equilibrium, is due to spin transitions induced by fluctuations of spin interactions such as dipole–dipole coupling between nuclei or nuclear quadrupole coupling to electric-field gradients. The stochastic time dependence of these fluctuations originates from molecular motions in the sense of rotational and translational diffusion. As already discussed above, two relaxation rates must be distinguished: (1) The spin–lattice (or longitudinal) relaxation rate T_1^{-1} as the inverse time constant with which the z component M_z (aligned along the external magnetic-field $\mathbf{B}_0$) of the magnetization approaches equilibrium, and (2) the transverse relaxation rate T_2^{-1} describing the irreversible decay of the transverse magnetization components usually represented in complex form

$$m = M_x + iM_y \quad (3.53)$$

The rates with which nonequilibrium magnetization components vary can be traced back to transitions between the states of the considered spin systems: In this sense, the relaxation rates can be defined as the weighted sum over all relevant *transition probabilities per unit time*, w_j :

$$\frac{1}{T_{1,2}} = \sum_j a_j w_j \quad (3.54)$$

The coefficients a_j depend on the number of spins involved in the transition and on the multiplicity of multiple-quantum transitions as will be outlined below. For example, the spin–lattice relaxation rate of dipolar-coupled two-spin $\frac{1}{2}$ systems of like dipoles is composed of single- (w_1) and double-quantum (w_2) transition probabilities according to

$$\frac{1}{T_1} = 2w_1(\omega_0) + 2w_2(2\omega_0) \quad (3.55)$$

as suggested by the Zeeman energy level scheme shown in Fig. 3.11. The detailed version of Eq. (3.55) will be presented in Eq. (3.138).

In the case of spin–lattice relaxation, the quantities w_j exclusively refer to transitions connected with *energy exchange* between the spin system and the molecular degrees of motional freedom. Depending on the responsible spin interactions and the dipole species, these processes can be single- and double-quantum transitions, and – as long as they do not conserve spin energy – zero-quantum transitions as well (e.g., compare the Zeeman energy level schemes shown in Figs. 3.11 and 3.12, for example).

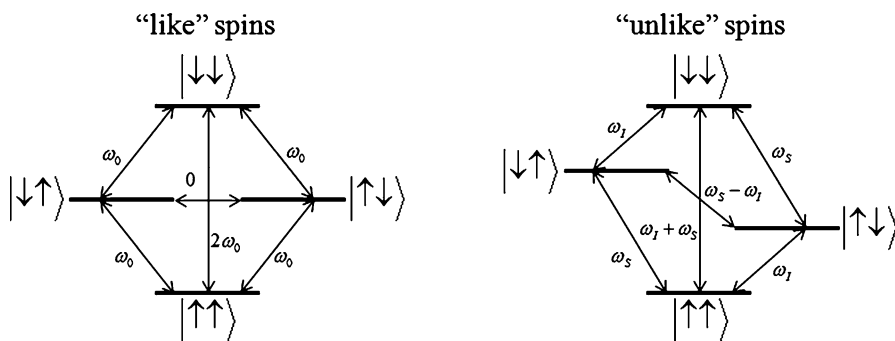
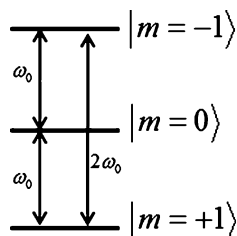
two-spin $\frac{1}{2}$ systems

Fig. 3.11 Zeeman energy levels $E_{m_I, m_S} = -\mu_{I,z}B_0 - \mu_{S,z}B_0 = -\gamma_I\hbar m_I B_0 - \gamma_S\hbar m_S B_0$ of like (left) and unlike (right) two-spin $\frac{1}{2}$ systems. The spin states are symbolized by kets $|\uparrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$, and $|\downarrow\downarrow\rangle$ for the diverse combinations of spin-up and spin-down states relative to the external magnetic flux density B_0 . In this representation, the flux density is assumed to point upward, and gyromagnetic ratios are chosen to be positive for both spin species as usual. The eigen-states correspond to the magnetic single-spin quantum numbers $m_I = 1/2$, $m_I = -1/2$, $m_S = 1/2$, and $m_S = -1/2$. The double arrows between the levels indicate the zero-, single-, and double-quantum transitions relevant for spin relaxation. The transition angular frequencies are indicated

Fig. 3.12 Zeeman energy levels of spin-1 nuclei in the high-field limit defined by $\langle\mathcal{H}_0\rangle \gg \langle\mathcal{H}_q\rangle$ for the expectation values of the Hamiltonians. Spin-1 particles have three eigenstates with the kets $|m = 1\rangle$, $|m = 0\rangle$, and $|m = -1\rangle$. The arrows between the levels indicate the single- and double-quantum transitions relevant for spin relaxation. The transition angular frequencies are indicated. In this representation, a positive gyromagnetic ratio was assumed



On the other hand, transverse relaxation does not necessarily stipulate transfer of spin energy to non-spin reservoirs. Rather, any spin transition induced by randomly fluctuating spin interactions will contribute. That is, zero-quantum transitions will be significant in any case. From the theoretical point of view, this is the main difference between transverse and spin–lattice relaxation.

The primary objective in the treatment of spin relaxation is consequently the determination of the spin transition probabilities per unit time, w_j , as a function of characteristics of thermal fluctuations. A tool appropriate for this task is *time-dependent perturbation theory* with spin couplings acting as perturbations. In the frame of this well-known-quantum-mechanical formalism, the first step to be established will be the derivation of the so-called *master equation*.¹⁰ The name of this equation of motion reminds of the general applicability to all observables and spin interactions relevant in the context of spin relaxation. Corresponding specifications can therefore be deferred to later stages of the theory.

3.1.5.2 The Master Equation

As the most popular spin-relaxation concept, we will refer to the *Bloch/Wangsness/Redfield (BWR) theory* [1, 4, 15]. The BWR theory is a density operator perturbation-theoretical approach of the so-called weak-collision case of fluctuating spin interactions. The technical term “weak collision” means that – contrary to *strong collisions* – the fluctuating perturbations are assumed to be small relative to the splitting energy in the external magnetic field. A discussion of this particular distinction of cases can be found in Ref. [18], but would be beyond the scope of this present representation.

The Hamiltonian describing a system of interacting spins can be analyzed by a stationary part, $\mathcal{H}_0$, and a relatively small time-dependent perturbation $\mathcal{H}_i(t)$:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_i(t) \quad (3.56)$$

The operator $\mathcal{H}_0$ primarily refers to Zeeman interaction between the nuclear dipole-moment $\boldsymbol{\mu}$ and the external magnetic flux density $\mathbf{B}_0$:

$$\mathcal{H}_Z = -\boldsymbol{\mu} \cdot \mathbf{B}_0 \quad (3.57)$$

$\mathcal{H}_0$ may also include any other time-independent contribution due to chemical or susceptibility shifts and spin interactions.

¹⁰ For the interested reader, it is noteworthy that an alternative derivation of the master equation exists which is not based on the standard perturbation theory [17]. The result is identical, but the formalism is more demanding.

The perturbative part, $\mathcal{H}_i(t)$, is due to the fluctuating part of spin interactions. As a consequence of the stochastic nature of these fluctuations, the ensemble average vanishes, $\overline{\mathcal{H}_i(t)} = 0$. Spin interactions of particular interest are dipolar and scalar coupling between nuclei and quadrupolar coupling between nuclear quadrupole moments and gradients of the electric field within molecules [1, 2, 15]. Let us briefly specify the corresponding Hamiltonians:

- (a) *Dipolar coupling between a pair of magnetic dipoles with the vector operators $\boldsymbol{\mu}_I$ and $\boldsymbol{\mu}_S$:*

$$\mathcal{H}_d = \frac{\mu_0}{4\pi} \frac{1}{r^3} \left\{ \boldsymbol{\mu}_I \cdot \boldsymbol{\mu}_S - \frac{3(\boldsymbol{\mu}_I \cdot \mathbf{r})(\boldsymbol{\mu}_S \cdot \mathbf{r})}{r^2} \right\} \quad (r > 0) \quad (3.58)$$

$\mathbf{r}$ is the distance vector between the dipoles. μ_0 is the magnetic-field constant.

- (b) *Scalar coupling between spins with (dimensionless) vector operators $\mathbf{I}$ and $\mathbf{S}$:*

$$\mathcal{H}_s = A \mathbf{I} \cdot \mathbf{S} \quad (3.59)$$

A is the scalar coupling constant.

- (c) *Quadrupole coupling of a nuclear spin with the vector operator $\mathbf{I}$ to the electric-field-gradient tensor $\tilde{\Gamma}$ in a molecule:*

$$\mathcal{H}_q = \frac{eQ}{2I(2I-1)} \mathbf{I} \cdot \tilde{\Gamma} \cdot \mathbf{I} \quad (3.60)$$

Q is the quadrupole moment of the nucleus with the spin quantum number I , and e is the positive elementary charge.

Explanations to these interactions and applications will follow below.

The general equation of motion for the density operator of a spin system is given in the form of the Liouville/von Neumann equation

$$\frac{d\rho}{dt} = -\frac{i}{\hbar} [\mathcal{H}_0 + \mathcal{H}_i, \rho] = -\frac{i}{\hbar} [\mathcal{H}_0, \rho] - \frac{i}{\hbar} [\mathcal{H}_i, \rho] \quad (3.61)$$

The brackets on the right-hand side indicate commutators of two operators. The commutator of the operators $\mathcal{H}_0$ and ρ , for example, is defined by $[\mathcal{H}_0, \rho] \equiv \mathcal{H}_0 \rho - \rho \mathcal{H}_0$. In order to get rid of the non-fluctuating operator $\mathcal{H}_0$, Eq. (3.61) can be transformed into the so-called *interaction representation*. Quantities referring to this picture will be marked by primes as used before. The unitary-transformation relations for the operators in Eq. (3.61) are

$$\rho = U \rho' U^{-1}; \quad \mathcal{H}_0 = U \mathcal{H}_0' U^{-1} \equiv \mathcal{H}_0'; \quad \mathcal{H}_i = U \mathcal{H}_i' U^{-1} \quad (3.62)$$

where¹¹

$$U \equiv e^{-(i/\hbar)\mathcal{H}_0 t} \quad (3.63)$$

In order to transform Eq. (3.61), the time derivative of the transformation relation of the density operator is needed. Deriving the first equation given in Eq. (3.62) gives in compact form

$$\frac{d\rho}{dt} = -\frac{i}{\hbar} U [\mathcal{H}'_0, \rho'] U^{-1} + U \frac{d\rho'}{dt} U^{-1} \quad (3.64)$$

Employing the transformation relations in Eq. (3.62) again, the right-hand side of Eq. (3.61) can be rewritten as

$$-\frac{i}{\hbar} [\mathcal{H}_0, \rho] - \frac{i}{\hbar} [\mathcal{H}_i, \rho] = -\frac{i}{\hbar} U [\mathcal{H}'_0, \rho'] U^{-1} - \frac{i}{\hbar} U [\mathcal{H}'_i, \rho'] U^{-1} \quad (3.65)$$

Equating Eqs. (3.64) and (3.65), and multiplying by U^{-1} from the left and by U from the right gives the *Liouville/von Neumann equation for the interaction reference frame*

$$\frac{d\rho'}{dt} = -\frac{i}{\hbar} [\mathcal{H}'_i, \rho'] \quad (3.66)$$

The integral thereof is

$$\rho'(t) = \rho'(0) - \frac{i}{\hbar} \int_0^t [\mathcal{H}'_i(t_1), \rho'(t_1)] dt_1 \quad (3.67)$$

Note that both results, Eq. (3.66) as well as Eq. (3.67), do no longer depend on the stationary Hamiltonian $\mathcal{H}_0$. The remaining Hamiltonian is $\mathcal{H}'_i(t)$, and this is the reason for the denotation “interaction representation.”

An approximate solution of the Liouville/von Neumann equation is found with the aid of the *Picard-iteration* variant of time-dependent perturbation theory. We start with the zeroth approximation

¹¹ In case $\mathcal{H}_0$ represents the Zeeman interaction of a *single* dipole species, so that according to Eq. (3.57) $\mathcal{H}_0 = -\boldsymbol{\mu} \cdot \mathbf{B}_0 = -\gamma \hbar \mathbf{I} \cdot \mathbf{B}_0$, these relations simultaneously mediate the transformation to a frame *resonantly rotating* with the Larmor frequency $\boldsymbol{\omega}_L = -\gamma \mathbf{B}_0$. However, quite often we will refer to spin systems consisting of two or more *different* spin species characterized by deviating gyromagnetic ratios. The transformation to the interaction representation nevertheless works, but, as a matter of course, it can no longer be identified with a “transformation to a resonantly rotating frame.” A colloquial wording used instead is sometimes “transformation to a double (or multiply) rotating reference frame.”

$$\rho'(t) \approx \rho'(0) \quad (3.68)$$

Replacing $\rho'(t)$ in the integral on the right-hand side of Eq. (3.67) by the zeroth approximation gives the first-order approximation

$$\rho'(t) \approx \rho'(0) - \frac{i}{\hbar} \int_0^t [\mathcal{H}'_i(t_1), \rho'(0)] dt_1 \quad (3.69)$$

Inserting this in turn into the integral on the right-hand side of Eq. (3.67) leads to the second approximation

$$\begin{aligned} \rho'(t) \approx & \rho'(0) - \frac{i}{\hbar} \int_0^t [\mathcal{H}'_i(t_2), \rho'(0)] dt_2 \\ & + \left(\frac{i}{\hbar}\right)^2 \int_0^t dt_2 \int_0^{t_2} dt_1 [\mathcal{H}'_i(t_2), [\mathcal{H}'_i(t_1), \rho'(0)]] \end{aligned} \quad (3.70)$$

and so on. Fortunately, it turns out that higher-order approximations are not necessary in the frame of any experimentally relevant accuracy.

The time derivative of Eq. (3.70) is

$$\frac{d\rho'}{dt} = -\frac{i}{\hbar} [\mathcal{H}'_i(t), \rho'(0)] - \frac{1}{\hbar^2} \int_0^t [\mathcal{H}'_i(t), [\mathcal{H}'_i(t_1), \rho'(0)]] dt_1 \quad (3.71)$$

With the substitution $t_1 = t - \tau$, this expression can be rewritten as

$$\frac{d\rho'}{dt} = -\frac{i}{\hbar} [\mathcal{H}'_i(t), \rho'(0)] - \frac{1}{\hbar^2} \int_0^t [\mathcal{H}'_i(t), [\mathcal{H}'_i(t - \tau), \rho'(0)]] d\tau \quad (3.72)$$

The time dependence $\mathcal{H}' = \mathcal{H}'_i(t)$ refers to the particular spin system under consideration. In reality, one is dealing with an ensemble of spin systems experiencing statistically varying functions $\mathcal{H}'_i(t)$. That is, quantities measured in experiments are averages over the variation of these time dependences. Notabene, this type of average must not be confused with the ensemble average inherent to the density operator discussed above. The density operator is an average over the distribution of *state vectors* in the ensemble (i.e., different compositions of eigenstates and different phases). Here we are dealing with the additional average over the *different time dependences* the fluctuating spin interactions in the ensemble are subjected to. Equation (3.72) must therefore be averaged correspondingly. In the following, this average will be indicated by a bar.

The spin interactions are assumed to fluctuate stochastically so that $\overline{\mathcal{H}'_i(t)} = 0$. Let us furthermore consider the time limit $t \gg \tau_c$, where τ_c is the correlation time of the spin interactions. The spin-interaction Hamiltonian at time t , $\mathcal{H}'_i(t)$, and the density operator at time 0, $\rho'(0)$, will be uncorrelated in this limit. They can therefore be averaged independently. That is,¹²

$$\overline{[\mathcal{H}'_i(t), \rho'(0)]} = \overline{[\mathcal{H}'_i(t), \overline{\rho'(0)}]} = 0 \quad \text{for } t \gg \tau_c \quad (3.73)$$

Since the average of the integrand in Eq. (3.72) vanishes for $t \gg \tau_c$, the upper integration limit can be equated with ∞ without loss of validity. The average of Eq. (3.72) thus obeys

$$\frac{d\overline{\rho'(t)}}{dt} = -\frac{1}{\hbar^2} \int_0^\infty \overline{[\mathcal{H}'_i(t), [\mathcal{H}'_i(t-\tau), \rho'(0)]]} d\tau \quad (3.74)$$

for $t \gg \tau_c$.

Let us now specify the time range of applicability of this expression in more detail. The iterative approximation procedure we have employed above starts with the zeroth-order $\rho'(t) \approx \rho'(0)$. As a consequence, this approach for the alteration rate of the density operator will be good only in the vicinity of time 0. The density operator is expected to vary significantly on the time scale of the relaxation times T_1 and T_2 . The requirement that the density operator is still close to its initial value thus stipulates $t < T_1, T_2$. On the other hand, the derivation of Eq. (3.74) demands $t \gg \tau_c$. That is, Eq. (3.74) holds good for the range $\tau_c \ll t < T_1, T_2$, that is, the time scale actually relevant in NMR relaxation experiments.

Introducing the stationary equilibrium density operator, $\rho'(\infty) = \rho'_0$, and omitting for simplicity the bar over the pure density operator terms from now on, the instantaneous deviation from equilibrium can be expressed as

$$\frac{d(\rho'(t) - \rho'_0)}{dt} = \frac{d\rho'(t)}{dt} = -\frac{1}{\hbar^2} \int_0^\infty \overline{[\mathcal{H}'_i(t), [\mathcal{H}'_i(t-\tau), (\rho'(t) - \rho'_0)]]} d\tau \quad (3.75)$$

This relation can be combined with the expectation value

$$\langle \mathcal{Q} \rangle' = \text{Tr}\{\rho'(t)\mathcal{Q}\} \quad (3.76)$$

¹²Note that the corresponding average of the Liouville/von Neumann equation, Eq. (3.66), does not vanish because the density operator and the Hamiltonian refer to the *same* time in that case.

of an observable $\mathcal{Q}$ of interest here. Examples are the components of the spin or dipole moment vector operators. The general result is the equation of motion for the expectation value $\langle \mathcal{Q} \rangle'$:

$$\begin{aligned} \frac{d\langle \mathcal{Q} \rangle'}{dt} &= \text{Tr} \left\{ \frac{d\rho'(t)}{dt} \mathcal{Q} \right\} \\ &= -\frac{1}{\hbar^2} \int_0^\infty \text{Tr} \left\{ \overline{[\mathcal{H}'_i(t), [\mathcal{H}'_i(t-\tau), (\rho'(t) - \rho'_0)]]} \mathcal{Q} \right\} d\tau \end{aligned} \quad (3.77)$$

Spelling the double commutator out, we obtain a linear combination of four terms which act as prefactors of the operator $\mathcal{Q}$. The operators in these terms can be rearranged in such a way that the factor $(\rho'(t) - \rho'_0)$ appears ahead of the other operators throughout.¹³ Recombining the four terms in the double-commutator symbolism results in the so-called *master equation*

$$\begin{aligned} \frac{d\langle \mathcal{Q} \rangle'}{dt} &= -\frac{1}{\hbar^2} \text{Tr} \left\{ (\rho'(t) - \rho'_0) \int_0^\infty \overline{[\mathcal{H}'_i(t-\tau), [\mathcal{H}'_i(t), \mathcal{Q}]]} d\tau \right\} \\ &= -\frac{1}{\hbar^2} \text{Tr} \{ (\rho'(t) - \rho'_0) \mathcal{P} \} \end{aligned} \quad (3.78)$$

where the *fluctuation operator* $\mathcal{P}$ is defined by

$$\mathcal{P} = \int_0^\infty \overline{[\mathcal{H}'_i(t-\tau), [\mathcal{H}'_i(t), \mathcal{Q}]]} d\tau \quad (3.79)$$

At this point, it should be recalled that the master equation refers to the interaction representation defined above. That is, the perturbation operator must be converted to this representation before being inserted into Eq. (3.78). Likewise, the solution of the master equation, that is, the time dependence of the expectation value of the observable $\langle \mathcal{Q} \rangle'$ applies to the interaction representation.

Equation (3.78) is of vast generality. It is suitable for treatments with any *spin quantum number* $\geq 1/2$, any *spin-interaction Hamiltonian* $\mathcal{H}'_i(t)$, and with any *observable* $\mathcal{Q}$, such as those relevant for longitudinal and transverse magnetization. In the present context, the most important spin interactions are dipolar and quadrupolar couplings which we have already specified in Eqs. (3.58) and (3.60), respectively. Other interactions possibly affecting spin relaxation under certain conditions are scalar coupling (see Eq. 3.59), chemical-shift anisotropy, spin-rotation

¹³ Here we exploit the rule $\text{Tr} \{ \mathcal{Q}\mathcal{P} \} = \text{Tr} \{ \mathcal{P}\mathcal{Q} \}$ for products of two operators $\mathcal{Q}$ and $\mathcal{P}$. That is, $\text{Tr} \{ [\mathcal{Q}, \mathcal{P}] \} = 0$.

coupling, and spin-phonon coupling. Since the special circumstances under which these latter interactions matter are of minor interest in the present context, the reader is referred to Refs. [1, 8, 15] for more details. Note furthermore that the term *observable* is used here in a generalized form. It may include also longitudinal order or multiple-quantum coherences that cannot be directly detected by RF signals. The existence of such phenomena manifests itself merely *indirectly* via indicative evolution features. This is however a field beyond the scope of this book. Those who are interested are referred to Refs. [1, 2], for instance, for further reading.

In the following, we will make use of Eq. (3.78) in particular by identifying the operator $\mathcal{Q}$, that is, the *observable* of interest, with the spin-operator components of interest, namely, $\mathcal{Q}$, where $j = x, y, z$. The expectation values of spin operators are proportional to the magnetization, the quantity to be actually measured in the experiments described in Sects. 3.1.3 and 3.1.4. The relation linking the magnetization vector with spin vector operators in a system containing a single-spin species is

$$\mathbf{M} = \frac{\gamma \hbar}{V} \sum_k \langle \mathbf{I}^{(k)} \rangle \quad (3.80)$$

where γ is the gyromagnetic ratio, $\hbar$ is Planck's constant divided by 2π , V is the sample volume, and $\langle \mathbf{I}^{(k)} \rangle$ is the expectation value vector of the (dimensionless) spin vector operator $\mathbf{I}^{(k)}$ of spin number k . The summation index k runs over all spins in the sample.

The second specification of the master equation needed for the derivation of spin-relaxation rates refers to the type of the fluctuating perturbation $\mathcal{H}'_i(t)$. Spins are subject to various interactions which tend to fluctuate as a consequence of molecular motions. The couplings most important in the present context have already been denominated in Eqs. (3.58), (3.59), and (3.60). As a first example, we will identify $\mathcal{H}'_i(t)$ with the Hamiltonian of dipolar-coupling $\mathcal{H}'_d(t)$ in the – notabene – interaction representation. Let us first discuss an important issue concerning the nature of dipolar-coupled spin systems and an important consequence for relaxation rates.

3.1.5.3 Classification of Dipolar-Coupled Spin Systems

At least as concerns protons, the nuclei of light hydrogen, dipolar interaction among nuclei is the prevailing origin of spin relaxation in soft-matter systems. The Hamiltonian Eq. (3.58) extended to multi-spin systems can be represented by

$$\mathcal{H}_d = \frac{\mu_0}{4\pi} \sum_{i < j} \frac{1}{r_{ij}^3} \left\{ \boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j - \frac{3(\boldsymbol{\mu}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\mu}_j \cdot \mathbf{r}_{ij})}{r_{ij}^2} \right\} \quad (r_{ij} > 0) \quad (3.81)$$

μ_0 is the magnetic-field constant. The sum runs over all dipole-moments $\boldsymbol{\mu}$ in the system in a pairwise fashion. $\mathbf{r}_{ij}$ is the distance vector between dipoles labeled by the

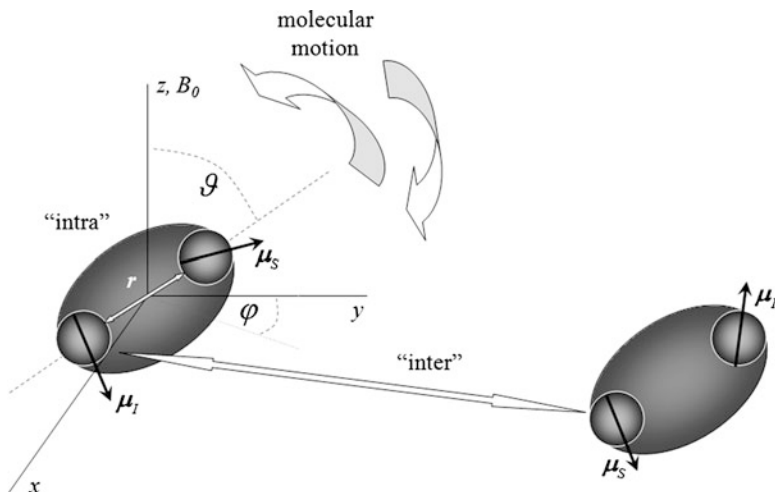


Fig. 3.13 Schematic illustration of dipolar coupling of dipole pairs μ_i and μ_s . The Hamiltonian is determined by the polar coordinates r , φ , ϑ of the dipole–dipole distance vector relative to the laboratory frame. The z -axis is aligned along the direction of the main magnetic field. Dipole pairs linked by dipolar interaction can be on the same molecule (*intramolecular coupling*) or on different particles (*intermolecular coupling*)

subscripts i and j . The magnetic dipole moment and the spin vector I of a particle are related by

$$\mu = \gamma \hbar I \quad (3.82)$$

where γ is the gyromagnetic ratio. If the interacting dipoles refer to the same particle species, that is, if the gyromagnetic ratios are the same, we speak of *like* dipoles. In case of different coupling partners, the dipoles are specified as *unlike*. The latter case refers to different species of nuclides or to nuclei coupled to unpaired electrons.

The Hamiltonian in Eq. (3.81) obviously couples *pairs* μ_i , μ_j of dipoles as illustrated in Fig. 3.13. Molecules normally contain more than two nuclear magnetic dipoles. The question is then whether the sum in Eq. (3.81) over all dipole pairs leads to a corresponding sum of spin-relaxation rates calculated for independent spin pairs. Actually, as already demonstrated in Ref. [19], this can be affirmed as long as cross-correlation effects due to *correlated fluctuations* of the spin system are negligible. Fortunately, even in cases of practically rigid atomic arrangements such as methyl groups or alkenes, perceptible cross-correlated relaxation effects will be restricted to high-resolution NMR in solutions of low viscosity.

In the present context, spin systems can thus be modeled safely as a set of independent two-spin systems. The accuracy of this approximation is much better than typical experimental errors. That is, spin relaxation by dipolar interaction can be treated as the sum of *two-spin-relaxation rates*

$$\frac{1}{T_{1,2}} = \sum_{i < j} \frac{1}{T_{1,2}^{(i,j)}} \quad (3.83)$$

as will become obvious after analyzing the dipolar Hamiltonian Eq. (3.81) in terms of spin-operator expressions according to Eqs. (3.88), (3.89), (3.90), and (3.91). The quantities $1/T_1^{(i,j)}$ and $1/T_2^{(i,j)}$ are the longitudinal or transverse relaxation rates, respectively, of a two-spin system composed of dipoles μ_i and μ_j . If the distance distribution of the dipoles in the sample is such that only isolated, that is, non-interacting dipole pairs are relevant, and if all dipole pairs are identical and fluctuate with the same statistics, it will be sufficient to consider just one dipole pair as a representative of all dipole pairs. In the theory to be outlined below, the sum in Eq. (3.83) can then be omitted.

In later stages of the treatment, we will prescind to some degree from this simplifying assumption by taking into account that a spin can be a partner in intra- and intermolecular pairs at the same time. This may be important since intramolecular interactions typically fluctuate due to *rotational* diffusion of molecules, whereas the coupling of intermolecular pairs is varied mainly by *translational* distance variations. Because of the shorter dipole–dipole distances, the contribution from intramolecular interactions normally dominates. However, at very low frequencies where the slowest motional components of molecular dynamics govern spin relaxation, significant contributions by intermolecular couplings may become important. If the rotational and translational fluctuations of dipolar couplings, a reference dipole is subjected to, can be assumed to be stochastically independent of each other, the effective relaxation rates can be expressed by the sums

$$\frac{1}{T_{1,2}} = \frac{1}{T_{1,2}^{\text{intra}}} + \frac{1}{T_{1,2}^{\text{inter}}} \quad (3.84)$$

In this approach, the sum in Eq. (3.81) is thus reduced to just two contributions a reference spin experiences, namely, intra- and intermolecular couplings.

3.1.5.4 Dipolar Coupling in Two-Spin Systems

The Dipolar Hamiltonian in the Laboratory Reference Frame

The ensemble of two-spin systems under consideration is assumed to be composed of pairs of a spin I and a spin S each. The dipole-moment vectors are

$$\mu_I = \gamma_I \hbar I \quad (3.85)$$

and

$$\mu_S = \gamma_S \hbar S \quad (3.86)$$

respectively. γ_I and γ_S are the (potentially different) gyromagnetic ratios of the spin species. For the moment, we do not yet distinguish whether the dipoles are “like” or

“unlike,” that is, whether the gyromagnetic ratios are the same or not. According to Eq. (3.81), the two-spin dipolar-coupling Hamiltonian is then given by

$$\mathcal{H}_d = \frac{\mu_0}{4\pi} \frac{1}{r^3} \left\{ \boldsymbol{\mu}_I \cdot \boldsymbol{\mu}_S - \frac{3(\boldsymbol{\mu}_I \cdot \mathbf{r})(\boldsymbol{\mu}_S \cdot \mathbf{r})}{r^2} \right\} \quad (r > 0) \quad (3.87)$$

where $\mathbf{r}$ is the distance vector between the dipoles $\boldsymbol{\mu}_I$ and $\boldsymbol{\mu}_S$. This Hamiltonian is now considered as time-dependent perturbation of the spin systems. That is, after having transformed $\mathcal{H}_d$ to the version in interaction representation, $\mathcal{H}'_d$, we set $\mathcal{H}'_i = \mathcal{H}'_d$ in the master equation given at Eq. (3.78). The fluctuating time dependence originates from molecular dynamics, that is, rotational and/or by translational diffusion (see Fig. 3.13), the vector $\mathbf{r} = \mathbf{r}(t)$ is subjected to.

The conversion to the interaction representation and the standard analysis by the so-called spin raising and lowering operators is best done by formally expanding $\mathcal{H}_d$ in terms of spatial functions $F^{(k)}$ and spin-operator expressions $\mathcal{O}^{(k)}$ according to

$$\mathcal{H}_d \equiv f_d \sum_{k=-2}^2 F^{(k)} \mathcal{O}^{(k)} \quad (3.88)$$

The prefactor implies the gyromagnetic ratios of the interacting nuclei:

$$f_d = \frac{\mu_0}{4\pi} \gamma_I \gamma_S \hbar^2 \quad (3.89)$$

The quantities $F^{(k)}(r, \varphi, \vartheta)$ are functions of the polar coordinates r, φ, ϑ describing the distance vector $\mathbf{r}$ between the interacting dipoles as illustrated in Fig. 3.13:

$$\begin{aligned} F^{(0)} &= F^{(0)*} = r^{-3} (1 - 3\cos^2\vartheta) = -\sqrt{\frac{16\pi}{5}} \frac{1}{r^3} Y_{2,0} \\ F^{(1)} &= F^{(-1)*} = r^{-3} (\sin\vartheta \cos\vartheta e^{-i\varphi}) = \sqrt{\frac{8\pi}{15}} \frac{1}{r^3} Y_{2,-1} = -\sqrt{\frac{8\pi}{15}} \frac{1}{r^3} Y_{2,1}^* \\ F^{(2)} &= F^{(-2)*} = r^{-3} (\sin^2\vartheta e^{-2i\varphi}) = \sqrt{\frac{32\pi}{15}} \frac{1}{r^3} Y_{2,-2} = \sqrt{\frac{32\pi}{15}} \frac{1}{r^3} Y_{2,2}^* \end{aligned} \quad (3.90)$$

$F^{(k)*} = F^{(-k)}$ is the complex conjugate of $F^{(k)}$. The sine and cosine terms can equivalently be expressed with the aid of second-degree spherical harmonics $Y_{2,\pm k}(\varphi, \vartheta)$ for $k = 0, \pm 1, \pm 2$ as specified in Eq. (1.8) and on the right-hand sides of the relations in Eq. (3.90). In the following, the spatial functions $F^{(k)}$ will be addressed shortly as *stochastic functions*.

The spin-operator expressions in Eq. (3.88) are defined by

$$\begin{aligned}
 \mathcal{O}^{(0)} &= I_z S_z - \frac{1}{4}(I^+ S^- + I^- S^+) \\
 \mathcal{O}^{(1)} &= -\frac{3}{2}(I^+ S_z + I_z S^+) \\
 \mathcal{O}^{(-1)} &= -\frac{3}{2}(I^- S_z + I_z S^-) \\
 \mathcal{O}^{(2)} &= -\frac{3}{4}I^+ S^+ \\
 \mathcal{O}^{(-2)} &= -\frac{3}{4}I^- S^-
 \end{aligned} \tag{3.91}$$

These are the operators acting on the spin states of the dipolar-coupled two-spin system under consideration. The operators I_z, I^+, I^- act exclusively on spin $\mathbf{I}$, and S_z, S^+, S^- solely affect the spin $\mathbf{S}$. The terms are composed of *raising and lowering* (or commonly *ladder*) *spin operators*:

$$\begin{aligned}
 I^+ &\equiv I_x + iI_y; & S^+ &\equiv S_x + iS_y \\
 I^- &\equiv I_x - iI_y; & S^- &\equiv S_x - iS_y
 \end{aligned} \tag{3.92}$$

which in turn are complex linear combinations of the spin-operator components I_x, I_y, I_z of spin $\mathbf{I}$, and S_x, S_y, S_z of spin $\mathbf{S}$. The ladder operators produce transitions between spin-down and spin-up eigen-states. The effect of the operators with the superscript “+” is that transitions are induced with changes $\Delta m_I = +1$ and $\Delta m_S = +1$ of the magnetic quantum number of spin $\mathbf{I}$ and spin $\mathbf{S}$, respectively. Likewise, operators with the superscript “-” produce $\Delta m_I = -1$ and $\Delta m_S = -1$ transitions of the respective spins. The z components I_z and S_z do not cause transitions.

If the total magnetic quantum number $m_{\text{tot}} = m_I + m_S$ of the spin states in a coupled two-spin system changes by $\Delta m_{\text{tot}} = \Delta m_I + \Delta m_S = \pm 1$ one speaks of *single-quantum transitions* produced by spin-operator terms in Eq. (3.91) such as $I^+ S_z, I^- S_z, I_z S^+,$ and $I_z S^-$. The application of the operator terms $I^+ S^+$ and $I^- S^-$ results in *double-quantum transitions* with the respective changes of the total magnetic quantum number $\Delta m_{\text{tot}} = \Delta m_I + \Delta m_S = +2$ and $\Delta m_{\text{tot}} = \Delta m_I + \Delta m_S = -2$. Likewise, the operator terms $I^+ S^-$ and $I^- S^+$ are responsible for *zero-quantum transitions* with $\Delta m_{\text{tot}} = \Delta m_I + \Delta m_S = 0$. By contrast, the term $I_z S_z$ is inert with respect to the induction of any spin transition and may again be associated with $\Delta m_{\text{tot}} = 0$ which is trivial in this case.¹⁴

Since the dipolar Hamiltonian is intrinsically a *two-particle* interaction, there will be no higher-order multiple-quantum transition than $\Delta m_{\text{tot}} = \pm 2$ even in cases

¹⁴ An important remark: The present statements on zero-, single-, and double-quantum transitions refer to the induction effects by *spin interactions*, in particular to dipolar and quadrupolar couplings. On the other hand, the interaction of *electromagnetic radiation* (i.e., photons with spin 1) with magnetic dipoles is known to induce exclusively single-quantum transitions with the selection rule $\Delta m = \pm 1$ as a consequence of the conservation of angular momentum. Multiple-quantum transitions are “forbidden” in this case and can therefore be detected only *indirectly* by

of high spin quantum numbers $I, S > 1/2$, and even in multi-spin systems being composed of more than two spins. As reflected by the sum in Eq. (3.81), the pair interactions are *additive* so that no spin operator of an order higher than that of the terms in Eq. (3.91) can arise.

The Dipolar Hamiltonian in the Interaction Representation

Let us now perform the transformation of the spin operator terms in Eq. (3.88) to the interaction representation as required for the application of the master equation given in Eq. (3.78). According to Eq. (3.62), this is performed by the “sandwich” expressions

$$\mathcal{O}^{(k)'} = U^{-1} \mathcal{O}^{(k)} U = e^{(i/\hbar)\mathcal{H}_0 t} \mathcal{O}^{(k)} e^{-(i/\hbar)\mathcal{H}_0 t} \quad (3.93)$$

The stationary part of the Hamiltonian, Eq. (3.56), is essentially due to the Zeeman interaction, Eq. (3.57), for the two-spin species:

$$\mathcal{H}_0 = -\hbar\omega_I I_z - \hbar\omega_S S_z \quad (3.94)$$

The individual angular resonance frequencies are $\omega_I = \gamma_I B_0$ and $\omega_S = \gamma_S B_0$. After transformation, we thus obtain the operator terms in the interaction representation¹⁵:

$$\begin{aligned} \mathcal{O}^{(0)'} &= I_z S_z - \frac{1}{4} I^+ S^- e^{-i(\omega_I - \omega_S)t} - \frac{1}{4} I^- S^+ e^{i(\omega_I - \omega_S)t} \\ \mathcal{O}^{(1)'} &= -\frac{3}{2} I^+ S_z e^{-i\omega_I t} - \frac{3}{2} I_z S^+ e^{-i\omega_S t} \\ \mathcal{O}^{(-1)'} &= -\frac{3}{2} I^- S_z e^{i\omega_I t} - \frac{3}{2} I_z S^- e^{+i\omega_S t} \\ \mathcal{O}^{(2)'} &= -\frac{3}{4} I^+ S^+ e^{-i(\omega_I + \omega_S)t} \\ \mathcal{O}^{(-2)'} &= -\frac{3}{4} I^- S^- e^{i(\omega_I + \omega_S)t} \end{aligned} \quad (3.95)$$

In the following, the *order* of the multiple-quantum transitions will be labeled by the superscript k , whereas the subscript l distinguishes which of the two spins flips up and which spin flips down. Referring to zero-, single-, and double-quantum transitions, the superscript k takes the respective values 0,

NMR spectroscopy [1]. The situation is different in NMR relaxometry: Transitions mediating spin relaxation are based on spin interactions not subject to this restriction since angular momentum is conserved by inclusion of the molecular degrees of motional freedom. As far as the operators in Eq. (3.91) allow for, multiple-quantum transitions are not forbidden in relaxometry.

¹⁵ Contrary to the operators $\mathcal{O}^{(k)'}$, ρ' etc., the components of spin operators, that is, I_j and S_j for $j = x, y, z$, will not be marked by primes in the interaction representation because they act on spin states irrespective of the representation.

± 1 and ± 2 . As concerns zero-quantum combinations of the spin states, that is, $\Delta m_{\text{tot}} = \Delta m_I + \Delta m_S = 0$, there are three variants linked by the spin-operator terms $I_z S_z$, $I^+ S^-$ and $I^- S^+$. They are numbered by subscripts $l = 0, 1, 2$. The single-quantum transition case is specified on the one hand by spin-operator terms $I^+ S_z$, $I^- S_z$ and $I_z S^+$, $I_z S^-$ on the other. The respective subscripts are $l = 1, 2$.

According to the transformed expressions given in Eq. (3.95), the dipolar Hamiltonian, Eq. (3.88), adopts the converted form

$$\mathcal{H}'_d = f_d \sum_{k,l} F^{(k)} \mathcal{O}_l^{(k)} e^{-i\omega_l^{(k)} t} \quad (3.96)$$

(valid in the interaction representation but expressed by – notabene – the original operators without primes as listed in Eq. (3.91)). In the sub- and superscript notation defined above, the new spin-operator terms $\mathcal{O}_l^{(k)}$ and the angular transition frequencies $\omega_l^{(k)}$ introduced in Eq. (3.96) can be paired as follows

$$\begin{aligned} \mathcal{O}_0^{(0)} &= I_z S_z & \omega_0^{(0)} &= 0 \\ \mathcal{O}_1^{(0)} &= -\frac{1}{4} I^+ S^- & \omega_1^{(0)} &= \omega_I - \omega_S \\ \mathcal{O}_2^{(0)} &= -\frac{1}{4} I^- S^+ & \omega_2^{(0)} &= \omega_S - \omega_I \\ \mathcal{O}_1^{(1)} &= -\frac{3}{2} I^+ S_z & \omega_1^{(1)} &= \omega_I \\ \mathcal{O}_2^{(1)} &= -\frac{3}{2} I_z S^+ & \omega_2^{(1)} &= \omega_S \\ \mathcal{O}_1^{(-1)} &= -\frac{3}{2} I^- S_z & \omega_1^{(-1)} &= -\omega_I \\ \mathcal{O}_2^{(-1)} &= -\frac{3}{2} I_z S^- & \omega_2^{(-1)} &= -\omega_S \\ \mathcal{O}_1^{(2)} &= -\frac{3}{4} I^+ S^+ & \omega_1^{(2)} &= \omega_I + \omega_S \\ \mathcal{O}_1^{(-2)} &= -\frac{3}{4} I^- S^- & \omega_1^{(-2)} &= -(\omega_I + \omega_S) \end{aligned} \quad (3.97)$$

Note that $\omega_l^{(k)} = -\omega_l^{(-k)}$ for $k \neq 0$, and $\omega_1^{(0)} = -\omega_2^{(0)}$. With this analysis of the dipolar Hamiltonian, we have prepared everything needed for the evaluation of the master equation represented by Eq. (3.78) for the particular case of dipolar coupling.

3.1.5.5 Spin–Lattice Relaxation in Dipolar-Coupled Two-Spin Systems

Master Equation for the Longitudinal Spin Operators

Spin–lattice relaxation refers to the z components of the partial magnetizations of the spin species. Since the operator of longitudinal magnetization is proportional to the respective spin-operator component, we express the operator of the observable $\mathcal{Q}$ in the master equation given in Eq. (3.78) by $\mathcal{Q} = I_z$ and $\mathcal{Q} = S_z$ depending on which spin species is referred to. Making use of the above analysis of

the dipolar Hamiltonian in the interaction representation as specified by Eq. (3.96) with the definitions given in Eqs. (3.90) and (3.97) and inserting this into Eq. (3.78) lead to the master equations for the special cases of the z components of the spin vectors of the two-spin species:

$$\begin{aligned}\frac{d\langle I_z \rangle'}{dt} &= \frac{d\langle I_z \rangle}{dt} = -\frac{1}{\hbar^2} \text{Tr}\{(\rho'(t) - \rho'_0) \mathcal{P}_z^I\} \\ \frac{d\langle S_z \rangle'}{dt} &= \frac{d\langle S_z \rangle}{dt} = -\frac{1}{\hbar^2} \text{Tr}\{(\rho'(t) - \rho'_0) \mathcal{P}_z^S\}\end{aligned}\quad (3.98)$$

The operators $\mathcal{P}_z^I$ and $\mathcal{P}_z^S$ are defined by

$$\begin{aligned}\mathcal{P}_z^I &= f_d^2 \int_0^\infty \overline{\left[\sum_{k,l} F^{(k)}(t-\tau) \mathcal{O}_l^{(k)} e^{-i\omega_l^{(k)}(t-\tau)}, \left[\sum_{k',l'} F^{(k')}(t) \mathcal{O}_{l'}^{(k')} e^{-i\omega_{l'}^{(k')}t}, I_z \right] \right]} d\tau \\ \mathcal{P}_z^S &= f_d^2 \int_0^\infty \overline{\left[\sum_{k,l} F^{(k)}(t-\tau) \mathcal{O}_l^{(k)} e^{-i\omega_l^{(k)}(t-\tau)}, \left[\sum_{k',l'} F^{(k')}(t) \mathcal{O}_{l'}^{(k')} e^{-i\omega_{l'}^{(k')}t}, S_z \right] \right]} d\tau\end{aligned}\quad (3.99)$$

Note that the left sides of the relations in Eq. (3.98) are the same for the original and the interaction representation since z components of spin operators are not affected by the transformation rules given in Eq. (3.62). The strategy for the solution of the rate equations given in Eq. (3.98) will now be to express both the operators $\mathcal{P}_z^I, \mathcal{P}_z^S$ and the density operators $\rho'(t), \rho'_0$ by manageable terms of spin operators so that the traces can be evaluated using standard spin operator relations. We will proceed in a number of steps modifying first the operators $\mathcal{P}_z^I, \mathcal{P}_z^S$ and analyzing afterward the density operators $\rho'(t), \rho'_0$.

Introduction of Dipolar Correlation and Intensity Functions

Separating the operators and the stochastic functions $F^{(k)}$ in the commutators and swapping the integration and the sum operations give

$$\begin{aligned}\mathcal{P}_z^I &= f_d^2 \sum_{k,l} \sum_{k',l'} \left\{ \int_0^\infty \overline{F^{(k)}(t-\tau) F^{(-k')*}(t)} e^{i\omega_l^{(k)}\tau} d\tau \right\} e^{-i(\omega_l^{(k)} + \omega_{l'}^{(k')})t} \left[\mathcal{O}_l^{(k)}, \left[\mathcal{O}_{l'}^{(k')}, I_z \right] \right] \\ \mathcal{P}_z^S &= f_d^2 \sum_{k,l} \sum_{k',l'} \left\{ \int_0^\infty \overline{F^{(k)}(t-\tau) F^{(-k')*}(t)} e^{i\omega_l^{(k)}\tau} d\tau \right\} e^{-i(\omega_l^{(k)} + \omega_{l'}^{(k')})t} \left[\mathcal{O}_l^{(k)}, \left[\mathcal{O}_{l'}^{(k')}, S_z \right] \right]\end{aligned}\quad (3.100)$$

The above expressions look still rather complicated but can be broken down to a manageable form as we will see soon. The first step will be to reduce the fourfold sums on the basis of the general properties of the correlation functions defined by

$$G_{k,-k'}(t, \tau) \equiv \overline{F^{(k)}(t - \tau) F^{(-k')*}(t)} \quad (3.101)$$

Actually, these functions will be decisive in the subsequent considerations because they are the entities reflecting the fluctuations of dipolar couplings due to thermal motions.

The fluctuations modulating spin interactions are assumed to be purely stochastic. They are therefore subject to the properties of *stationarity* and *time-reversal invariance*. That is, the correlation functions are independent of the absolute time and of the sign of the interval τ . Furthermore, we may assume that the spatial configuration of the ensemble of spin systems is *isotropic* as it is the case for disordered materials permitting unrestricted orientations of the inter-dipole vectors. There is consequently no correlation among the polar coordinates r, φ, ϑ , and the stochastic functions $F^{(k)}$ of different orders k are *uncorrelated*. In summary, the stationarity, time-reversal invariance, and isotropy conditions can be represented by

$$\begin{aligned} G_{k,-k'}(t, \tau) &= \delta_{k,-k'} G_k(|\tau|) \\ &= \overline{F^{(k)}(0) F^{(k)*}(\tau)} \end{aligned} \quad (3.102)$$

where $\delta_{k,-k'}$ is the Kronecker symbol¹⁶ and $G_k(|\tau|)$ is the (even) *autocorrelation function* of order k . As a consequence of the Kronecker symbol inherent to the correlation function Eq. (3.102), the number of sums in Eq. (3.100) will be reduced by one. The only correlation functions that must be distinguished in the following treatment are defined by

$$G_k(\tau) \equiv \left\langle F^{(k)}(0) F^{(k)*}(\tau) \right\rangle \quad (3.103)$$

for the positive orders $k = 0, 1, 2$. The bar in Eqs. (3.102) and in the previous equations has now been replaced by angle brackets with the identical meaning “ensemble average.” This notation will be used from now on. With these modifications, the operators in Eq. (3.100) adopt the form

$$\begin{aligned} \mathcal{P}_z^I &= f_d^2 \sum_k \sum_{l,l'} \left\{ \int_0^\infty G_k(\tau) e^{i\omega_l^{(k)} \tau} d\tau \right\} e^{-i(\omega_l^{(k)} + \omega_{l'}^{(-k)})t} \left[\mathcal{O}_l^{(k)}, \left[\mathcal{O}_{l'}^{(-k)}, I_z \right] \right] \\ \mathcal{P}_z^S &= f_d^2 \sum_k \sum_{l,l'} \left\{ \int_0^\infty G_k(\tau) e^{i\omega_l^{(k)} \tau} d\tau \right\} e^{-i(\omega_l^{(k)} + \omega_{l'}^{(-k)})t} \left[\mathcal{O}_l^{(k)}, \left[\mathcal{O}_{l'}^{(-k)}, S_z \right] \right] \end{aligned} \quad (3.104)$$

¹⁶ The Kronecker symbol is defined by $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ otherwise.

Instead of fourfold sums, we have now only three different running indices.

The correlation functions are furthermore even, that is, $G_k(\tau) = G_k(-\tau)$. As a consequence, the integrals in Eq. (3.104) can be replaced by the identity

$$\int_0^{\infty} G_k(\tau) e^{i\omega_l^{(k)} \tau} d\tau \equiv \frac{1}{2} \int_{-\infty}^{\infty} G_k(\tau) e^{i\omega_l^{(k)} \tau} d\tau + i \int_0^{\infty} G_k(\tau) \sin(\omega_l^{(k)} \tau) d\tau \quad (3.105)$$

The integrals are thus split into real and imaginary parts. Contributions due to the imaginary terms would be oscillatory and would therefore vanish in the subsequent treatment. Actually, this is a manifestation of the intrinsically aperiodic character of relaxation. The imaginary parts can therefore be dropped already at the present stage of the formalism.

The left integral on the right-hand side of Eq. (3.105), that is, the real part, is one half times the Fourier transform of the autocorrelation function of order k . The expression thus conforms to the usual convention for Fourier transformations. In the nomenclature of the *Wiener/Khintchine theorem* (e.g., see Ref. [20]), we denote this Fourier integral as *intensity function* or *spectral density* at the angular-frequency $\omega_l^{(k)}$

$$J^{(k)}(\omega_l^{(k)}) = \int_{-\infty}^{\infty} G_k(\tau) e^{-i\omega_l^{(k)} \tau} d\tau \quad (3.106)$$

for $k = 0, 1, 2$. This is the second type of function describing the fluctuations of dipolar couplings due to thermal motions. While the correlation function Eq. (3.103) refers to the time domain, the spectral density is the conjugate counterpart in the frequency regime.

Further Simplification of the Operators $\mathcal{P}_z^I$ and $\mathcal{P}_z^S$

In terms of intensity functions, the expressions in Eq. (3.104) can be rewritten in the form

$$\begin{aligned} \mathcal{P}_z^I &= f_d^2 \sum_k \sum_{l,l'} \frac{1}{2} J^{(k)}(\omega_l^{(k)}) e^{-i(\omega_l^{(k)} + \omega_{l'}^{(-k)})t} \left[\mathcal{O}_l^{(k)}, \left[\mathcal{O}_{l'}^{(-k)}, I_z \right] \right] \\ \mathcal{P}_z^S &= f_d^2 \sum_k \sum_{l,l'} \frac{1}{2} J^{(k)}(\omega_l^{(k)}) e^{-i(\omega_l^{(k)} + \omega_{l'}^{(-k)})t} \left[\mathcal{O}_l^{(k)}, \left[\mathcal{O}_{l'}^{(-k)}, S_z \right] \right] \end{aligned} \quad (3.107)$$

Let us now have a closer look at the angular frequencies $\omega_l^{(k)}$ specified in Eqs. (3.97). Obviously, in the cases $l = l'$, $k \neq 0$; $l = 1$, $l' = 2$, $k = 0$ and $l = 2$, $l' = 1$, $k = 0$,

we have $\omega_l^{(k)} = -\omega_{l'}^{(-k)}$ so that the exponential functions in Eqs. (3.107) take the value 1, and the time dependences vanish. The *time-independent* terms produced in this way are denoted as *secular*. Actually, these expressions will form the crucial basis of the relaxation equations we are aiming at.

This is in contrast to the time-dependent *non-secular* terms arising for indices l, l', k not complying with the above conditions. In this case, the exponential functions will cause rapid oscillations on the time scale of relaxation. In the average, the influence of these terms will therefore cancel. As a consequence, the triple sums in Eqs. (3.107) can be reduced to double sums of the secular terms by discarding the running index l' .

Inserting the operator expressions Eqs. (3.97) into Eqs. (3.107) truncated in this way leads to

$$\begin{aligned}
 \mathcal{P}_z^I &= \frac{1}{2} f_d^2 \sum_{k,l} J^{(k)}(\omega_l^{(k)}) \left[\mathcal{O}_l^{(k)}, \left[\mathcal{O}_{l'}^{(-k)}, I_z \right] \right] \\
 &= \frac{1}{16} f_d^2 J^{(0)}(\omega_I - \omega_S) [I^+ S^-, [I^- S^+, I_z]] + \text{H. c.} \\
 &\quad + \frac{9}{4} f_d^2 J^{(1)}(\omega_I) [I^+ S_z, [I^- S_z, I_z]] + \text{H. c.} \\
 &\quad + \frac{9}{16} f_d^2 J^{(2)}(\omega_I + \omega_S) [I^+ S^+, [I^- S^-, I_z]] + \text{H. c.} \\
 \mathcal{P}_z^S &= \frac{1}{2} f_d^2 \sum_{k,l} J^{(k)}(\omega_l^{(k)}) \left[\mathcal{O}_l^{(k)}, \left[\mathcal{O}_{l'}^{(-k)}, S_z \right] \right] \\
 &= \frac{1}{16} f_d^2 J^{(0)}(\omega_S - \omega_I) [S^+ I^-, [S^- I^+, S_z]] + \text{H. c.} \\
 &\quad + \frac{9}{4} f_d^2 J^{(1)}(\omega_S) [S^+ I_z, [S^- I_z, S_z]] + \text{H. c.} \\
 &\quad + \frac{9}{16} f_d^2 J^{(2)}(\omega_I + \omega_S) [S^+ I^+, [S^- I^-, S_z]] + \text{H. c.} \quad (3.108)
 \end{aligned}$$

The abbreviation H. c. (Hermitian conjugate) represents the preceding expression with all operators replaced by their adjoint forms, and all complex functions substituted by their conjugate complex counterparts. Rules for the evaluation of the double commutators in Eqs. (3.108) can be found in Ref. [1], Part IV, for instance. The relations relevant in the present case are

$$\begin{aligned}
 [I^+ S_z, [I^- S_z, I_z]] &= 2I_z S_z^2 \\
 [I^+ S^-, [I^- S^+, I_z]] &= 2I_z (S_x^2 + S_y^2) - 2S_z (I_x^2 + I_y^2) \\
 [S^+ I^+, [S^- I^-, I_z]] &= I_z (S_x^2 + S_y^2 + S_z^2) + 2S_z (I_x^2 + I_y^2 + I_z^2) \quad (3.109)
 \end{aligned}$$

plus the same expressions with the symbols I and S interchanged.

After having established Eqs. (3.108) for the operators $\mathcal{P}_z^I$ and $\mathcal{P}_z^S$ as functions of the diverse spin operators, the next problem will be to put the density operators $\rho'(t), \rho'_0$ in the rate equations (3.98) on the same basis. Inserting the above expressions for the operators $\mathcal{P}_z^I$ and $\mathcal{P}_z^S$ into the equations of motion for the expectation values of the longitudinal spin components, Eqs. (3.98), leads to trace terms of the type $\text{Tr}\{\rho' I_z S_j^2\}$, $\text{Tr}\{\rho'_0 I_z S_j^2\}$, $\text{Tr}\{\rho' S_z I_j^2\}$, $\text{Tr}\{\rho'_0 S_z I_j^2\}$, $\text{Tr}\{\rho' I_z S_z\}$, and $\text{Tr}\{\rho'_0 I_z S_z\}$, where the subscript j stands for any of the coordinates x, y, z . In order to be able to evaluate the traces, we must first express the density operators ρ'_0 and ρ' in terms of spin operators.

Equilibrium Density Operator

According to Eq. (3.76), the equilibrium magnetizations $M'_{I,0}$ and $M'_{S,0}$, for the spins I and S , respectively, that is, the expectation values of the respective magnetization operators M'_I and M'_S , are given by the relations

$$\begin{aligned} M'_{I,0} &\equiv \langle M'_I \rangle_0 = \text{Tr}\{\rho'_0 M'_I\} \\ M'_{S,0} &\equiv \langle M'_S \rangle_0 = \text{Tr}\{\rho'_0 M'_S\} \end{aligned} \quad (3.110)$$

The definition of the equilibrium density operator reads

$$\rho_0 = \frac{\exp\{-\mathcal{H}_0/k_B T\}}{\text{Tr}\{\exp\{-\mathcal{H}_0/k_B T\}\}} \quad (3.111)$$

where the Zeeman Hamilton operator of the two-spin systems under consideration is given by

$$\mathcal{H}_0 = -\hbar\gamma_I B_0 I_z - \hbar\gamma_S B_0 S_z \quad (3.112)$$

According to the transformation relation Eq. (3.93), this Hamiltonian is invariant under transformation to the interaction representation, that is, $\mathcal{H}_0 = \mathcal{H}'_0$. The equilibrium density operator and the equilibrium magnetizations therefore obey likewise

$$\begin{aligned} \rho'_0 &= \rho_0 \\ M'_{I,0} &= M_{I,0} \\ M'_{S,0} &= M_{S,0} \end{aligned} \quad (3.113)$$

The next step is to exploit the high-temperature limit defined in Eq. (3.7). This is the usual and safely justified assumption in standard NMR theories. In linear

approximation, the equilibrium density operator given by Eqs. (3.111) and (3.113) is thus approached by

$$\rho'_0 \approx \frac{1 + \hbar B_0(\gamma_I I_z + \gamma_S S_z)k_B^{-1}T^{-1}}{\text{Tr}\{1 + \hbar B_0(\gamma_I I_z + \gamma_S S_z)k_B^{-1}T^{-1}\}} \quad (3.114)$$

According to the $\pm$ symmetry of the distribution of the spin energy levels, the denominator can be replaced by $\text{Tr}\{1 + \hbar B_0(\gamma_I I_z + \gamma_S S_z)k_B^{-1}T^{-1}\} = \text{Tr}\{\varepsilon\}$, where ε is the unit operator for the two-spin system:

$$\begin{aligned} \rho'_0 &= \frac{1}{\text{Tr}\{\varepsilon\}} + \frac{\hbar B_0 \gamma_I}{k_B T \text{Tr}\{\varepsilon\}} I_z + \frac{\hbar B_0 \gamma_S}{k_B T \text{Tr}\{\varepsilon\}} S_z \\ &= a + b_0 I_z + c_0 S_z \end{aligned} \quad (3.115)$$

In the case of like dipoles, that is, $\gamma_I = \gamma_S$, the coefficients b_0 and c_0 coincide of course. In this way, we have decomposed the *equilibrium* density operator ρ'_0 for the two-spin system into a linear combination of the spin operators I_z and S_z with constant coefficients a, b_0, c_0 .

Non-equilibrium Density Operator

Let us now turn to the *nonequilibrium* density operator ρ' required for the evaluation of the rate equations in Eq. (3.98). The relaxation experiments described in Sects. 3.1.4.1, 3.1.4.2, 3.1.4.3, and 3.1.4.4 start with the preparation of a non-equilibrium magnetization. In the case of the field-cycling NMR relaxometry technique, the nonequilibrium is reached by abruptly changing the magnitude of the external magnetic flux density B_0 . That is, the coefficients in Eq. (3.115) adopt nonequilibrium values b and c , whereas the spin-operator structure is retained:

$$\rho'(t) = a + bI_z + cS_z \quad (3.116)$$

It is then a matter of relaxation how fast the coefficient b and c evolve toward equilibrium again, whereas the constant term a does not matter in the present context.

Other relaxation techniques employ RF pulses for the generation of nonequilibrium spin populations. The situation is then a bit more complicated. If so, we must in particular distinguish whether the RF pulse affects both spin species, that is, if $\gamma_I = \gamma_S$ and consequently $b_0 = c_0$, or whether it is resonant to only one of them. The latter will be the case for strongly deviating gyromagnetic ratios, $\gamma_I \neq \gamma_S$, so that $b_0 \neq c_0$.

For example, the 90° RF pulse of the saturation/recovery method applied to *like dipoles* produces¹⁷

$$\rho'(0+) = a + b_0(I_y + S_y) \quad (3.117)$$

as suggested by Eq. (3.28) (for the particular RF pulse phase assumed there). According to the rules for traces of spin-operator terms, the trace expressions of the type $\text{Tr}\{\rho'(0+)I_zS_j^2\}$, $\text{Tr}\{\rho'(0+)S_zI_j^2\}$ and $\text{Tr}\{\rho'(0+)I_zS_z\}$ mentioned above vanish in this case. In other words, the longitudinal magnetization is zero at this instant. In the course of spin–lattice relaxation, the population difference of the spin states grows again toward equilibrium so that the z components of the spin operators will become effective again:

$$\rho'(t) = b(t)I_z + c(t)S_z + \text{irrelevant terms} \quad (3.118)$$

The coefficients b and c can be different if the two dipoles, though being like, are individually subjected to different interactions and, hence, to different relaxation properties. Otherwise, they will be equal of course. The density operator terms relevant for spin–lattice relaxation will thus be the same as in Eq. (3.116).

If the 90° RF pulse is applied to *unlike dipoles* and hence acts selectively to only one of the spin species, for example, the I -spins, we have

$$\rho'(0+) = a + b_0I_y + c_0S_z \quad (3.119)$$

instead of Eq. (3.117). The equilibrium populations of the S -spin states will initially not be perturbed. The populations will however evolve by spin–lattice relaxation owing to the mutual coupling, so that Eq. (3.119) will soon adopt the same structure as Eqs. (3.116) and (3.118) with respect to the z components of the spin operators.

Evaluation of the Traces

Having the equilibrium and nonequilibrium density operators Eqs. (3.115) and (3.118), respectively, at our disposal, we can straightforwardly calculate the linear combinations of the traces $\text{Tr}\{\rho'I_zS_j^2\}$, $\text{Tr}\{\rho'_0I_zS_j^2\}$, $\text{Tr}\{\rho'S_zI_j^2\}$, $\text{Tr}\{\rho'_0S_zI_j^2\}$, $\text{Tr}\{\rho'I_zS_z\}$, $\text{Tr}\{\rho'_0I_zS_z\}$ etc., into which the rate equations given in Eq. (3.98) can be broken down. For this purpose, we use known relations such as

¹⁷ The effect of RF pulses on density operators is extensively described and explained in textbooks such as Refs [1, 2] and in a recommendable review article in Ref. [21].

$$\begin{aligned}
\langle \tilde{m}_I, \tilde{m}_S | S_x^2 | m_I, m_S \rangle &= \frac{1}{3} S(S+1) \delta_{\tilde{m}_I, m_I} \delta_{\tilde{m}_S, m_S} \\
\sum_{m_I, m_S} \langle m_I, m_S | \rho' I_z | m_I, m_S \rangle &= \langle I_z \rangle
\end{aligned} \tag{3.120}$$

(e.g., see Ref. [1]) leading to results such as

$$\begin{aligned}
\text{Tr}\{\rho' I_z S_z\} &= \langle I_z S_z \rangle' \\
&= \sum_{m_I, m_S} \langle m_I, m_S | \rho I_z S_z | m_I, m_S \rangle = 0 \\
\text{Tr}\{\rho' I_z S_x^2\} &= \langle I_z S_x^2 \rangle' \\
&= \sum_{m_I, m_S} \langle m_I, m_S | \rho' I_z S_x^2 | m_I, m_S \rangle \\
&= \sum_{m_I, m_S} \sum_{\tilde{m}_I, \tilde{m}_S} \langle m_I, m_S | \rho' I_z | \tilde{m}_I, \tilde{m}_S \rangle \langle \tilde{m}_I, \tilde{m}_S | S_x^2 | m_I, m_S \rangle \\
&= \langle I_z \rangle \frac{1}{3} S(S+1)
\end{aligned} \tag{3.121}$$

The trace terms for ρ'_0 and for the other components of the spin operators $\mathbf{I}$ and $\mathbf{S}$ can be derived analogously. The numbers m_I and m_S are the eigen-values of the (dimensionless) spin operators I_z and S_z , respectively. The quantity S is the spin quantum number for the spin operator $\mathbf{S}$. Below, the spin quantum number of the spin operator $\mathbf{I}$ will likewise be denoted by I . $\delta_{\tilde{m}_I, m_I}$ and $\delta_{\tilde{m}_S, m_S}$ are Kronecker symbols as defined in footnote 16. Note that the density operator coefficients b, b_0, c, c_0 in Eqs. (3.115) and (3.118) are *implicitly* involved in the expectation values resulting from the above operations.

Final Equations of Motion for the Expectation Values $\langle I_z \rangle$ and $\langle S_z \rangle$

In summary, the above formalism leads straightforwardly from Eq. (3.98) to the following system of rate equations for the expectation values of the longitudinal spin operators:

$$\begin{aligned}
\frac{d\langle I_z \rangle}{dt} &= -\frac{1}{T_1^{II}} (\langle I_z \rangle - \langle I_z \rangle_0) - \frac{1}{T_1^{IS}} (\langle S_z \rangle - \langle S_z \rangle_0) \\
\frac{d\langle S_z \rangle}{dt} &= -\frac{1}{T_1^{SI}} (\langle I_z \rangle - \langle I_z \rangle_0) - \frac{1}{T_1^{SS}} (\langle S_z \rangle - \langle S_z \rangle_0)
\end{aligned} \tag{3.122}$$

The functions $\langle I_z \rangle$ and $\langle S_z \rangle$ are the instantaneous expectation values of the z components of spins $\mathbf{I}$ and $\mathbf{S}$, respectively. The equilibrium expectation values are denoted by $\langle I_z \rangle_0$ and $\langle S_z \rangle_0$. The diverse rate constants (or longitudinal relaxation times) are given by

$$\begin{aligned}
\frac{1}{T_1^H} &= \left(\frac{\mu_0}{4\pi}\right)^2 \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \left[\frac{1}{12} J^{(0)}(|\omega_I - \omega_S|) + \frac{3}{2} J^{(1)}(\omega_I) + \frac{3}{4} J^{(2)}(\omega_I + \omega_S) \right] \\
\frac{1}{T_1^{IS}} &= \left(\frac{\mu_0}{4\pi}\right)^2 \gamma_I^2 \gamma_S^2 \hbar^2 I(I+1) \left[-\frac{1}{12} J^{(0)}(|\omega_I - \omega_S|) + \frac{3}{4} J^{(2)}(\omega_I + \omega_S) \right] \\
\frac{1}{T_1^{SI}} &= \left(\frac{\mu_0}{4\pi}\right)^2 \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \left[-\frac{1}{12} J^{(0)}(|\omega_I - \omega_S|) + \frac{3}{4} J^{(2)}(\omega_I + \omega_S) \right] \\
\frac{1}{T_1^{SS}} &= \left(\frac{\mu_0}{4\pi}\right)^2 \gamma_I^2 \gamma_S^2 \hbar^2 I(I+1) \left[\frac{1}{12} J^{(0)}(|\omega_I - \omega_S|) + \frac{3}{2} J^{(1)}(\omega_S) + \frac{3}{4} J^{(2)}(\omega_I + \omega_S) \right]
\end{aligned} \tag{3.123}$$

The spectral densities $J^{(k)}$ are defined in Eq. (3.106) for the orders $k = 0, 1, 2$. From the angular transition frequencies specified in Eq. (3.97), merely ω_I , ω_S , $|\omega_I - \omega_S|$, and $\omega_I + \omega_S$ remain, where $\omega_I = |\gamma_I|B_0$ and $\omega_S = |\gamma_S|B_0$. Note that the signs of the gyromagnetic ratios γ_I , γ_S and of the difference $\omega_I - \omega_S$ do not matter. This is why we have indicated the magnitudes of these quantities.

Examining the arguments of the spectral densities of the orders $k = 0, 1, 2$ reveals that the transition rates are determined by the respective expressions for *zero*-, *single*-, and *double-quantum transitions*, just as expected in view of the spin-operator terms of the dipolar Hamiltonian (see the ladder operator terms in Eq. (3.97)). The relevant transitions in two-spin $\frac{1}{2}$ systems can be illustrated by the Zeeman energy diagrams for like and unlike dipoles as depicted in Fig. 3.11.

Partial Magnetizations for the Spins I and S

According to Eq. (3.80), the longitudinal partial magnetizations of the two-spin species in homogeneous samples are defined by

$$\begin{aligned}
M_{I,z} &= n_I \gamma_I \hbar \langle I_z \rangle \\
M_{S,z} &= n_S \gamma_S \hbar \langle S_z \rangle
\end{aligned} \tag{3.124}$$

where n_I and n_S are the respective number densities of the spins. The system of rate equations given in Eq. (3.122) can thus be converted to

$$\begin{aligned}
\frac{dM_{I,z}}{dt} &= -\frac{1}{T_1^H} (M_{I,z} - M_{I,0}) - \frac{1}{T_1^{IS}} (M_{S,z} - M_{S,0}) \\
\frac{dM_{S,z}}{dt} &= -\frac{1}{T_1^{SI}} (M_{I,z} - M_{I,0}) - \frac{1}{T_1^{SS}} (M_{S,z} - M_{S,0})
\end{aligned} \tag{3.125}$$

where $M_{I,0}$ and $M_{S,0}$ are the Curie's magnetizations of the two-spin species (see Eqs. (3.110) and (3.113)). We thus arrive at the equations of motion of the longitudinal magnetizations subjected to fluctuating dipolar coupling.

The relaxation functions resulting as solutions are obviously linear combinations of two exponential functions in each case. As concerns experimental investigations, such superpositions are unfavorable and a bit tricky to evaluate. For the limiting cases relevant in the most important applications, the situation is fortunately less complicated: One distinguishes in particular the *like-spin* and the *S-spin-equilibrium* limits, where the system Eq. (3.125) reduces to single differential equations. The solutions will consequently be mono-exponential as it was predicted already by the rotating-frame Bloch equation given in Eq. (3.21) and as it was anticipated for the applications to the various experimental protocols outlined in Sect. 3.1.4. These limits will be elucidated in detail in the following sections. Prior to that, let us insert a short section on important definitions which will be used in this context.

3.1.5.6 Reduced Dipolar Correlation and Intensity Functions

In the course of the above relaxation formalism, we have defined the original dipolar autocorrelation and intensity functions of order $k = 0, 1, 2$ as the Fourier transform pairs Eqs. (3.103) and (3.106):

$$G_k(\tau) = \langle F^{(k)}(\tau) F^{(-k)}(0) \rangle \propto \left\langle \frac{1}{r^3(\tau)} Y_{2,k}(\tau) \frac{1}{r^3(0)} Y_{2,-k}(0) \right\rangle$$

$$J^{(k)}(\omega) = \int_{-\infty}^{\infty} G_k(\tau) e^{-i\omega\tau} d\tau \quad (3.126)$$

for $k = 0, 1, 2$. The relevant angular frequencies are specified in Eq. (3.123) and for the case of two-spin $\frac{1}{2}$ systems, in Fig. 3.11. The quantities $F^{(k)}$ are functions of the fluctuating polar laboratory-frame coordinates $r(\tau)$, $\varphi(\tau)$, $\vartheta(\tau)$ of the inter-dipole vector $\mathbf{r} = \mathbf{r}(\tau)$. They are best expressed in terms of second-degree spherical harmonics $Y_{2,k}(\tau)$ as listed in Eq. (3.90).

The initial values of the autocorrelation functions are equal to the mean square fluctuations of the stochastic functions, that is, $G_k(0) = \langle |F^{(k)}|^2 \rangle$. In disordered systems, the inter-dipole vectors can be assumed to be randomly oriented within the envisaged ensemble of two-spin systems, and that – in the ergodic sense – all orientations can be reached by each dipole pair on the correlation time scale with the same probability density. It can readily be shown that the mean square fluctuations of the stochastic functions are then related as

$$\langle |F^{(0)}|^2 \rangle : \langle |F^{(1)}|^2 \rangle : \langle |F^{(2)}|^2 \rangle = \frac{12}{15} \left\langle \frac{1}{r^6} \right\rangle : \frac{2}{15} \left\langle \frac{1}{r^6} \right\rangle : \frac{8}{15} \left\langle \frac{1}{r^6} \right\rangle = 6 : 1 : 4 \quad (3.127)$$

The definitions referred to so far are specific for interactions of two magnetic dipoles. According to the general philosophy of the present treatise favoring representations of correlation functions applicable to non-NMR techniques as well, it is however more appropriate to consider *normalized* (or synonymously: *reduced*) versions $\mathcal{G}_k(\tau)$ instead of the original dipolar-correlation functions $G_k(\tau)$ given in Eqs. (3.126):

$$\mathcal{G}_k(\tau) = \frac{\langle F^{(k)}(0)F^{(-k)}(\tau) \rangle}{\langle |F^{(k)}|^2 \rangle} \quad (3.128)$$

where the attribute “normalized” means that the initial values are

$$\mathcal{G}_k(0) = 1 \quad (3.129)$$

Intramolecular Dipolar Coupling

If the relaxation mechanism is dominated by *intramolecular* dipolar coupling, the magnitude r of the inter-dipole distance can normally be approached by a fixed value not subjected to major thermal fluctuations (see Fig. 3.13). In this case, the reduced correlation functions of dipolar fluctuations can be expressed in the simple form

$$\mathcal{G}_k(\tau) \approx (-1)^k 4\pi \langle Y_{2,k}(0)Y_{2,-k}(\tau) \rangle \quad (3.130)$$

with $k = 0, 1, 2$.

Furthermore, as long as the system is disordered and molecular reorientations are not restricted by topological or sterical constraints, the normalized correlation functions will not depend on the order k . In this case, one may equate

$$\mathcal{G}_0(\tau) = \mathcal{G}_1(\tau) = \mathcal{G}_2(\tau) \equiv \mathcal{G}(\tau) \quad (3.131)$$

Examples demonstrating the equivalence for different orders of the spherical harmonics will explicitly be figured out in Sect. 3.1.7.1 for *isotropic rotational diffusion* and in Sect. 5.4.3.7 for *Rouse dynamics* of polymers.

In ordered systems or in cases where molecular reorientations are strongly restricted by topological constraints, the ensemble averages in Eqs. (3.127) and (3.131) will no longer imply all orientations in space. These relations can nevertheless be taken as good approximations relative to experimental errors. Practically, it will be unnecessary in most cases to distinguish the individual normalized correlation functions $\mathcal{G}_0(\tau)$, $\mathcal{G}_1(\tau)$, $\mathcal{G}_2(\tau)$ for intra-molecular interactions.

It suffices to consider one of the orders of the fluctuating spherical harmonics, for example,

$$Y_{2,\pm 1}(\varphi, \vartheta) = \mp \sqrt{\frac{15}{8\pi}} \sin \vartheta \cos \vartheta e^{\pm i\varphi} \quad (3.132)$$

to obtain a normalized correlation function $\mathcal{G}(\tau)$ representative for intra-molecular dipolar interactions.

According to the stationarity and time-reversal invariance of stochastic fluctuations, correlation functions are even functions of the interval τ at any time. We may therefore equate $\mathcal{G}(\tau) = \mathcal{G}(|\tau|)$. The overall correlation time of the fluctuations of the spin couplings is defined by

$$\tau_c = \int_0^{\infty} \mathcal{G}(\tau) d\tau \quad (3.133)$$

provided that $\mathcal{G}(0) = 1$ and $\mathcal{G}(\infty) = 0$ (see Eq. (1.7)).

The reduced dipolar intensity function conjugate to $\mathcal{G}(\tau)$ is

$$I(\omega) = \int_{-\infty}^{+\infty} \mathcal{G}(\tau) e^{-i\omega\tau} d\tau \quad (3.134)$$

with the property

$$I(0) = \int_{-\infty}^{+\infty} \mathcal{G}(\tau) d\tau = 2\tau_c \quad (3.135)$$

$I(\omega) \equiv I(|\omega|)$ is an even and real function of the angular frequency. It obeys the normalization condition

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} I(\omega) d\omega = \mathcal{G}(0) = 1 \quad (3.136)$$

Note that although the normalized correlation functions $\mathcal{G}(\tau)$ normally do not depend on the order of the spherical harmonics, the contributions of the reduced spectral densities $I(\omega)$ to dipolar relaxation rates will be weighted according to the different prefactors specified in Eq. (3.90) and related in Eq. (3.127). This will be the basis of the weighting factors in the formulas for the dipolar-coupling-based relaxation rates given in Eqs. (3.139), (3.144), (3.154), (3.155), (3.164), and (3.167).

Intermolecular Dipolar Coupling

The second case illustrated in Fig. 3.13 is *intermolecular* interaction between dipoles on different molecules. If this coupling contributes significantly, distance fluctuations $r = r(\tau)$ must be taken into account in addition. Quite often, intermolecular contributions are negligible because of the relatively large inter-dipole distances. However, especially at low fields (or frequencies), it may be necessary to consider such *translational* fluctuations. The representation of the reduced correlation function by spherical harmonics according to Eq. (3.130) is then no longer adequate. We will shortly get back to this case in Sect. 3.1.9.

3.1.5.7 Like Dipoles

Let us now resume the treatment of relaxation rates in the case of dipolar coupled two-spin systems. The most important case of NMR relaxometry is that of like dipoles, that is, $\gamma_I \equiv \gamma_S \equiv \gamma$ and $\omega_I \equiv \omega_S = \omega_0 = \gamma B_0$. With $\langle I_z \rangle = \langle S_z \rangle$ and $\langle I_z \rangle_0 = \langle S_z \rangle_0$, the system of relaxation equations, Eq. (3.122), merges into

$$\frac{d\langle I_z \rangle}{dt} = -\frac{1}{T_1} (\langle I_z \rangle - \langle I_z \rangle_0) \quad (3.137)$$

The general set of spin–lattice relaxation rates given in Eq. (3.123) can thus be reduced to a single rate according to

$$\frac{1}{T_1} = \frac{1}{T_1^H} + \frac{1}{T_1^S} = \left(\frac{\mu_0}{4\pi} \right)^2 \frac{3}{2} \gamma^4 \hbar^2 I(I+1) \left[J^{(1)}(\omega_0) + J^{(2)}(2\omega_0) \right] \quad (3.138)$$

In terms of the reduced intensity function (Eq. 3.134), this expression can be rewritten for a fixed inter-nuclear distance r in the form

$$\frac{1}{T_1} = \left(\frac{\mu_0}{4\pi} \right)^2 \frac{1}{5r^6} \gamma^4 \hbar^2 I(I+1) [I(\omega_0) + 4I(2\omega_0)] \quad (3.139)$$

Under the same prerequisites as for Eq. (3.131), different orders of spherical harmonics need not be distinguished. The factor of 4 in the brackets accounts for the different prefactors of the spherical harmonics as specified in Eq. (3.127). Double-quantum transitions are four times more efficient than the single-quantum counterpart. Equation (3.139) is also known as the *Bloembergen/Purcell/Pound (BPP) formula* [22]. The solutions of Eq. (3.137), that is, the relaxation curves for like spins, are again mono-exponential in accordance with the Bloch equation for the z magnetization, Eq. (3.29).

Zero-quantum transitions do not contribute in this case since they conserve the Zeeman energy of the spin system as illustrated in Fig. 3.11. There is no energy

exchange with the lattice, so that no contribution to spin–lattice relaxation can arise on this basis. This is in contrast to transverse relaxation as will be shown in Sect. 3.1.5.11.

Examples closely fulfilling the condition of isolated spin pairs are the protons of crystal water molecules in gypsum [23] or the protons in uracil [1]. For spin systems consisting of more than two dipolar-coupled spins, the dipolar Hamiltonian (Eq. 3.81) implies a sum over all pairs a given spin participates. Provided that the pair motions are independent of each other, the contributions from each of these pairs can be added according to

$$\frac{1}{T_1} = \frac{3}{2} \left(\frac{\mu_0}{4\pi} \right)^2 \gamma^4 \hbar^2 I(I+1) \sum_j \left[J_j^{(1)}(\omega_0) + J_j^{(2)}(2\omega_0) \right] \quad (3.140)$$

The sum index j runs over all dipoles interacting with the reference particle (see Eq. (3.83)).

3.1.5.8 S-Spin-Equilibrium Limit

For unlike dipoles, that is, $\gamma_I \neq \gamma_S$, the rate equations given in Eq. (3.122) and the respective longitudinal relaxation rates represented by Eq. (3.123) are of relatively general validity. They can however be simplified considerably for the following scenario which normally dominates in practical relaxation studies of unlike dipoles.

The RF pulses are considered to be tuned to the resonance of the I spins, whereas the off-resonant S spins merely take effect as interaction partners and are not subject to RF excitation. Furthermore, the S -spin populations are assumed to stay in their thermal equilibrium irrespective of what happens with the I spins. This is a frequent scenario arising if the S spins experience an additional coupling which is much stronger than the coupling to the I spins.¹⁸ Spin–lattice relaxation of the S spins can then be assumed to be fast enough to ensure permanent equilibrium. A typical example is electron-paramagnetic particles (atoms, ions, molecules, free radicals) characterized by unpaired electrons with spin S . Nuclear spins I interacting with spins S of unpaired electrons thus form two-spin systems with a resonant and a nonresonant partner, respectively. A further situation where this sort of two-spin system applies is the coupling of dipolar nuclei (resonant) with quadrupole nuclei (nonresonant). Both unpaired electrons and quadrupole nuclei are subject to additional and independent spin-relaxation mechanisms ineffective for their dipolar-coupling partners possessing not these attributes. The spin populations of unpaired electrons are efficiently kept in permanent thermal equilibrium by spin–orbit coupling. Likewise quadrupole nuclei are subject to a strong interaction

¹⁸ This refers predominantly to *dipolar coupling*. In the case of unpaired electrons, *scalar coupling* can be effective as well (see Sect. 3.1.5.9).

between the electric quadrupole moment and electric-field gradients intrinsic to molecules and their aggregates (see Sect. 3.1.5.9).

In the formalism, the permanent equilibrium of the S spins is taken into account by equating

$$\langle S_z(t) \rangle \approx \langle S_z(0) \rangle = \langle S_z \rangle_0 \quad (3.141)$$

Under these conditions, the system of master equations (3.122) reduces to

$$\begin{aligned} \frac{d\langle I_z \rangle}{dt} &= -\frac{1}{T_1} (\langle I_z \rangle - \langle I_z \rangle_0) \\ \frac{d\langle S_z \rangle}{dt} &\approx 0 \end{aligned} \quad (3.142)$$

Recalling the proportionality between the expectation value of the z component of the I spins and the z magnetization of this spin species, we see that the *rotating-frame Bloch equation* for the latter quantity has been reproduced in this way (see Eq. (3.29)). The solution is a mono-exponential relaxation function. According to Eq. (3.123), the spin–lattice relaxation rate of the I spins is given by

$$\begin{aligned} \frac{1}{T_1} &\equiv \frac{1}{T_1^H} \\ &= \left(\frac{\mu_0}{4\pi} \right)^2 \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \\ &\quad \times \left[\frac{1}{12} J^{(0)}(\omega_I - \omega_S) + \frac{3}{2} J^{(1)}(\omega_I) + \frac{3}{4} J^{(2)}(\omega_I + \omega_S) \right] \end{aligned} \quad (3.143)$$

where $\omega_I = \gamma_I B_0$ and $\omega_S = \gamma_S B_0$.

In terms of the reduced intensity functions defined in Eq. (3.134), this rate can be rewritten for a fixed interparticle distance r as

$$\frac{1}{T_1} = \left(\frac{\mu_0}{4\pi} \right)^2 \frac{1}{15 r^6} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) [I(\omega_I - \omega_S) + 3I(\omega_I) + 6I(\omega_I + \omega_S)] \quad (3.144)$$

Following the argument in the context of Eq. (3.131), the functions $I(\omega)$ need not be distinguished for different orders of spherical harmonics. Their contributions are, however, weighted according to the prefactors given in Eq. (3.90) and related in Eq. (3.127). The zero-, single-, and double-quantum transitions corresponding to the three angular transition frequencies in the arguments of the spectral densities in Eqs. (3.143) or (3.144) are illustrated by the Zeeman energy level scheme on the right-hand side of Fig. 3.11. The transition energy quanta are $|\omega_S - \omega_I| \hbar$ (zero-quantum transition), $\omega_I \hbar$ (I -spin single-quantum transitions), and $(\omega_S + \omega_I) \hbar$ (double-quantum transition). Zero-quantum transitions contribute to spin–lattice relaxation in the present case since they do not conserve spin energy (in contrast to

the like-dipole case). Single-quantum transitions of the S spins do not directly appear in Eqs. (3.143) or (3.144), since the S spins are assumed to stay in equilibrium all the time.

The level schemes in Fig. 3.11 refer to two-spin systems with spin quantum numbers $I = 1/2$ and $S = 1/2$. Note, however, that the spectral-density composition of the above result would be valid even if the spin system would consist of more than two spins and even if the spin quantum numbers would be larger than $1/2$. Merely the coefficients would be subject to slight modifications if cross-correlation effects among different spin pairs matter.

3.1.5.9 Spin–Lattice Relaxation by Other Interaction Types

As mentioned above, the master equation given in Eq. (3.78) is of a rather general applicability. Certainly, fluctuations of the dipolar couplings treated so far are the almost ubiquitous origin of spin–lattice relaxation. There is however a number of other and possibly additional interactions that matter under certain conditions to be specified in each case. The contributions of these interactions can be treated in the same way as in the case of dipolar coupling by just replacing the perturbation Hamiltonian.

Spin–Lattice Relaxation due to Scalar-Coupling of Unlike Dipoles ($\gamma_I \neq \gamma_S$)

The first case where scalar coupling matters refers to nuclei coupled to *unpaired electrons* having a finite probability to reside temporally in the resonant nucleus. Under such conditions, the electron–nucleus distance is zero, so that the validity of the dipolar-coupling Hamiltonian (Eq. 3.87) is violated. Instead, the electron/nuclear spin coupling adopts the scalar form of the *Fermi contact interaction*. The relevant spin–interaction Hamiltonian

$$\mathcal{H}_s = A \mathbf{I} \cdot \mathbf{S} = \frac{A}{2} [(I^+ S^- + I^- S^+) + 2I_z S_z] \quad (3.145)$$

consists of an orientation-independent scalar product of the two-spin vector operators. This is in contrast to dipolar interaction which has the orientation properties of a second-rank tensor. A is the coupling constant which implies the probability density of finding the electron in the resonant nucleus. A typical example for relaxation phenomena based on this interaction is observed with hydrated paramagnetic ions such as Mn^{2+} [11].

The second variant of scalar coupling refers to *indirect spin–spin coupling* of the resonant nucleus to a quadrupole nucleus in the same molecule via the surrounding electron orbitals. In this case, one of the interaction partners is subjected to additional relaxation mechanisms by quadrupole interactions. In the motional-averaging limit, when only the isotropic part of the coupling tensor matters, the Hamiltonian has again a scalar form analogous to Eq. (3.145). An example where

this interaction gives rise to significant low-field or low-frequency relaxation effects is water containing ^{17}O in enriched or in natural abundance as quadrupolar species [24–26].

The scalar-interaction Hamiltonian (Eq. 3.145) can be transformed to the interaction representation according to Eq. (3.93). The master equation (Eq. 3.78) can then be established for the observable $\mathcal{Q} = I_z$. The treatment is already implied in the formalism for dipolar coupling because the spin-operator terms in Eq. (3.145) are part of the dipolar Hamiltonian as well. The additional *scalar spin–lattice relaxation* rate term can thus readily be derived as

$$\left(\frac{1}{T_1}\right)_{\text{scal}} = \frac{1}{3} \left(\frac{A}{\hbar}\right)^2 S(S+1) I(\omega_S - \omega_I) \quad (3.146)$$

where $\omega_S = \gamma_S B_0$ and $\omega_I = \gamma_I B_0$ refer to the off- and on-resonant spin species, respectively. The quantities $I(\omega) = \mathcal{F}\{G(\tau)\}$ and $G(\tau)$ form the conjugate Fourier transform pair of the reduced spectral density and the normalized correlation function for scalar interaction in analogy to Eq. (3.134). As suggested by the Hamiltonian (Eq. 3.145), the scalar coupling mechanism produces only zero-quantum (or “flip-flop”) spin transitions (see Fig. 3.11, right-hand side).

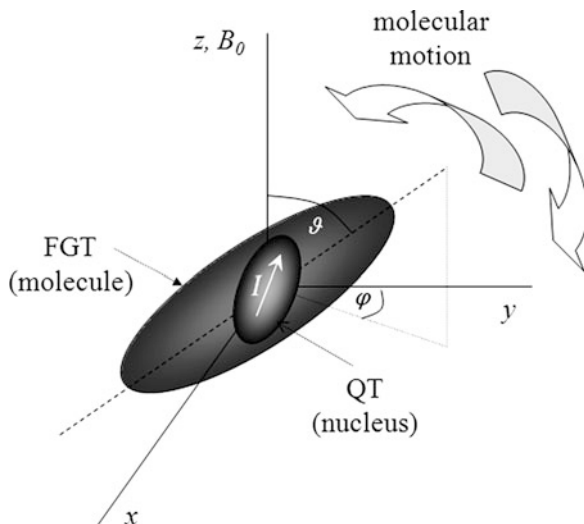
The analytical form of the scalar Hamiltonian furthermore stipulates that scalar interaction is inherently insensitive to rotational diffusion. Its fluctuations arise either from fast spin–lattice relaxation of the nonresonant interaction partner or from chemical exchange separating the resonant nucleus from the coupled spin in the sense of distance fluctuation. The former case is referred to as *scalar relaxation of the second kind* [15]. The condition is that the spin-flip rate caused by additional interaction mechanisms selectively acting on this particle is sufficiently high.

Spin–Lattice Relaxation of Spin-1 Nuclei due to Quadrupolar Coupling in the High-Field Limit

Electric-field gradients are ubiquitous in molecules and molecular aggregates as a consequence of nonuniform charge distributions. Nuclei with spin quantum numbers $I > 1/2$ possess an electric quadrupole moment that interacts with these electric-field gradients. An illustration of the respective tensors is shown in Fig. 3.14. This so-called *quadrupole coupling* tends to be much stronger than dipolar coupling to the same or other nuclear species. If present, it therefore tends to be the dominant source of relaxation.

An example is relaxation of deuterons ($I = 1$) in D_2O on the one hand and in HDO molecules on the other. HDO molecules unavoidably occur in mixtures of light and heavy water due to chemical exchange. In both cases, spin–lattice relaxation of the deuterons is dominated by quadrupole coupling. The respective contributions by dipolar coupling, that is, from deuteron to deuteron in the D_2O case or from deuteron to proton ($I = 1/2$) in HDO molecules, are negligible regardless of the coupling partner. For this reason, relaxation of quadrupole nuclei

Fig. 3.14 Schematic representation of electric-field gradient (FGT) and quadrupole (QT) tensors



is a matter of single particles. Even in solids, the effective spin “system” consists just of a single member.

Quadrupole nuclei with spin 1 are of particular interest in the present context. Apart from deuterons, ^{14}N is a further example often encountered in NMR studies of soft matter. The quadrupole-coupling Hamiltonian is given by [1, 15]

$$\mathcal{H}_q = \frac{eQ}{2I(2I-1)} I \cdot \tilde{\Gamma} \cdot I \quad (3.147)$$

with I the nuclear spin quantum number, e the positive elementary charge, Q the nuclear quadrupole moment, I the dimensionless spin vector operator, and $\tilde{\Gamma}$ the electric-field gradient tensor fixed in the molecular system hosting the quadrupole nucleus. Equation (3.147) obviously represents a single-spin Hamiltonian in contrast to the dipolar and scalar couplings treated above.

The *high-field limit* for quadrupole nuclei is defined by $\langle \mathcal{H}_0 \rangle \gg \langle \mathcal{H}_q \rangle$. The expectation value of the Zeeman Hamiltonian, Eq. (3.1), is then much greater than the expectation value of the quadrupolar-interaction Hamiltonian, Eq. (3.147). That is, the external magnetic-field $\mathbf{B}_0$ defines the quantization direction, whereas quadrupolar coupling acts as a small perturbation. Relative to the external magnetic field, the Hamiltonian of this perturbation can be analyzed in complete analogy to the dipolar case specified in Eqs. (3.88), (3.89), (3.90), and (3.91). We are again dealing with a series of products of second-degree spherical harmonics $Y_{2,m}(\varphi, \vartheta)$, $m = 0, \pm 1, \pm 2$, and spin-operator terms. The azimuthal and polar angles φ and ϑ refer to the orientation of the field-gradient tensor in its principal-axes representation relative to the laboratory reference frame where the external flux density $\mathbf{B}_0$ is aligned along the z -axis. As a consequence of molecular motions, the angles φ , ϑ , and hence the quadrupolar Hamiltonian will fluctuate as a function of time.

The above BWR formalism thus predicts the induction of spin transitions manifesting themselves as spin relaxation.

On this basis, the BWR master equation (Eq. 3.78) leads to the spin–lattice relaxation rate of the observable $\mathcal{Q} = I_z$, that is, the *quadrupolar spin–lattice relaxation rate for spins 1* in the high-field limit:

$$\frac{1}{T_1} = \frac{3}{80} \left(\frac{e^2 q Q}{\hbar} \right)^2 \left(1 + \frac{\eta^2}{3} \right) [\mathcal{I}(\omega_0) + 4\mathcal{I}(2\omega_0)] \quad (3.148)$$

where $\omega_0 = \gamma B_0$ as before. The parameters $q = \Gamma_{33}/e$ and $\eta = (\Gamma_{11} - \Gamma_{22})/\Gamma_{33}$ characterize the electric field gradient at the position of the nucleus, where the principal-axes values of the field-gradient tensor obey the inequality $|\Gamma_{33}| \geq |\Gamma_{22}| \geq |\Gamma_{11}|$. The reduced spectral densities $\mathcal{I}(\omega_0)$ are defined analogous to Eq. (3.134) and refer in principle to the reduced autocorrelation function of quadrupolar couplings in terms of spherical harmonics $Y_{2,m}(\varphi, \vartheta)$ of order $m = \pm 1, \pm 2$. Under the premises mentioned in the context of Eq. (3.131), the order of the spherical harmonics considered is normally irrelevant. Merely the factor of 4 in the brackets in Eq. (3.148) accounts for the different prefactors with which the spherical harmonics are weighted in the quadrupole Hamiltonian. As in the dipolar-coupling case, double-quantum transitions are four times more efficient than the single-quantum counterpart.

There is a striking similarity between Eqs. (3.148) and (3.139) for *quadrupolar* spin–lattice relaxation of spins 1 and *dipolar* spin–lattice relaxation of two-spin systems, respectively. The reason is that the Hamiltonians in both cases imply spin-operator terms causing single- as well as double-quantum transitions as reflected by the respective intensity function terms for once and twice the resonance frequency. For an illustration, see the Zeeman energy level scheme for spin-1 particles shown in Fig. 3.12.

The situation is more complicated for nuclei with spins greater than 1. Examples are lithium, sodium, and chlorine. In these cases, the relaxation equation deviates substantially from the Bloch equation. Since nuclear magnetic resonance of such nuclides is of minor interest in the present context, we will omit any further discussion.

Spin–Lattice Relaxation by Chemical-Shift Anisotropy (CSA)

As a further mechanism that can be treated on the basis of the BWR master equation given in Eq. (3.78), the *anisotropy of the chemical-shift tensor* can provide a significant contribution in certain cases to be specified below. The chemical-shift Hamiltonian [1, 2, 15]

$$\mathcal{H}_{cs} = \hbar \gamma \mathbf{I} \cdot \underline{\underline{\sigma}} \cdot \mathbf{B}_0 \quad (3.149)$$

accounts for the modified flux density at the position of a nuclear spin $\mathbf{I}$. The reason for this modification is the so-called “shielding” of the external field $\mathbf{B}_0$ by the

electron shell of the molecule. The term shielding suggests a diamagnetic effect, that is, a reduction of the external flux density. However, it should be kept in mind that the effect can also be of a paramagnetic nature depending on the orbital wave functions. The shielding tensor σ fluctuates as a consequence of molecular tumbling in the course of thermal motions. It thus produces transverse field components which are able to induce single-quantum spin transitions.

For axially symmetric molecules, the CSA *spin-lattice relaxation rate* straightforwardly following from Eq. (3.78) for the observable $Q = I_z$ is

$$\frac{1}{T_1} \propto \gamma^2 B_0^2 (\sigma_{33} - \sigma_i)^2 I(\omega_0) \quad (3.150)$$

where σ_{33} is the (largest) principal-axes value of the shielding tensor. σ_i is the isotropic chemical shielding constant. The reduced spectral density $I(\omega_0)$ is defined in analogy to Eq. (3.134) for the normalized autocorrelation function of the Hamiltonian (Eq. 3.149). By contrast to the other spin couplings treated so far, the coupling constant of the chemical-shift anisotropy mechanism varies with the external flux density. This manifests itself by the characteristic factor B_0^2 .

Relaxation due to CSA becomes important at high fields (above about 6 T), and may even prevail in case the competitive spin couplings are weak enough. Relevant scenarios are dipole nuclei on isolated positions and quadrupole nuclei in cubic or tetrahedral structures where electric-field gradients vanish. Nuclear species predestinated for CSA-induced relaxation are ^{13}C and ^{31}P .

3.1.5.10 Rotating-Frame Spin-Lattice Relaxation by Dipolar Coupling

In laboratory-frame experiments, the *direction of quantization* is aligned along the external magnetic-field B_0 . This is in contrast to the so-called rotating-frame experiments. In this case, the direction of quantization is *tilted* by not necessarily but typically 90° relative to B_0 as already outlined in Sect. 3.1.4.5. The experimental pulse scheme for achieving this scenario is shown in Fig. 3.8. The magnetic field effective during the relaxation interval is then the RF field amplitude B_1 of the spin-lock pulse.

The treatment follows the same principles as applied in the case of laboratory-frame spin-lattice relaxation. In order to obtain a convenient reference frame, all fields are transformed from the rotating frame x', y', z' to the rotating frame x'', y'', z'' tilted by 90° relative to the z' direction. The z'' -axis, that is, the new quantization direction, is then aligned along the RF field amplitude B_1 . Note that this vector rotates in the transverse plane of the laboratory frame but is statically aligned along the z'' -axis of the tilted rotating frame. In the case of the RF pulse phases assumed in the scheme Fig. 3.8, the quantizing field B_1 along the z'' -axis thus coincides with the y' -axis of the untilted rotating frame.

As before, all operators must be transformed to the interaction representation. The coefficients in the expression for the (high-temperature) equilibrium density operator for an ensemble of two-spin systems,

$$\begin{aligned}\rho_0'' &= a + b_0 I_z + c_0 S_z && \text{(unlike dipoles)} \\ \rho_0'' &= a + b_0 (I_z + S_z) && \text{(like dipoles)}\end{aligned}\quad (3.151)$$

refer to the effective field $\mathbf{B}_1$ acting during the spin-lock pulse instead of $\mathbf{B}_0$ (compare Eq. (3.115)) and are accordingly small. Note that the spin operators I_z and S_z now act *relative to the tilted rotating reference frame*.

The nonequilibrium density operator $\rho''(t)$ describing the evolution during the spin-lock relaxation interval again refers to components of the spin operators $\mathbf{I}$ and $\mathbf{S}$. For *like dipoles*, it will be of a structure

$$\rho''(t) = a + b(t)I_z + c(t)S_z \quad (3.152)$$

The coefficients b and c will be identical if the interactions to which the spins are subjected are equivalent. The respective relation for *unlike dipoles* with resonant $\mathbf{I}$ spins is

$$\rho''(t) = a + b(t)I_z + c(t)S_z + \text{transverse components} \quad (3.153)$$

The nonresonant species contribute temporally with their transverse components as well, and the longitudinal component starts with the coefficient $c(0+) = 0$. The terms “transverse” and “longitudinal” refer again to the tilted rotating frame, of course.

The spin operator corresponding to the partial magnetization to be observed in the experiment is identified with the observable $\mathcal{Q}$ in the master equation given in Eq. (3.78). The rate equation established in this way permits the evaluation of the -rotating-frame spin-lattice relaxation rate for dipolar-coupled pairs of *like* dipoles with a fixed internuclear distance r . In terms of reduced spectral densities, the result is

$$\frac{1}{T_{1\rho}} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{1}{10r^6} \gamma^4 \hbar^2 I(I+1) [3I(2\omega_1) + 5I(\omega_0) + 2I(2\omega_0)] \quad (3.154)$$

The reduced spectral densities $I(\omega)$ are defined in Eq. (3.134) and are weighted according to the different prefactors of the spherical harmonics in Eq. (3.90) (see Eq. (3.127)). Apart from $\omega_0 = \gamma B_0$, Eq. (3.154) depends on $\omega_1 = \gamma B_1$ as a further angular frequency. Since $\omega_0 \gg \omega_1$, rotating-frame spin-lattice relaxometry offers the possibility to examine low frequencies with high-field instruments.

In the case of dipolar-coupled pairs of *unlike* dipoles, we must distinguish which of the spin species is resonant. If the $\mathbf{I}$ spins are resonant and if the $\mathbf{S}$ spins are remaining in permanent equilibrium, the rotating-frame spin-lattice relaxation rate of the $\mathbf{I}$ spins can be derived as

$$\begin{aligned}\frac{1}{T_{1\rho}} &= \left(\frac{\mu_0}{4\pi}\right)^2 \frac{1}{30r^6} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \\ &\quad [4I(\omega_1) + I(\omega_I - \omega_S) + 3I(\omega_I) + 6I(\omega_S) + 6I(\omega_I + \omega_S)]\end{aligned}\quad (3.155)$$

The angular-frequency $\omega_1 = \gamma_I B_1$ refers to the resonant $\mathbf{I}$ spins, whereas $\omega_S = \gamma_S B_0$ and $\omega_I = \gamma_I B_0$ as before.

3.1.5.11 Transverse Relaxation in the Motional-Averaging Limit

As concerns transverse relaxation, the validity of the BWR theory is restricted to the motional-averaging limit which anticipates that the spin-interaction fluctuations are fast on the basic time scale of transverse relaxation. This time scale can be defined via the coherence attenuation time to be expected in the absence of motions, that is, for the so-called rigid-lattice case. The rigid-lattice line width $(\Delta\omega)_{\text{rl}}$ originates from secular spin couplings. The time scale corresponding to this line width is then given by the reciprocal value. Expressed by the so-called *local fields*, the motional averaging condition can be formulated as

$$(\Delta\omega)_{\text{rl}} = \gamma \sqrt{\langle B_{\text{loc}}^2 \rangle} \tau_c \ll 1 \quad (3.156)$$

where τ_c is the correlation time of the fluctuating spin interactions.

Transverse relaxation experiments usually start with 90° RF pulse exciting the spin coherences of interest as described in Sects. 3.1.4.6 and 3.1.4.7. Suitable RF pulse schemes are depicted in Figs. 3.9 and 3.10. If the RF phase of the preparation pulse is assumed to correspond to the x' -axis of the rotating frame, the initial coherence phase direction immediately after the preparation pulse is then the y' direction. The (high-temperature) equilibrium density operator for an ensemble of two-spin systems consisting of the spins I and S and *like dipoles*,

$$\rho'_0 = a + b_0(I_z + S_z) \quad (3.157)$$

(see Eq. (3.115)) is thus converted to the nonequilibrium density operator

$$\begin{aligned} \rho'(0+) &= a + b_0(I_y + S_y) \\ \rho'(t) &= a + \text{transverse components} \\ &\quad + \text{irrelevant longitudinal components} \end{aligned} \quad (3.158)$$

(compare Eq. (3.117)). In the case of *unlike dipoles*, the respective relations are

$$\rho'_0 = a + b_0 I_z + c_0 S_z \quad (3.159)$$

and

$$\begin{aligned} \rho'(0+) &= a + b_0 I_y + c_0 S_z \\ \rho'(t) &= a + \text{transverse components} \\ &\quad + \text{irrelevant longitudinal components} \end{aligned} \quad (3.160)$$

where it is assumed that the I spins are resonant (compare Eqs. (3.115) and (3.119)).

The observables to be inserted into the BWR master (Eq. 3.78) for the derivation of the transverse relaxation equation are $\mathcal{Q} = I_y$ and $\mathcal{Q} = S_y$. The equilibrium expectation values are $\langle I_y \rangle_0 = 0$ and $\langle S_y \rangle_0 = 0$ in accordance with Curie's law, that is, Eqs. (3.157) and (3.159). Analogous to Eqs. (3.122), the transverse relaxation equations for dipolar coupling between two spins I and S result as

$$\begin{aligned}\frac{d\langle I_y \rangle}{dt} &= -\frac{1}{T_2^{II}} \langle I_y \rangle - \frac{1}{T_2^{IS}} \langle S_y \rangle \\ \frac{d\langle S_y \rangle}{dt} &= -\frac{1}{T_1^{SI}} \langle I_y \rangle - \frac{1}{T_1^{SS}} \langle S_y \rangle\end{aligned}\quad (3.161)$$

The solutions of this system of differential equations are linear combinations of exponential functions. These reduce to mono-exponential versions in the two limits already discussed in the context of spin-lattice relaxation, namely the *S-spin-equilibrium limit* and the case of *like dipoles*.

In the *S-spin-equilibrium limit*, Eqs. (3.161) reduces to a Bloch-type relaxation equation for the resonant **I** spins

$$\frac{d\langle I_y \rangle}{dt} = -\frac{1}{T_2} \langle I_y \rangle \quad (3.162)$$

whereas the **S** spins reside permanently in equilibrium. For single-quantum coherences of *dipolar-coupled* two-spin systems, the transverse relaxation rate of the **I** spins is found to be

$$\begin{aligned}\frac{1}{T_2} &= \left(\frac{\mu_0}{4\pi}\right)^2 \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \\ &\quad \left[\frac{1}{6} J^{(0)}(0) + \frac{1}{24} J^{(0)}(\omega_I - \omega_S) + \frac{3}{4} J^{(1)}(\omega_I) + \frac{3}{2} J^{(1)}(\omega_S) + \frac{3}{8} J^{(2)}(\omega_I + \omega_S) \right]\end{aligned}\quad (3.163)$$

where $\omega_S = \gamma_S B_0$ and $\omega_I = \gamma_I B_0$ refer to the off- and on-resonant spin species, respectively, as before. Remarkably, a spectral-density term $J^{(0)}(0)$ appears which is specific for transverse relaxation. In terms of the reduced intensity function (Eq. 3.134), and for a fixed interdipole distance r , the transverse relaxation rate is converted to

$$\begin{aligned}\frac{1}{T_2} &= \left(\frac{\mu_0}{4\pi}\right)^2 \frac{2}{15 r^6} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \\ &\quad \left[I(0) + \frac{1}{4} I(\omega_I - \omega_S) + \frac{3}{4} I(\omega_I) + \frac{3}{2} I(\omega_S) + \frac{3}{2} I(\omega_I + \omega_S) \right]\end{aligned}\quad (3.164)$$

If *scalar coupling* due to Fermi contact interaction of unpaired electrons, that is, the **S** spins, with an $I = 1/2$ nucleus exists, the contribution to the transverse relaxation rate of the **I** spins is

$$\left(\frac{1}{T_2}\right)_{\text{scal}} = \frac{1}{6} \left(\frac{A}{\hbar}\right)^2 S(S+1) [I(0) + I(\omega_S - \omega_I)] \quad (3.165)$$

in addition to the dipolar relaxation rate (Eq. 3.164). The reduced spectral densities in this expression are understood as the scalar analogues to the dipolar variant defined in Eq. (3.134).

In the case of *like dipoles*, the analytic form of the relaxation equation given in Eq. (3.162) holds true again. The corresponding transverse relaxation rate for single-quantum coherences of *dipolar-coupled* two-spin systems is

$$\frac{1}{T_2} = \left(\frac{\mu_0}{4\pi}\right)^2 \gamma^4 \hbar^2 I(I+1) \left[\frac{3}{8} J^{(0)}(0) + \frac{15}{4} J^{(1)}(\omega_0) + \frac{3}{8} J^{(2)}(2\omega_0) \right] \quad (3.166)$$

where $\omega_0 = \gamma B_0$. As in the *S*-spin-equilibrium limit, a secular spectral-density term $J^{(0)}(0)$ appears again. In terms of reduced intensity functions, Eq. (3.166) can be rewritten for a fixed inter-dipole distance r as

$$\frac{1}{T_2} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{1}{10r^6} \gamma^4 \hbar^2 I(I+1) [3I(0) + 5I(\omega_0) + 2I(2\omega_0)] \quad (3.167)$$

The effect of *quadrupole interactions* on transverse relaxation can again be treated with the aid of the BWR theory in a totally analogous manner. For nuclei with spin quantum numbers $I = 1$, that is, the quadrupole nuclei most important in the present context, the BWR theory predicts the transverse relaxation rate

$$\frac{1}{T_2} = \frac{3}{160} \left(\frac{e^2 q Q}{\hbar} \right)^2 \left(1 + \frac{\eta^2}{3} \right) [3I(0) + 5I(\omega_0) + 2I(2\omega_0)] \quad (3.168)$$

for single-quantum coherences. As in the case of spin–lattice relaxation, the reduced spectral densities $I(\omega)$ are the Fourier conjugates of the autocorrelation function of quadrupole interaction in analogy to Eq. (3.134). The definitions of the symbols in the factors preceding the brackets are the same as in Eqs. (3.147) and (3.148). Nuclear species with spins $I > 1$ are of minor interest in soft-matter science. The relaxation behavior turns out to be more complicated in this case since substantial deviations from Bloch-type relaxation equations arise.

3.1.6 Anderson/Weiss Theory for Transverse Relaxation in the Presence of Residual Spin Couplings

This section is devoted to transverse relaxation in the case when the motional-averaging limit Eq. (3.156), $\gamma \sqrt{\langle B_{\text{loc}}^2 \rangle} \tau_c \ll 1$, is not or only with respect to certain anisotropic components of molecular motions fulfilled. For the viscous and structured materials with which one is normally dealing in the frame of soft-matter science, such conditions quite often apply. The BWR theory fails then. For the treatment of the equilibration of transverse magnetization, one uses local-field

approaches instead. In the following, we will focus on the most elementary and most useful local-field theory, namely the *Anderson/Weiss (AW) formalism* [27].

The applicability ranges of the BWR and AW approaches are overlapping. However, they are not of an entirely complementary nature. Secular terms of spin couplings are relevant in both formalisms. These are operator terms generating energy-conserving spin transitions or are inert with respect to transitions. In the case of dipolar interaction, the terms containing spin operators of the form $I_z S_z$ and – in the like-dipole case – $(I^+ S^- + I^- S^+)$ are secular (see Eq. (3.91)). Both types of operator produce the so-called *local fields* causing a distribution of spin energy levels and consequently varying precession frequencies so that coherences decay fast. The operator term $(I^+ S^- + I^- S^+)$ has a second effect: It induces *flip-flop spin transitions* which also destroy the precession phase coherence as a consequence of the random nature of the perturbative fields.

The AW concept anticipates that transverse relaxation is governed solely by a spin-coupling-induced distribution of precession frequencies in the sense of the before-mentioned local fields. This effect certainly arises in the absence of motional averaging. On the other hand, in the realm of motional averaging where the BWR theory is adequate the secular flip-flop term can contribute not only in this way but also via random spin transitions in addition (apart from the action of the *non-secular terms*, i.e., terms producing spin transitions that do not conserve spin energy). The inconsistencies arising in principle when considering the crossover between the rigid-lattice and complete-motional averaging limits, that is, the two formalisms, are however of minor significance and can be ignored in the frame of the accuracy needed for the interpretation of experimental data.

The local field produced by spin interactions causes local offsets of the angular precession frequency, $\Omega \equiv \omega - \omega_0 = \gamma B_{\text{loc}}$, relative to the angular resonance frequency $\omega_0 = \gamma B_0$. For a spin ensemble, one speaks of an *inhomogeneous* distribution of the angular-frequency offsets. The normalized free-induction decay (FID) of the NMR signal resulting from the superposition of such offsets is given as the ensemble average of the precession phase factors:

$$A(t) = \frac{m(t)}{m(0)} = \langle e^{i\Omega t} \rangle = \langle e^{i\varphi(t)} \rangle \quad (3.169)$$

where $m(t) = M_x + iM_y$ is the complex transverse magnetization relative to the rotating frame.

The relation $\varphi = \Omega t$ between the offset phase angle and the offset frequency implicitly used in Eq. (3.169) is what one expects in the static case. The situation is different if molecular motion modulates the spin interactions and, hence, the frequency offsets. That is, the precession phase angle is then accumulated in an interval $0 \dots t$ according to

$$\varphi(t) = \int_0^t \Omega(t') dt' \quad (3.170)$$

where the angular offset frequency $\Omega = \Omega(t)$ fluctuates due to molecular dynamics. The expression to be evaluated is therefore

$$A(t) = \left\langle \exp \left\{ i \int_0^t \Omega(t') dt' \right\} \right\rangle \quad (3.171)$$

The ensemble average can be derived with the aid of the distribution function $P(\varphi, t)$ of the phase shifts φ accumulated in a time t :

$$A(t) = \int_{-\infty}^{\infty} P(\varphi, t) e^{i\varphi} d\varphi \quad (3.172)$$

Expanding the exponential function and forming the ensemble average of each expansion term lead to the moment series

$$\begin{aligned} A(t) &= \int_{-\infty}^{\infty} P(\varphi, t) \left(1 + i \frac{\varphi}{1!} - \frac{\varphi^2}{2!} - i \frac{\varphi^3}{3!} + \frac{\varphi^4}{4!} \pm \dots \right) d\varphi \\ &= 1 - \frac{\langle \varphi^2 \rangle}{2!} + \frac{\langle \varphi^4 \rangle}{4!} - \frac{\langle \varphi^6 \rangle}{6!} \pm \dots \end{aligned} \quad (3.173)$$

All odd moments vanish because the phase-shift distribution is an *even* function of the phase shifts.

Under normal circumstances, the local field a nucleus experiences is a superposition of contributions of numerous interaction partners. Therefore, the *central-limit theorem* (see e.g. Refs. [20] or [28]) applies. It expresses that the accumulative sum of a sufficiently large number of random contributions is distributed according to a Gauss function irrespective of how the contributions themselves are distributed. If the angular-frequency offsets Ω caused by the local fields are Gauss distributed, the phase shift accumulated in a time interval t is Gauss distributed as well because φ is a linear combination (in the form of an integral) of the Gauss-distributed offsets Ω . Thus,

$$P(\varphi, t) = \frac{1}{\sqrt{2\pi\langle\varphi^2\rangle}} \exp \left\{ -\frac{\varphi^2}{2\langle\varphi^2\rangle} \right\} \quad (3.174)$$

The even moments of a Gaussian distribution can be derived from its second moment according to the rule

$$\langle \varphi^{2N} \rangle = 1 \cdot 3 \cdot 5 \dots (2N - 1) \langle \varphi^2 \rangle^N \quad (N = 1, 2, 3 \dots) \quad (3.175)$$

The evaluation of the expansion (Eq. 3.173) thus results in

$$\begin{aligned}
A(t) &= 1 - \frac{\frac{1}{2}\langle\varphi^2\rangle}{1!} + \frac{\left(\frac{1}{2}\langle\varphi^2\rangle\right)^2}{2!} - \frac{\left(\frac{1}{2}\langle\varphi^2\rangle\right)^3}{3!} \pm \dots \\
&= \exp\left\{-\frac{1}{2}\langle\varphi^2\rangle\right\}
\end{aligned} \tag{3.176}$$

The second moment of the precession phase distribution after the time interval t can be rewritten in the form

$$\begin{aligned}
\langle\varphi^2\rangle &= \left\langle \left[\int_0^t \Omega(t') dt' \right]^2 \right\rangle = \left\langle \int_0^t dt' \int_0^t dt'' \Omega(t') \Omega(t'') \right\rangle \\
&= \int_0^t dt' \int_0^t dt'' \underbrace{\langle \Omega(t') \Omega(t'') \rangle}_{G_\Omega}
\end{aligned} \tag{3.177}$$

where we have introduced the *correlation function of the local resonance offsets*, $G_\Omega = \langle \Omega(t') \Omega(t'') \rangle$. According to the stationarity requirement for stochastic processes, it depends on the time difference rather than on the absolute time. Furthermore, it does not matter which of the two times t' and t'' is first, so that the correlation function must be even as symbolized by the magnitude of the time argument:

$$G_\Omega = G_\Omega(|t'' - t'|) \tag{3.178}$$

The two time variables t' and t'' can be substituted by the new variable pair $\tau = t'' - t'$ and t' . With this substitution, the second moment given in Eq. (3.177) is converted to

$$\begin{aligned}
\langle\varphi^2\rangle &= \int_0^t dt' \int_0^t dt'' G_\Omega(|t'' - t'|) \\
&= \underbrace{\int_0^t d\tau \left[G_\Omega(|\tau|) \int_0^{t-\tau} dt' \right]}_{\text{positive } \tau \text{ values}} + \underbrace{\int_{-t}^0 d\tau \left[G_\Omega(|\tau|) \int_{|\tau|}^t dt' \right]}_{\text{negative } \tau \text{ values}} \\
&= 2 \int_0^t d\tau \left[G_\Omega(|\tau|) \int_0^{t-\tau} dt' \right] \\
&= 2 \int_0^t (t - \tau) G_\Omega(\tau) d\tau
\end{aligned} \tag{3.179}$$

Inserting this result into Eq. (3.176) gives the *Anderson/Weiss formula* for the envelope of the free-induction decay for equivalent spins:

$$A(t) = \exp \left\{ -\langle \Omega_{\text{H}}^2 \rangle \int_0^t (t - \tau) \mathcal{G}(\tau) d\tau \right\} \quad (3.180)$$

where the normalized correlation function of the local offset frequencies is defined by $\mathcal{G}(\tau) \equiv \mathcal{G}_{\Omega}(\tau) / \langle \Omega^2 \rangle$. That is, $\mathcal{G}(0) = 1$. The factor $\langle \Omega_{\text{H}}^2 \rangle$ is the *second moment* of the resonance line in the absence of molecular motion, that is, for stationary local fields as expected in the *rigid-lattice* limit. The root mean square angular offset frequency, $\sqrt{\langle \Omega_{\text{H}}^2 \rangle}$, characterizes the line width in this limit. The result given in Eq. (3.180) can also be obtained in the frame of the more general *Kubo/Tomita theory* using the stochastic Liouville/von Neumann equation supplemented by an additional Markov operator term [29].

In terms of the reduced intensity function, the FID envelope (Eq. 3.180) can be reformulated by replacing $\mathcal{G}(\tau)$ by its Fourier transform

$$\mathcal{G}(\tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} I(\Omega) \exp\{i\Omega\tau\} d\Omega \quad (3.181)$$

Interchanging the time integral in Eq. (3.180) and the angular-frequency integral of the Fourier transformation and carrying out the time integration lead to

$$A(t) = \exp \left\{ -\frac{1}{\pi} \int_0^{\infty} \frac{\langle \Omega_{\text{H}}^2 \rangle}{\Omega^2} I(\Omega) [1 - \cos(\Omega t)] d\Omega \right\} \quad (3.182)$$

With this spectral-density representation of the Anderson/Weiss formula, it becomes evident that the FID envelope is dominated by *slow fluctuations* with rates $\Omega \leq \sqrt{\langle \Omega_{\text{H}}^2 \rangle}$.

For discussion purposes and for simplicity, let us assume an exponential correlation function for the moment:

$$\mathcal{G}(\tau) = \exp\{-|\tau|/\tau_{\Omega}\} \quad (3.183)$$

Such a relationship arises, for instance, if any change of the local field entails the total loss of correlation. In this case, the correlation time τ_{Ω} is identical with the mean lifetime of the local fields, that is, of the local resonance frequency. The *rigid-lattice limit* is then defined by the condition $\tau_{\Omega} \gg (\langle \Omega_{\text{H}}^2 \rangle)^{-1/2}$. The experimental time window, that is, the acquisition time T_{a} is adjusted in such a way that the whole

timescale of perceptible FID signals is covered. According to the basic rules of Fourier transform NMR spectroscopy [1–7], it is ensured in this way that the resonance line will completely be resolved. In the rigid-lattice limit, the signal acquisition time must therefore correspond to the inverse line width of the rigid-lattice spectrum, that is, $T_a \approx (\langle \Omega_{\text{rl}}^2 \rangle)^{-1/2}$. Since there will practically be no fluctuations of the angular offset frequencies Ω on this time scale, we may equate $G(\tau) \approx 1$. The Anderson/Weiss formula (Eq. 3.180) thus converges to the rigid-lattice version

$$A(t) = \exp \left\{ -\frac{1}{2} \langle \Omega_{\text{rl}}^2 \rangle t^2 \right\} \quad (3.184)$$

corresponding to the limit $\tau_\Omega \rightarrow \infty$. The line-shape conjugate to this Gaussian FID is again a Gaussian function:

$$f_{\text{Gauss}}(\omega) = \exp \left\{ -\omega^2 / 2 \langle \Omega_{\text{rl}}^2 \rangle \right\} \quad (3.185)$$

as illustrated in Fig. 3.15 in comparison to the Fourier transform pair exponential FID versus Lorentzian line shape.

In the opposite limit, $\tau_\Omega \ll (\langle \Omega_{\text{rl}}^2 \rangle)^{-1/2}$, the angular offset frequencies Ω fluctuate rapidly on the minimum time scale for the acquisition of the NMR signal, that is $T_a \gg (\langle \Omega_{\text{rl}}^2 \rangle)^{-1/2} \gg \tau_\Omega$. The consequence is *motional averaging* of the frequency offsets. The autocorrelation function of the frequency offsets therefore decays correspondingly fast. The exponent in Eq. (3.180) can then be approximated by

$$\int_0^t (t - \tau) G(\tau) d\tau \approx t \int_0^\infty G(\tau) d\tau = t\tau_\Omega \quad (3.186)$$

The argument leading to this result is that the integrand can be neglected for $\tau \gg \tau_\Omega$ because $G(\tau)$ has then decayed already to insignificantly low values. That is, the upper integration limit can be equated with ∞ . On the other hand, the τ range in which the integrand perceptibly contributes to the integral is $\tau < \tau_\Omega \ll t$. The integration variable τ in the factor $(t - \tau)$ can therefore be neglected relative to t . In the motional-averaging limit, the Anderson/Weiss formula (Eq. 3.180) thus takes the form of an exponential decay function,

$$A(t) \approx \exp \left\{ -\langle \Omega_{\text{rl}}^2 \rangle \tau_\Omega t \right\} \quad (3.187)$$

for $\tau_\Omega \ll (\langle \Omega_{\text{rl}}^2 \rangle)^{-1/2}$. The Fourier transform yields a Lorentz line-shape function

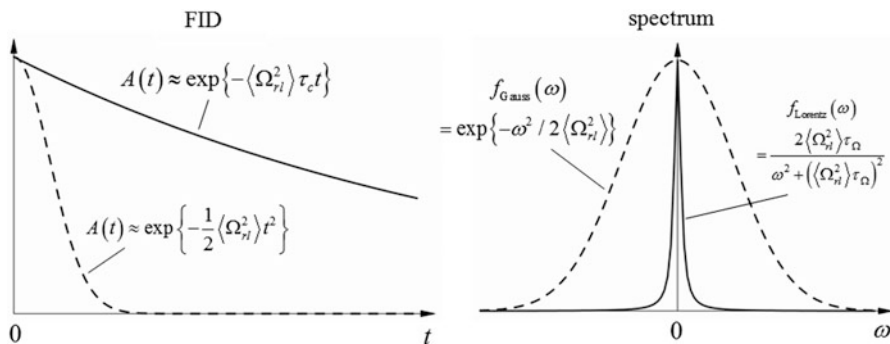


Fig. 3.15 Lorentzian and Gaussian line shapes in the frequency domain (*right-hand side*) are Fourier conjugated to exponential and Gaussian free-induction decays (*left side*), respectively

$$f_{\text{Lorentz}}(\omega) = \frac{2\langle\Omega_{\text{H}}^2\rangle\tau_{\Omega}}{\omega^2 + (\langle\Omega_{\text{H}}^2\rangle\tau_{\Omega})^2} \quad (3.188)$$

with a full line width at half maximum

$$\Delta\Omega_{\text{FWHM}} = 2\langle\Omega_{\text{H}}^2\rangle\tau_{\Omega} \quad (3.189)$$

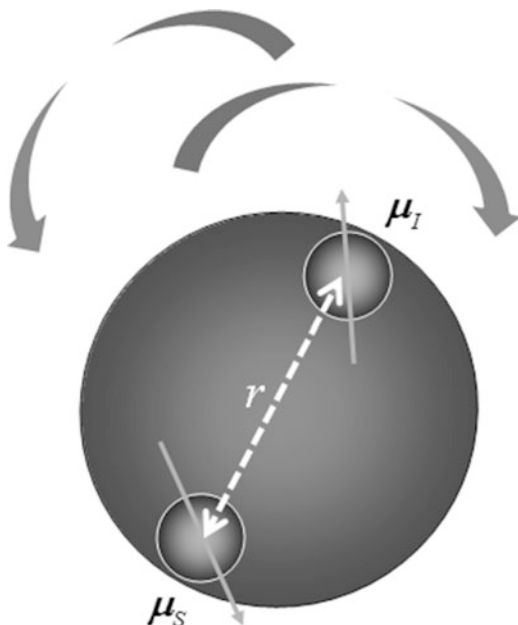
The shorter the correlation time τ_{Ω} is, the narrower is the resonance line.¹⁹ The interrelation between FID and resonance line is again illustrated in Fig. 3.15.

3.1.7 A First Example of Correlation Functions: The Isotropic Rotational Diffusion Model

Up to now, we have established NMR relaxation and line-shape theories in terms of correlation functions of spin interactions fluctuating as a consequence of molecular motions. No specification of the type of the correlation decays to be expected has been made so far. At this point, the proper character of molecular dynamics comes into play. Molecular dynamics in soft matter reflect all the complexities intrinsic to this sort of systems. Constraints due to obstacles, confinements, pores, surface

¹⁹Note that “motional averaging” in the present context specifically refers to the reduction of *inhomogeneous line broadening* which is the result of a distribution of local resonance frequencies. This is in contrast to the additional *lifetime narrowing* effect predicted by the BWR theory in the sense of Heisenberg’s uncertainty principle. The rationale of this lifetime phenomenon is the following: The mean lifetime of spin states is characterized by the transverse relaxation time in the BWR sense. It can be traced back to spin transitions induced by molecular motions modulating spin interactions. Faster molecular motions stipulate longer mean lifetimes and, hence, narrower resonance lines.

Fig. 3.16 Illustration of isotropic rotational diffusion of an isolated spherical molecule in a viscous medium. The molecule is assumed to contain two magnetic dipoles in a fixed distance r



adsorption and ordering, domains, anisotropy, excluded volume, polymer-chain connectivity, etc., will be reflected by special features of the correlation functions. This is the realm of modeling molecular dynamics in terms of characteristic correlation functions. One of the major objectives of the subsequent chapters will be to establish corresponding relationships for scenarios of interest. For didactic reasons and for comparisons with other techniques, we will restrict ourselves by now to the simplest molecular-dynamics model as an introductory example, namely, isotropic rotational diffusion.

3.1.7.1 Autocorrelation Function and Spectral Density

Let us resume the discussion of rotational diffusion in Sect. 2.5.3 by considering an ensemble of spherically shaped, isolated molecules. As the most important spin interaction, we assume *dipolar coupling*, but keep in mind that other spin interactions would lead to equivalent results. Each molecule is assumed to contain two dipolar-coupled spins in a fixed distance r as illustrated in Fig. 3.16. The molecules are thought to tumble randomly, independently and isotropically in a viscous medium. The rotational nature of this motion and the constant inter-nuclear distance suggest to express the functions $F^{(m)}(\varphi, \vartheta)$ in Eq. (3.90) by spherical harmonics $Y_{2,-m}(\varphi, \vartheta)$ according to

$$\begin{aligned}
F^{(0)} &= r^{-3} (1 - 3\cos^2\vartheta) \propto Y_{2,0}(\vartheta) = \sqrt{\frac{5}{16\pi}} [3\cos^2\vartheta(t) - 1] \\
F^{(1)} &= r^{-3} (\sin\vartheta \cos\vartheta e^{-i\varphi}) \propto Y_{2,-1}(\varphi, \vartheta) = \sqrt{\frac{15}{8\pi}} \sin\vartheta(t) \cos\vartheta(t) e^{-i\varphi(t)} \\
F^{(2)} &= r^{-3} (\sin^2\vartheta e^{-2i\varphi}) \propto Y_{2,-2}(\varphi, \vartheta) = \sqrt{\frac{15}{32\pi}} \sin^2\vartheta(t) e^{-2i\varphi(t)} \quad (3.190)
\end{aligned}$$

where φ and ϑ are the azimuth and polar angles, respectively, of the internuclear vector relative to the laboratory frame of reference (compare Fig. 3.13). The z-axis of this frame coincides with the main magnetic-field $\mathbf{B}_0$. The internuclear distance vector $\mathbf{r}$ is assumed to have a fixed magnitude determined by the molecular structure. It is thus merely its orientation that will be subject to molecular dynamics.

The unit vector $\mathbf{u}(t) = \mathbf{r}(t)/r$ with the polar coordinates $\varphi(t)$, $\vartheta(t)$, $u = 1$ defines the orientation of the internuclear vector $\mathbf{r}(t)$ at time t . Let us now consider the time interval between $t = 0$ and $t = \tau$. With the identities $\varphi(0) \equiv \varphi_i$, $\vartheta(0) \equiv \vartheta_i$, $\mathbf{u}(0) \equiv \mathbf{u}_i$ and $\varphi(\tau) \equiv \varphi_f$, $\vartheta(\tau) \equiv \vartheta_f$, $\mathbf{u}(\tau) \equiv \mathbf{u}_f$ for the respective initial and final orientations, the normalized autocorrelation function for dipolar coupling at fixed inter-dipole distance can be expressed as

$$\begin{aligned}
G_m(\tau) &= \frac{\langle F^{(m)}(0) F^{(-m)}(\tau) \rangle}{\langle |F^{(m)}|^2 \rangle} \\
&= 4\pi(-1)^m \langle Y_{2,-m}(\mathbf{u}_i) Y_{2,m}(\mathbf{u}_f) \rangle \quad (3.191)
\end{aligned}$$

where $m = 0, 1, 2$. The angle brackets indicate ensemble averages regarding the initial and final orientations $\mathbf{u}_i$ and $\mathbf{u}_f$, respectively. As already argued in the context of Eq. (3.131) and as will be shown in the following, the order m of the spherical harmonics does not matter since in all three cases the same correlation function comes out.

The partial average over all final orientations $\mathbf{u}_f$ can be calculated with the aid of the probability density $P(\mathbf{u}_i, 0; \mathbf{u}_f, \tau)$ that the initial unit vector is $\mathbf{u}_i$ and that the final orientation is given by $\mathbf{u}_f$ ²⁰:

²⁰ In this context, the term *probability density* refers to solid angles. The probability that the final unit vector $\mathbf{u}_f$ points in a solid-angle element $d\Omega_f = \sin\vartheta_f d\vartheta_f d\varphi_f$ and that the initial unit vector $\mathbf{u}_i$ points in the solid-angle element $d\Omega_i = \sin\vartheta_i d\vartheta_i d\varphi_i$ is thus equal to $P(\mathbf{u}_i, 0; \mathbf{u}_f, \tau) \sin\vartheta_f \sin\vartheta_i d\vartheta_f d\varphi_f d\vartheta_i d\varphi_i$, where $P(\mathbf{u}_i, 0; \mathbf{u}_f, \tau)$ is the corresponding probability density. Likewise, the a priori probability that the unit vector $\mathbf{u}_i$ points in a solid-angle element $d\Omega_i = \sin\vartheta_i d\vartheta_i d\varphi_i$ equals $p(\mathbf{u}_i) \sin\vartheta_i d\vartheta_i d\varphi_i$, where $p(\mathbf{u}_i)$ is the a priori probability density. Finally, the conditional probability that the final unit vector $\mathbf{u}_f$ points in the solid-angle element $d\Omega_f = \sin\vartheta_f d\vartheta_f d\varphi_f$ if the initial unit vector is $\mathbf{u}_i$ is defined by $P_c(\mathbf{u}_i, \mathbf{u}_f, \tau) \sin\vartheta_f d\vartheta_f d\varphi_f$, where $P_c(\mathbf{u}_i, \mathbf{u}_f, \tau)$ is the conditional probability density.

$$\begin{aligned}
G_m(\tau) &= 4\pi(-1)^m \langle Y_{2,m}\{\mathbf{u}_i\} Y_{2,-m}\{\mathbf{u}_f\} \rangle \\
&= 4\pi(-1)^m \left\langle \int_0^{2\pi} d\varphi_f \int_0^\pi d\vartheta_f P(\mathbf{u}_i, 0; \mathbf{u}_f, \tau) Y_{2,m}(\mathbf{u}_i) Y_{2,-m}(\mathbf{u}_f) \sin \vartheta_f \right\rangle_{\mathbf{u}_i} \\
&= 4\pi(-1)^m \int_0^{2\pi} d\varphi_f \int_0^\pi d\vartheta_f \langle P(\mathbf{u}_i, 0; \mathbf{u}_f, \tau) Y_{2,m}(\mathbf{u}_i) \rangle_{\mathbf{u}_i} Y_{2,-m}(\mathbf{u}_f) \sin \vartheta_f \quad (3.192)
\end{aligned}$$

The subscript $\mathbf{u}_i$ at the brackets indicates that the remaining part of the ensemble average concerns the initial orientations. The probability density $P(\mathbf{u}_i, 0; \mathbf{u}_f, \tau)$ can be factorized into two terms. $p(\mathbf{u}_i)$ is the *a priori probability density* for the initial orientation. The second term is the *conditional-probability density* $P_c(\mathbf{u}_i, \mathbf{u}_f, \tau)$ that the final orientation after the interval τ will be $\mathbf{u}_f$ provided that the initial orientation was $\mathbf{u}_i$:

$$P(\mathbf{u}_i, 0; \mathbf{u}_f, \tau) = p(\mathbf{u}_i) P_c(\mathbf{u}_i, \mathbf{u}_f, \tau) \quad (3.193)$$

Under isotropic conditions, the *a priori probability* for a certain orientation is given by the solid-angle ratio

$$p(\mathbf{u}_i) \sin \vartheta_i d\vartheta_i d\varphi_i = \frac{d\Omega_i}{4\pi} = \frac{1}{4\pi} \sin \vartheta_i d\vartheta_i d\varphi_i \quad (3.194)$$

For continuous rotational diffusion, the conditional probability density obeys the rotational variant of the diffusion equation (see Eq. (2.179))

$$\frac{\partial P_c(\mathbf{u}_i, \mathbf{u}_f, \tau)}{\partial \tau} = D_r \nabla^2 P_c(\mathbf{u}_i, \mathbf{u}_f, \tau) \quad (3.195)$$

where D_r is the rotational diffusion coefficient and ∇^2 is the Laplace differential operator for polar coordinates r, φ, ϑ . With Dirac's delta function, the initial condition can be expressed as

$$P_c(\mathbf{u}_i, \mathbf{u}_f, 0) = \delta(\mathbf{u}_f - \mathbf{u}_i) \quad (3.196)$$

Regarding the spherical-harmonics basis of the autocorrelation function, Eq. (3.191), it is favorable to make use of the expansion

$$P_c(\mathbf{u}_i, \mathbf{u}_f, \tau) = \sum_{l', m'} c_{l', m'}(\tau) Y_{l', m'}(\mathbf{u}_f) \quad (3.197)$$

for the separation of time and orientation dependences. The former is implied in the coefficients $c_{l', m'}(\tau)$, the latter is reflected by the spherical harmonics $Y_{l', m'}(\mathbf{u}_f)$.

Further steps of the treatment are the following: (1) Eq. (3.197) is inserted into the rotational diffusion equation, Eq. (3.195). (2) The Laplace operator terms acting on spherical harmonics are replaced by the known eigenvalue equation

$$\begin{aligned}\nabla^2 Y_{l,m} &= \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial Y_{l,m}}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 Y_{l,m}}{\partial \varphi^2} \\ &= -l(l+1) Y_{l,m}(\vartheta, \varphi)\end{aligned}\quad (3.198)$$

where the degree l can in general adopt integer values, $l = 0, 1, 2, \dots$ and where the order m will be shown below to be irrelevant for the final result. (2) Both sides of the resulting equation are multiplied by conjugate complex function $Y_{l,m}^*(\mathbf{u}_f)$ and integrated over the full solid-angle range with respect to the final orientations $\mathbf{u}_f$. (4) Furthermore, the orthonormal property of spherical harmonics is employed. That is,

$$\int_0^{2\pi} d\varphi \int_0^\pi d\vartheta \sin \vartheta Y_{l,m}^*(\vartheta, \varphi) Y_{l',m'}(\vartheta, \varphi) = \delta_{ll'} \delta_{mm'} \quad (3.199)$$

where $\delta_{ll'}$ and $\delta_{mm'}$ are Kronecker symbols (see footnote 16).

On this basis, a linear differential equation for the time-dependent coefficients $c_{l,m}$ can be derived straightforwardly from the rotational diffusion equation (Eq. 3.195):

$$\frac{dc_{l,m}}{d\tau} = -D_r l(l+1) c_{l,m} \quad (3.200)$$

The initial condition for Eq. (3.200) can be obtained in the following manner: (1) The ansatz equation (3.197) is multiplied by $Y_{l,m}^*(\mathbf{u}_f)$ on both sides. (2) The left- and right-hand sides are then integrated over the full solid-angle range with respect to $\mathbf{u}_f$. (3) The orthonormal property of spherical harmonics, Eq. (3.199), is again taken into account. (4) Finally, the initial condition for $P_c(\mathbf{u}_i, \mathbf{u}_f, 0)$, Eq. (3.196), is inserted. The result is

$$c_{l,m}(0) = Y_{l,-m}(\mathbf{u}_i) \quad (3.201)$$

The solution of Eq. (3.200) is thus established as

$$c_{l,m} = Y_{l,-m}(\mathbf{u}_i) \exp\{-D_r l(l+1) \tau\} \quad (3.202)$$

Combining this result with the ansatz equation (3.197) yields the conditional probability

$$P_c(\mathbf{u}_i, \mathbf{u}_f, \tau) = \sum_{l,m} Y_{l,-m}(\mathbf{u}_i) Y_{l,m}(\mathbf{u}_f) \exp\{-D_r l(l+1) \tau\} \quad (3.203)$$

which, in turn, can be associated with Eqs. (3.192) and (3.193). Utilizing the orthonormal property of spherical harmonics again leads to the *exponential* auto-correlation function of second-degree spherical harmonics ($l = 2$)

$$G_m(\tau) = 4\pi(-1)^m \langle Y_{2,m}[\mathbf{u}(0)] Y_{2,-m}[\mathbf{u}(\tau)] \rangle = \exp\{-|\tau|/\tau_c\} \quad (3.204)$$

The time constant τ_c is the *rotational correlation time* given by

$$\tau_c = [l(l+1)D_r]^{-1} = (6D_r)^{-1} \quad (3.205)$$

Note that Eq. (3.204) for the normalized correlation function does *not* depend on the order m as already mentioned in the context of Eq. (3.131). This subscript can therefore be omitted. The different m values will however be significant for the original versions of the correlation functions via the different prefactors of the spherical harmonics in Eq. (3.190). The original correlation functions $\langle F^{(m)}(0) F^{(-m)}(\tau) \rangle$ are weighted by different numerical factors for the different m values, while the time dependences are identical as a consequence of the isotropy anticipated in this model.

Combining Eq. (3.205) with the Stokes/Einstein/Debye relation given in Eq. (2.204) finally leads to

$$\tau_c = \frac{4\pi\eta a_h^3}{3k_B T} \quad (3.206)$$

η is the dynamic viscosity of the medium, and a_h is the hydrodynamic radius of the particle.

The reduced intensity function, that is the Fourier conjugate to the normalized, exponential autocorrelation function $G_m(\tau)$, is calculated as the *Lorentz* function

$$I(\omega) = \mathcal{F}\{G(\tau)\} = \frac{2\tau_c}{1 + \omega^2\tau_c^2} \quad (3.207)$$

ω represents any of the angular resonance frequencies such as ω_0 , ω_I , ω_S , and $\omega_I \pm \omega_S$, referred to in the relaxation formulas derived in Sect. 3.1.5.

Graphical representations and characteristic properties of this spectral density can be found in Figs. 3.17 and 3.18. The angular-frequency dependence is characterized by a crossover from a plateau $I(\omega\tau_c \ll 1) \approx 2\tau_c$ in the low frequency limit to the high-frequency regime $I(\omega\tau_c \gg 1) = 2/(\omega^2\tau_c)$. The spectral density adopts the value τ_c at the crossover condition $\omega\tau_c = 1$. With increasing correlation time τ_c , the crossover region is shifted to lower frequencies, and the plateau value increases. This is the origin of the $T_1(\tau_c)$ minimum (or the $T_1^{-1}(\tau_c)$ maximum) to be discussed later.

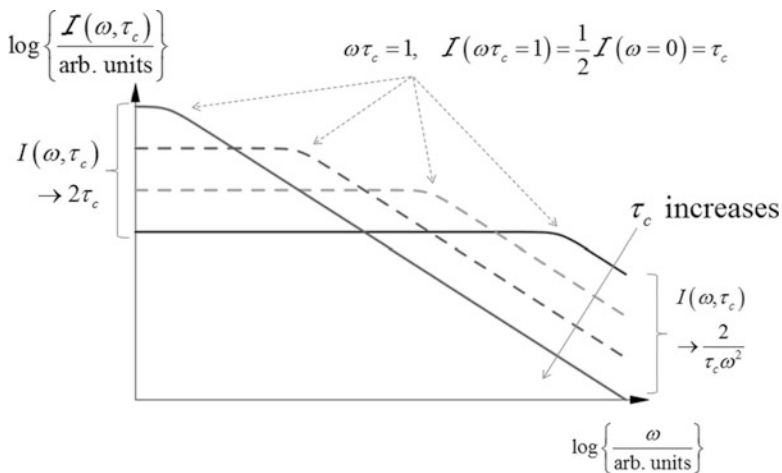


Fig. 3.17 Double logarithmic plot of the Lorentzian spectral density Eq. (3.207) as a function of the angular-frequency ω for various correlation times τ_c

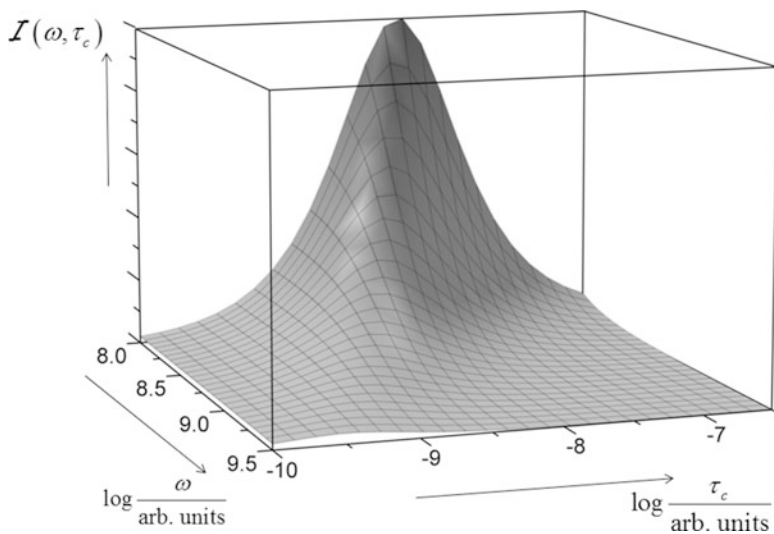


Fig. 3.18 Lorentzian spectral density Eq. (3.207) as a function of the angular-frequency ω and the correlation time τ_c . Along the τ_c axis, a maximum appears for the condition $\omega \tau_c = 1$

3.1.7.2 Frequency and Temperature Dependences of Relaxation Times for Dipolar-Coupled Pairs of Like Dipoles with Spins $\frac{1}{2}$

Let us now examine how the isotropic rotational diffusion model manifests itself by certain features of the relaxation behavior. As the standard scenario, we consider systems of two like and dipolar-coupled dipoles with spins $\frac{1}{2}$. Inserting

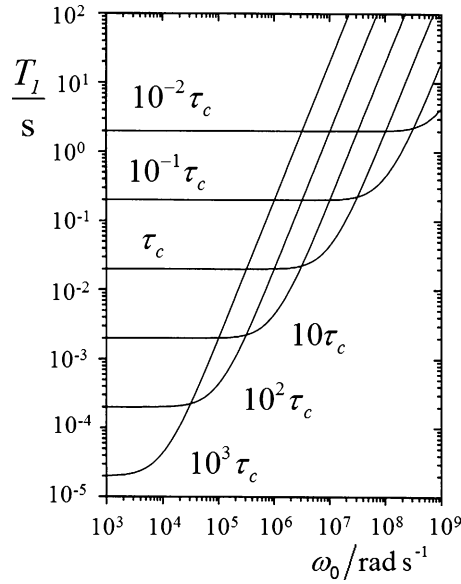


Fig. 3.19 Double logarithmic plot of the (laboratory-frame) spin-lattice relaxation time T_1 as a function of the angular-frequency $\omega_0 = \gamma B_0$. The data have been calculated on the basis of the BPP expression given in Eq. (3.208) (a) for different rotational correlation times. The theory is valid for a two-spin 1/2 ensemble of like dipoles subject to intramolecular dipolar interactions with fixed internuclear distance r . Fluctuations of this coupling are assumed to originate from isotropic rotational diffusion leading to a mono-exponential correlation function. All parameter values have been chosen arbitrarily but in typical orders of magnitude. The curves reflect the characteristics of the Lorentzian spectral density shown in Fig. 3.17. The crossover from the low-frequency plateau in the limit $\omega_0 \tau_c \ll 1$ to the high-frequency regime $T_1 \propto \tau_c^{-1} \omega_0^{-2}$ for $\omega_0 \tau_c \gg 1$ occurs at $\omega_0 \approx \tau_c^{-1}$ (Reproduced from Ref. [9] with kind permission of © Elsevier 2004)

the Lorentz-shaped intensity function derived in the previous section into the BWR relations (Eqs. (3.139), (3.154), and (3.167)) gives

$$\begin{aligned}
 \frac{1}{T_1} &= \left(\frac{\mu_0}{4\pi}\right)^2 \frac{3}{10r^6} \gamma^4 \hbar^2 \left[\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right] & (\rightarrow \text{lab. frame}) & \quad (a) \\
 \frac{1}{T_{1\rho}} &= \left(\frac{\mu_0}{4\pi}\right)^2 \frac{3}{20r^6} \gamma^4 \hbar^2 \left[\frac{3\tau_c}{1 + 4\omega_1^2 \tau_c^2} + \frac{5\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right] & (\rightarrow \text{rot. frame}) & \quad (b) \\
 \frac{1}{T_2} &= \left(\frac{\mu_0}{4\pi}\right)^2 \frac{3}{20r^6} \gamma^4 \hbar^2 \left[3\tau_c + \frac{5\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right] & (\rightarrow \text{lab. frame}) & \quad (c)
 \end{aligned}
 \tag{3.208}$$

These expressions are often referred to as *Bloembergen/Purcell/Pound (BPP) equations* as well. The relevant angular frequencies are $\omega_0 = \gamma B_0$ and $\omega_1 = \gamma B_1$.

The plots in Figs. 3.19, 3.20, and 3.21 show the diverse relaxation times as functions of the angular frequency and the reciprocal absolute temperature expected on this basis. The frequency dependence of T_1 , Fig. 3.19, is characterized by a crossover from a low-frequency plateau for $\omega_0 \tau_c \ll 1$ to a steep dispersion regime

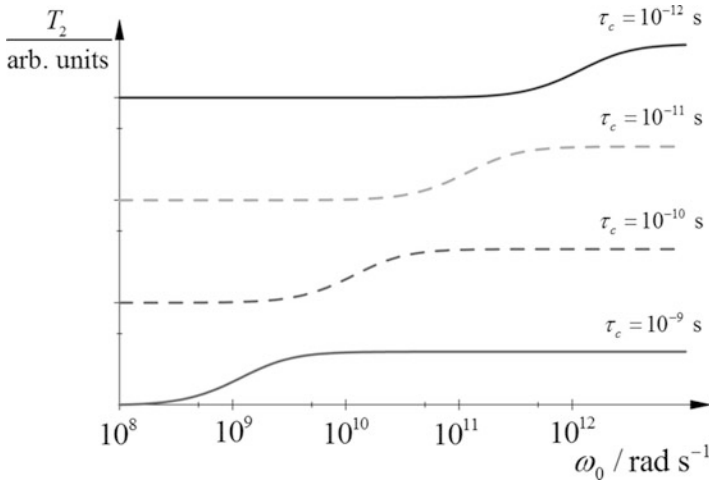


Fig. 3.20 Double logarithmic plot of the angular-frequency dependence of the transverse relaxation time T_2 . The data have been calculated on the basis of the BPP expression given in Eq. (3.208c) for typical rotational correlation times. The crossover from the low- to the high-frequency plateaus appears at $\omega_0 \approx \tau_c^{-1}$. The step height between the plateau values given by Eqs. (3.209) and (3.210) corresponds to a factor $10/3$

$T_1 \propto \omega_0^2$ in the limit $\omega_0 \tau_c \gg 1$. The crossover position obeys the condition $\omega_0 \tau_c \approx 0.6$. The temperature dependences of T_1 and $T_{1\rho}$, Fig. 3.21, show minima for the same condition and for $\omega_1 \tau_c = 1$, respectively. This phenomenon reflects the maximum of the spectral density upon variation of the (temperature-dependent) correlation time shown in Fig. 3.18.

The temperature dependence of T_2 , Fig. 3.21, is a function smoothly decaying with increasing reciprocal temperature. However, unlike the spin-lattice relaxation times T_1 and $T_{1\rho}$, no minimum appears. At sufficiently low temperatures, the T_2 data merge into the temperature-independent *rigid-lattice limit*, where the motional-average formula Eq. (3.208c) resulting from the BWR theory is no longer valid. The problem is that transverse relaxation decays adopt a non-exponential shape in this limit which is described more appropriately by the Anderson/Weiss formalism outlined in Sect. 3.1.6.

The frequency dependence of T_2 , Fig. 3.20, is characterized by a step centered at the position $\omega_0 \tau_c \approx 1$. The transverse relaxation rate in the so-called *extreme-narrowing limit* $\omega_0 \tau_c \ll 1$ for very short correlation times and/or for very low angular frequencies is

$$\frac{1}{T_2} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{3}{2} \frac{1}{r^6} \gamma^4 \hbar^2 \tau_c = \frac{1}{T_1} \quad (3.209)$$

This is to be distinguished from the ordinary *motional-averaging* situation determined on the one hand by the root mean square of the angular offset frequency in the rigid-lattice limit, $\sqrt{\langle \Omega_{\text{rl}}^2 \rangle}$, and the angular resonance frequency ω_0 on the other.

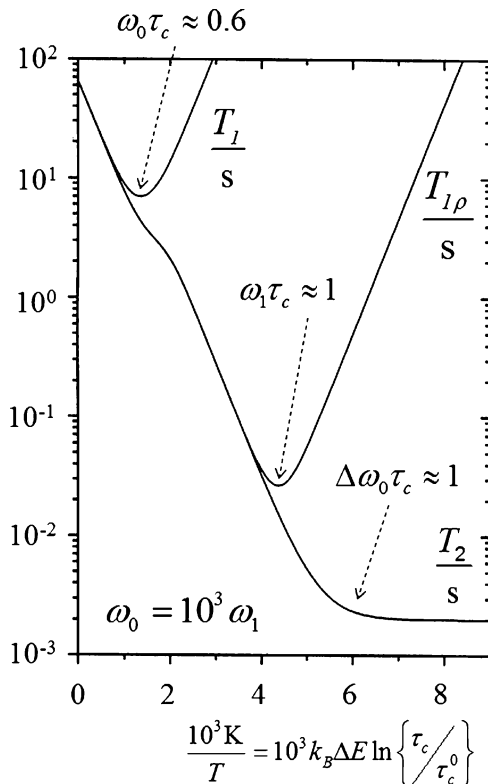


Fig. 3.21 Temperature dependences of the spin-relaxation times T_1 , $T_{1\rho}$, T_2 calculated on the basis of the BPP expressions given in Eq. (3.208a–c). The theory is valid for two-spin 1/2 ensembles of like dipoles subject to intramolecular dipolar interactions with fixed internuclear distance r . Fluctuations of this coupling are assumed to originate from isotropic rotational diffusion leading to mono-exponential correlation functions. For the temperature dependence of the correlation time of this process, the Arrhenius law $\tau_c = \tau_c^0 \exp\{\Delta E/k_B T\}$ was assumed, where ΔE is the activation energy and τ_c^0 is the correlation time in the limit of infinite temperature. All parameter values have been chosen arbitrarily but in typical orders of magnitude. The condition $\Delta\omega_0\tau_c = \tau_c\sqrt{\langle\Omega_{rl}^2\rangle} = 1$ indicates the crossover from the (temperature-independent) rigid-lattice limit to motional averaging. $\sqrt{\langle\Omega_{rl}^2\rangle}$ is the root mean square angular-frequency offset in the absence of motions (Reproduced from Ref. [9] with kind permission of © Elsevier 2004)

The quantity $\sqrt{\langle\Omega_{rl}^2\rangle}$ characterizes the residual spin couplings not averaged out by molecular motions as already discussed in the context of the Anderson/Weiss theory. In combined form, the condition for motional averaging thus is $1/\omega_0 \ll \tau_c \ll 1/\sqrt{\langle\Omega_{rl}^2\rangle}$ which is equivalent to the two inequalities $\tau_c\sqrt{\langle\Omega_{rl}^2\rangle} \ll 1$ and $\omega_0\tau_c \gg 1$. Under these circumstances, that is, for high angular frequencies and/or long correlation times, Eq. (3.208c) is reduced to

$$\frac{1}{T_2} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{9}{20} \frac{1}{r^6} \gamma^4 \hbar^2 \tau_c \quad (3.210)$$

The height of the dispersion step between the low- and high-frequency regimes corresponds to a factor of 10/3.

3.1.7.3 Spin-Relaxation Features of Pairs of Unlike Dipoles Subject to Exponential Correlation Functions

After having discussed the spin-relaxation behavior for the case of like dipoles, let us now turn to unlike dipoles in the S -spin equilibrium limit. In terms of general spectral densities, the I -spin-relaxation rates in dipolar-coupled I, S pairs (with spin quantum numbers $I = 1/2$; S arbitrary) were found to obey Eqs. (3.144), (3.155), and (3.164). Inserting the Lorentzian spectral density Eq. (3.207) gives

$$\frac{1}{T_1} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{2}{15r^6} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \left[\frac{\tau_{\text{dip}}}{1 + (\omega_I - \omega_S)^2 \tau_{\text{dip}}^2} + \frac{3\tau_{\text{dip}}}{1 + \omega_I^2 \tau_{\text{dip}}^2} + \frac{6\tau_{\text{dip}}}{1 + (\omega_I + \omega_S)^2 \tau_{\text{dip}}^2} \right] \quad (a)$$

$$\frac{1}{T_{1\rho}} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{1}{15r^6} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \left[\frac{4\tau_{\text{dip}}}{1 + \omega_I^2 \tau_{\text{dip}}^2} + \frac{\tau_{\text{dip}}}{1 + (\omega_I - \omega_S)^2 \tau_{\text{dip}}^2} + \frac{3\tau_{\text{dip}}}{1 + \omega_I^2 \tau_{\text{dip}}^2} + \frac{6\tau_{\text{dip}}}{1 + \omega_S^2 \tau_{\text{dip}}^2} + \frac{6\tau_{\text{dip}}}{1 + (\omega_I + \omega_S)^2 \tau_{\text{dip}}^2} \right] \quad (b)$$

$$\frac{1}{T_2} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{1}{15r^6} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \left[4\tau_{\text{dip}} + \frac{\tau_{\text{dip}}}{1 + (\omega_I - \omega_S)^2 \tau_{\text{dip}}^2} + \frac{3\tau_{\text{dip}}}{1 + \omega_I^2 \tau_{\text{dip}}^2} + \frac{6\tau_{\text{dip}}}{1 + \omega_S^2 \tau_{\text{dip}}^2} + \frac{6\tau_{\text{dip}}}{1 + (\omega_I + \omega_S)^2 \tau_{\text{dip}}^2} \right] \quad (c)$$

(3.211)

where $\omega_I = \gamma_I B_0$ and $\omega_S = \gamma_S B_0$ are the angular resonance frequencies of the two spin species. The correlation time τ_c has now been renamed by τ_{dip} indicating that this correlation time is valid for dipolar coupling for reasons to be discussed below. The above equations are often referred to as the *Bloembergen/Solomon equations*. More detailed monographs focusing on relaxation mechanisms by interactions to unlike dipoles are Refs. [11, 30].

Figure 3.22 shows the frequency dispersion of the longitudinal and transverse relaxation times of the I spins for two different correlation times. The particles bearing the I spins are assumed to be protons, and the S spins refer to unpaired electrons. In this case, the quotient of the gyromagnetic ratios and consequently of the resonance frequencies is $|\gamma_S/\gamma_I| = 661$. Two dispersion regimes appear at frequencies around the conditions $\omega_I \tau_{\text{dip}} = 1$ and $\omega_S \tau_{\text{dip}} = 1$. They are shifted relative to each other by the factor $|\gamma_S/\gamma_I| = 661$.

A typical example where this sort of relaxation dispersion applies is an aqueous solution of paramagnetic ions such as Cu^{2+} forming hydration complexes. The effective proton relaxation rates of the water are then composed of a like-dipole and an unlike-dipole contribution,

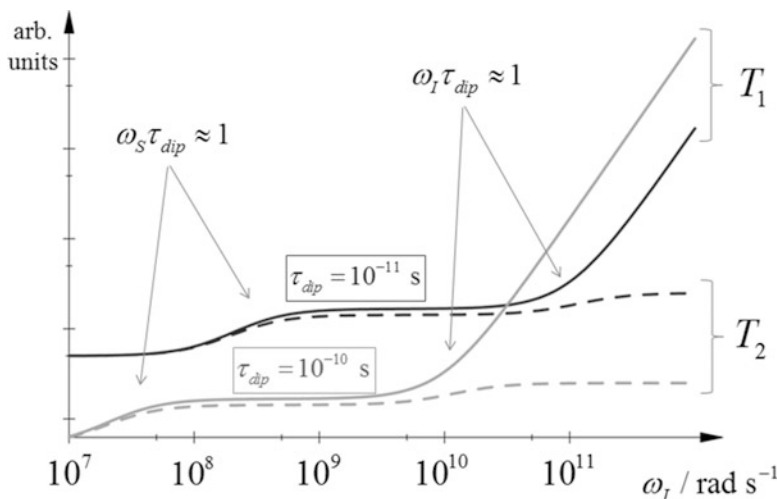


Fig. 3.22 Frequency dependences of T_1 and T_2 of I spins dipolar coupled to S -spins in thermal equilibrium. Two different rotational correlation times of dipolar coupling are assumed (see Eq. 3.211a, c). As I - and S -spin species, protons and unpaired electrons are assumed so that $\omega_S \approx 661\omega_I$

$$\frac{1}{T_{1,2}} = \frac{1}{T_{1,2}^{\text{like}}} + z \frac{n_S}{n_I} \frac{1}{T_{1,2}^{\text{unlike}}} \quad (3.212)$$

The first term on the right-hand side reflects the like-dipole contribution, that is, dipolar proton–proton coupling. In addition to this, the protons are temporally coupled to the S spins giving rise to the second term. “Temporally” means that fast exchange on the relaxation time scale is assumed between the hydration complexes and the bulk water (details of exchange phenomena will be treated in Sect. 3.4.3.2). The weighting factor before the second term, zn_S/n_I , is the probability of finding a given proton in a hydration complex. z (≈ 12) is the hydrogen coordination number of the ion hydration complex. n_I and n_S are the number densities of the hydrogen nuclei and the paramagnetic ions, respectively. $1/T_{1,2}^{\text{unlike}}$ represents the two-spin expressions (Eq. 3.211a or c).

There are three mechanisms causing fluctuations of the dipolar interaction between protons and unpaired electrons in an ion hydration complex: (1) rotational diffusion of the whole hydration complex with a rate given by Eq. (3.205), that is, $\tau_r^{-1} = 6D_r$; (2) exchange between the hydration shell and bulk water with a rate τ_{ex}^{-1} . The consequence of this exchange process is that the electron–proton distance fluctuates between the molecular dimension of the hydration complexes and far beyond such values. (3) S -spin fluctuation with a rate τ_S^{-1} due to S -spin–lattice relaxation. The origin of the latter mechanism can be a further, independent relaxation mechanism such as spin–orbit coupling which is selectively effective for electrons. Spin–lattice relaxation of the S spins therefore tends to be particularly fast, and dipolar coupling of the S spins to the I spins fluctuates correspondingly.

All three processes are of a purely Markovian nature, and they are entirely independent of each other. They can therefore be described by exponential correlation functions $\mathcal{G}_r(\tau)$, $\mathcal{G}_{\text{ex}}(\tau)$, and $\mathcal{G}_S(\tau)$, respectively. In terms of probability theory, the probability that *none* of the three independent events has yet occurred is the product of the three individual probabilities that the event did not yet happen. This is the probabilistic meaning of the normalized correlation function. The total correlation function of dipolar coupling between a hydration proton and the unpaired electron of the ion is hence given by the product of the three exponential functions

$$\mathcal{G}_{\text{dip}}(\tau) = \mathcal{G}_r(\tau)\mathcal{G}_{\text{ex}}(\tau)\mathcal{G}_S(\tau) = \exp\{-|\tau|/\tau_{\text{dip}}\} \quad (3.213)$$

where the effective correlation time is composed according to

$$\frac{1}{\tau_{\text{dip}}} = \frac{1}{\tau_r} + \frac{1}{\tau_{\text{ex}}} + \frac{1}{\tau_S} \quad (3.214)$$

Normally the limit $\tau_r \ll \tau_{\text{ex}}, \tau_S$ applies, so that $\tau_{\text{dip}} \approx \tau_r$.

If scalar coupling contributes as it is the case with aqueous solutions of Mn^{2+} ions or rare-earth contrast agents in NMR tomography, for instance, additional relaxation rate terms are relevant. For more details, the reader is referred to Refs. [11, 15, 30], or [31]. According to Eq. (3.146), these additional relaxation rates in combination with Lorentzian spectral densities are represented by

$$\begin{aligned} \left(\frac{1}{T_1}\right)_{\text{scal}} &= \frac{2}{3} \left(\frac{A}{\hbar}\right)^2 S(S+1) \frac{\tau_{\text{scal}}}{1 + (\omega_I - \omega_S)^2 \tau_{\text{scal}}^2} \\ \left(\frac{1}{T_2}\right)_{\text{scal}} &= \frac{1}{3} \left(\frac{A}{\hbar}\right)^2 S(S+1) \left[\tau_{\text{scal}} + \frac{\tau_{\text{scal}}}{1 + (\omega_I - \omega_S)^2 \tau_{\text{scal}}^2} \right] \end{aligned} \quad (3.215)$$

As suggested by the name, scalar coupling is insensitive to rotational diffusion. The correlation function of scalar coupling is thus reduced according to

$$\mathcal{G}_{\text{scal}}(\tau) = \mathcal{G}_{\text{ex}}(\tau)\mathcal{G}_S(\tau) = \exp\{-|\tau|/\tau_{\text{scal}}\} \quad (3.216)$$

with the effective correlation time

$$\frac{1}{\tau_{\text{scal}}} = \frac{1}{\tau_{\text{ex}}} + \frac{1}{\tau_S} \quad (3.217)$$

If $\tau_s \ll \tau_{\text{ex}}$, the scalar correlation time will be dominated by the electron spin–lattice relaxation time which in turn is a function of the electron Larmor frequency, that is, $\tau_{\text{scal}} \approx \tau_S(\omega_S)$. As a consequence, the frequency dispersion of the relaxation rates can adopt quite complicated features as outlined in Ref. [11], for example.

3.1.8 *Quadrupole Dips or Peaks by Cross Relaxation from Dipole to Quadrupole Nuclei*

A particular situation arises if the I spins are dipolar coupled to quadrupole nuclei with spins S . Typical quadrupolar nuclides are ^2H , ^{14}N , ^{35}Cl , or ^{37}Cl . The S spins are then subjected to an additional quadrupole interaction with the electric-field gradients in the molecules hosting the quadrupole nuclei. In the partial or complete absence of motional averaging, quadrupole interaction gives rise to *zero-field splitting* of the energy levels of the S spins. For $B_0 \rightarrow 0$, the electric-field gradient acts as quantization field (*low-field limit*). If the external magnetic flux density B_0 is increased to higher and higher values, a crossover to the *high-field limit* will take place, where the ordinary Zeeman splitting of the S -spin energies prevails, so that B_0 plays the role of the quantization field. In both limits, spin–lattice relaxation of the S spins will be fast due to strong perturbations either by Zeeman coupling in the low-field limit or by quadrupole interaction in the high-field regime. That is, the S spins will permanently remain in thermal equilibrium irrespective of the experimental protocol subjected to the I spins. This is another variant of the S -spin-equilibrium limit discussed above.

The magnitude of the gyromagnetic ratio of the dipolar I -spin nuclei is usually much larger than that of the quadrupolar S spin nuclei, $|\gamma_I| \gg |\gamma_S|$. The resonance of the I spins (determined by Zeeman interaction) will therefore cross the resonance(s) of the S spins at certain magnetic flux densities where the S spins are still in the low-field limit, that is, where the splitting is still governed by quadrupole interaction.

At these resonance crossings, the difference of the angular resonance frequencies vanishes: $\omega_I - \omega_S^{(i)} = 0$, where $\omega_S^{(i)}$ is any of the unaveraged low-field resonances of the quadrupole nuclei and $\omega_I = \gamma_I B_0$. The “flip-flop” (or zero-quantum) spectral density terms in Eqs. (3.211)

$$I(\omega_I - \omega_S^{(i)}) \propto \frac{\tau_{\text{dip}}}{1 + (\omega_I - \omega_S^{(i)})^2 \tau_{\text{dip}}^2} \quad (3.218)$$

accordingly adopt peaks centered at $\omega_I = \omega_S^{(i)}$. Likewise, the relaxation rates and times as a function of the magnetic flux density will display the so-called *quadrupole peaks* and *dips*, respectively. That is, the magnetization of the I -spin nuclei (usually protons) dipolar coupled to quadrupole nuclei is relaxed particularly efficiently when the resonance frequencies of the two nuclear species approach each other. Phenomena of this sort can be observed in solid, solid-like or ordered systems containing quadrupole nuclei dipolar coupled to abundant spin $\frac{1}{2}$ species. Typical applications have been reported in Refs. [32] (proteins and tissue) and [33, 34] (liquid crystals), for instance.

3.1.9 Translational Diffusion as Dipolar or Scalar Spin-Relaxation Mechanism

In Sect. 3.1.7, *rotational diffusion* of molecules, be it isotropic or not, was identified as the most efficient origin of dipolar fluctuations inducing spin relaxation. A further source of spin relaxation can arise from *translational diffusion* modulating the internuclear distance. Depending on the experimental conditions, the contribution by this fluctuation can be significant. Of course, single-spin interactions such as quadrupole and anisotropic–chemical-shift couplings are insensitive to translational diffusion by definition. However, dipolar and scalar couplings as two-spin interactions depend on the interparticle distance, and will hence be subject to molecular fluctuations.

In the case of scalar coupling between nuclei and unpaired electrons, distance fluctuations even tend to be the most important relaxation mechanism since this interaction is insensitive to rotational diffusion. Implicitly, we have already referred to this sort of fluctuation in the sense of *exchange* between the hydration and the bulk phases of water, that is, by a more or less abrupt variation of the distance between the interacting spins.

Dipolar couplings are less selective. They can be modulated by rotational as well as translational diffusion. The normally dominating contribution arises from intramolecular interaction characterized by practically fixed and relatively short inter-dipole distances. Spin relaxation due to dipolar coupling therefore tends to be governed by rotational diffusion at least at frequencies close to or higher than intramolecular fluctuation rates. However, there are two scenarios where a contribution by translational diffusion is expected to be significant [35–39].

Intermolecular dipole–dipole distances vary from values close to intramolecular dimensions up to lengths beyond perceptibility of the interaction. An illustration is shown in Fig. 3.23a. As a consequence of the long-distance scale, fluctuations of the intermolecular dipole–dipole vector by translational diffusion will be slow in the average relative to rotational diffusion. Significant contributions to spin relaxation will therefore arise only at relatively low frequencies as they are typically probed by field-cycling NMR relaxometry, rotating-frame relaxation, and transverse relaxation.

As the characteristic time for the translational-diffusion mechanism of spin relaxation, one can define the mean diffusion time over a distance of the order of the molecular diameter, τ_{trans} . The angular-frequency regime of interest is then $\omega_0 < \tau_{\text{trans}}^{-1}$. The reduced spectral density for fluctuations by translational diffusion is predicted for this case as [15, 35]

$$I(\omega_0) = I(0) - c\omega_0^{1/2} \quad (3.219)$$

where c is a constant. Equation (3.219) was verified in a field-cycling NMR relaxometry study of plastic cyclohexane, for example [36]. The contribution of the translational relaxation mechanism relative to the total spin–lattice relaxation rate was estimated to be 20% or less.

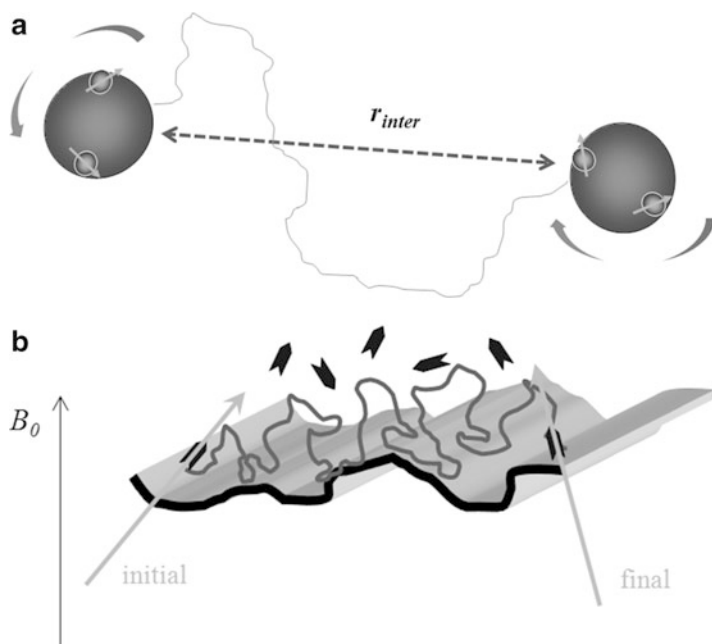


Fig. 3.23 Schematic illustration of direct and indirect influences of translational diffusion on spin relaxation. **(a)** Intermolecular distance fluctuations. **(b)** *Reorientation mediated by translational displacements* (RMTD) on a rough surface. Anisotropic molecules (represented by the *short arrow symbols*) adopt the local orientation of the surface when being adsorbed. Readsorption after desorption and translational migration to another surface site leads to reorientation of the molecule as specified by the *long arrows*. *Translations thus cause rotations*

The formalism behind Eq. (3.219) and the experimental data for plastic cyclohexane refer to *normal* diffusion in the Fickian sense. *Anomalous* displacements (see Sect. 2.5.2) as they are expected in polymer melts, for instance, can also be studied based on the same principle after appropriate modifications of the theory. Actually, such relaxation experiments can be used for measurements of translational diffusion on time and length scales not covered by the proper diffusometry techniques [37, 38].

The second relaxation mechanism based on translational diffusion is an indirect one. In this case, the origin of the fluctuations of dipolar interaction is primarily rotation (“reorientation”) of molecules, but the reorientation is the *result* of translational displacements. This in particular refers to adsorbate molecules diffusing along rough surfaces in a sequence of more or less cyclic desorption, bulk diffusion, and readsorption processes as illustrated in Fig. 3.23b. If this *reorientation mediated by translational displacements* (RMTD) occurs, it will dominate spin relaxation on a time scale longer than that of local motions. We will get back to this relaxation mechanism in the context of liquid crystals and fluids confined in porous media.

3.2 Field-Gradient NMR Diffusometry

3.2.1 The Principle

As already outlined in Sect. 2.5, diffusive displacements of molecules are characterized by the propagator $P(\mathbf{r}, t)$, that is, the probability density for a displacement vector $\mathbf{r}$ in a time interval t . On this basis, the mean square displacement $\langle r^2 \rangle$ and – in the case of normal diffusion – the diffusion coefficient D can be evaluated. In field-gradient NMR diffusometry [40–44], the molecular displacements are probed via the displacement of spins.

The detection of displacements requires *spatial encoding* of the spin positions. Experimentally, this is performed with the aid of strong gradients $\mathbf{g}$ superimposed to the quantizing field (i.e., $\mathbf{B}_0$ in the laboratory frame or $\mathbf{B}_1$ in the case of rotating-frame techniques [45]). Typical values of field gradients range from 0.1 to 100 T/m. The signals to be detected and evaluated are generally spin echoes. The most popular variants to be outlined below are based on *Hahn* and *stimulated echoes*. Other spin echo-phenomena based on multiple-quantum coherence transfer, rotating-frame techniques, for example, may be of interest as well but are less common. Let us explain the principle with the simplest refocusing phenomenon, namely, the *gradient reversal echo*, and return later to practically more significant diffusometry techniques.

Figure 3.24 shows a scheme illustrating the generation of gradient reversal echoes. The experiment starts with a 90° radio frequency pulse flipping the equilibrium magnetization $\mathbf{M}_0$ into the plane transverse to the external magnetic flux density $\mathbf{B}_0$. The transverse magnetization generated in this way precesses then with the angular Larmor frequency $\omega_0 = \gamma B_0$. In order to achieve spatial encoding of *local transverse magnetizations*,²¹ the homogeneity of the external magnetic field is intentionally deteriorated by superimposing a strong field gradient produced by auxiliary gradient coils. For practical reasons, the field gradients must be spatially constant, that is,

$$\mathbf{g} = \nabla B = \text{const} \quad (3.220)$$

The gradient direction is usually (but arbitrarily) chosen along the z -axis of the laboratory frame. The magnitude of the main magnetic flux density is thus given by

²¹ We use the term *local magnetization* in order to avoid the term *spin* which strictly speaking represents a quantum mechanical operator. The attribute *local* refers to a volume small enough to ensure a reasonably well defined Larmor frequency in an inhomogeneous field. In the case of a spatially constant gradient, this means that the extension of the volume in gradient direction is small relative to the helix pitch (see Fig. 3.24), that is, it is given by a thin slice perpendicular to the gradient. The quantity *magnetization* indicates that we are referring to an expectation value vector rather than to a vector operator.

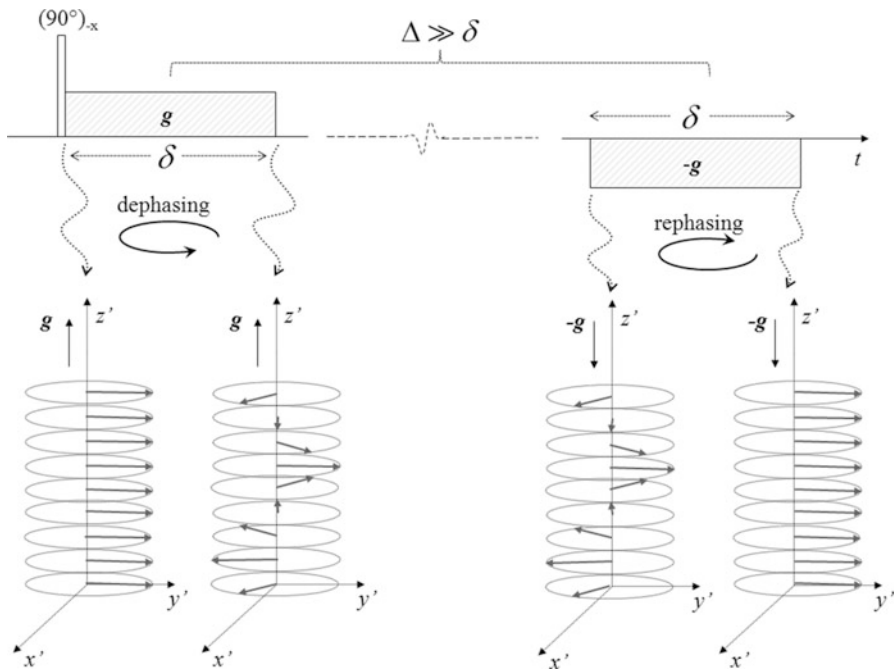


Fig. 3.24 Formation of a *gradient reversal echo* by inverting the polarity of the gradient pulse. The rotating frame of reference, x' , y' , z' , is to rotate with the *mean* Larmor frequency about the external magnetic-field B_0 . The 90° RF pulse with a phase corresponding to the $-x'$ direction of the rotating frame flips the magnetization into the transverse plane. Initially, all local magnetizations are aligned along the y' -axis. Owing to the field gradient, the Larmor frequency is distributed along the z' direction, and the local magnetizations will consequently be dephased at the end of the gradient pulse. The local magnetization is so-to-speak wound up in the form of a *helix* along the gradient direction. The pitch of the helix is equal to $2\pi/q$ where $q = \gamma g \delta$ is the so-called *wave number* and δ is the time the local magnetizations have precessed in the presence of the gradient g . Applying a second gradient pulse of the same length and magnitude, but inverted polarity, refocuses the local magnetizations. A gradient reversal spin echo is formed, and all local magnetizations are aligned along the y' direction again. However, if spins are subjected to translational diffusion and are displaced along the gradient direction during the pulse sequence, refocusing will be incomplete. The attenuation of the echo signal on these grounds is thus indicative for diffusion

$B(z) = B_0 + gz$. The magnitude of the local Larmor frequency is consequently a linear function of the position as well:

$$\omega = \omega(z) = \gamma B(z) = \omega_0 + \gamma gz \quad (3.221)$$

Since the induction-voltage signal recorded with the pickup RF coil is composed of all frequencies induced by Larmor precession, the superposition becomes destructive, and the FID drops away faster than expected by transverse relaxation. The crucial point is now that the dephasing of the precessing local magnetizations can be refocused by a second gradient pulse of identical length and magnitude

but inverted polarity. The helix is wound back again as illustrated in Fig. 3.24. The amplitude of the gradient reversal echo formed in this way would ideally be identical to the initial amplitude of the FID after the initial 90° RF pulse if *irreversible attenuation processes* would be absent. As such, two mutually independent phenomena must be considered, namely, translational diffusion of the spin-bearing particles and transverse relaxation.²²

In complex notation, the local transverse magnetization at a position z is

$$m(z) = M_x(z) + iM_y(z) \quad (3.222)$$

where “local” is meant in the sense defined in footnote 21. Assume now that the spin-bearing particle initially resides at the position z_0 . Referring to the pulse scheme shown in Fig. 3.24, the local transverse magnetization immediately after the first gradient pulse of duration δ , that is, at time $t \approx 0$, will be

$$m(z_0) = i|m(z_0)| \exp\{i\varphi(z_0, \delta)\} \quad (3.223)$$

where we assume for the moment that the gradient pulse is extremely short so that all irreversible effects by transverse relaxation and diffusion can be neglected in this particular interval. The right-hand side has been multiplied by the imaginary unit i in order to account for the particular phase of the excitation RF pulse assumed in Fig. 3.24. That is, immediately after the excitation pulse, the transverse magnetization is aligned along the y' -axis of the rotating frame. During the gradient pulse duration δ , the local precession phase shift at the particle position z_0 will be

$$\varphi(z_0, \delta) = \omega(z_0)\delta = \gamma g z_0 \delta = q z_0 \quad (3.224)$$

where $\omega(z_0) = \gamma g z_0$ is the local angular precession frequency offset acting on the spin at the position z_0 . Here we have introduced the so-called *wave number*

$$q = \gamma g \delta \quad (3.225)$$

for a spatially constant gradient g .

After an interval Δ , the second, again extremely short-gradient pulse is applied with opposite polarity. In the meantime, the spin-bearing particle may have diffused from the initial position z_0 to the new position z_Δ . The precession frequency offset experienced by the spins during the second gradient pulse will consequently be $\omega(z_\Delta) = -g\gamma z_\Delta$ leading to the additional local precession phase shift

$$\varphi(z_\Delta, \delta) = \omega(z_\Delta)\delta = -\gamma g z_\Delta \delta = -q z_\Delta \quad (3.226)$$

²² Here and in the following, the term “independent” implies that molecular diffusion is not affected by RF pulses, and transverse as well as longitudinal spin relaxation processes are insensitive to field gradients at strengths usual in field-gradient NMR diffusometry.

The minus sign indicates the reversal of the second gradient pulse.

The resulting local transverse magnetization at the time $t \approx \Delta$ will consequently be related to $m(z_0)$ by

$$\begin{aligned} m(z_\Delta) &= i|m(z_0)| \exp\{i\varphi_0(z, \delta) + i\varphi_\Delta(z, \delta)\} a_{\text{relax}}(\Delta) \\ &= i|m(z_0)| \exp\{iqz_0 - iqz_\Delta\} a_{\text{relax}}(\Delta) \end{aligned} \quad (3.227)$$

The factor $a_{\text{relax}}(\Delta)$ accounts for attenuation by transverse relaxation during the time interval Δ . Forming the average over all local positions within the sample provides

$$\left\langle \frac{m(z_\Delta)}{|m(z_0)|} \right\rangle = ia_{\text{relax}}(\Delta) \langle \exp\{iqz_0 - iqz_\Delta\} \rangle \quad (3.228)$$

as the total attenuation factor of the amplitude of the gradient reversal echo.

According to Eq. (3.220), the field gradient was assumed to be *constant* across the sample. This implies that the average over all sample positions is identical to an *ensemble average* over all spin-bearing particles. Using the relations²³ $qz_0 = \mathbf{q} \cdot \mathbf{R}_0$ and $qz_\Delta = \mathbf{q} \cdot \mathbf{R}_\Delta$, the right-hand side of Eq. (3.228) can be rewritten in terms of position vectors as

$$\left\langle \frac{m(z_\Delta)}{|m(z_0)|} \right\rangle = ia_{\text{relax}}(\Delta) \langle \exp\{i\mathbf{q} \cdot \mathbf{R}_0 - i\mathbf{q} \cdot \mathbf{R}_\Delta\} \rangle \quad (3.229)$$

$\mathbf{R}_0$ and $\mathbf{R}_\Delta$ specify the positions of the considered particle at times 0 and Δ , respectively. Since the attenuation factor by transverse relaxation, $a_{\text{relax}}(\Delta)$, is either known or can be kept constant in the course of an experiment, the primary quantity probed by field-gradient NMR diffusometry is the last term on the right-hand side of Eq. (3.229), namely, the *incoherent dynamic structure factor*

$$\mathcal{G}_{\text{inc}}(\Delta) = \langle \exp\{-i\mathbf{q} \cdot [\mathbf{R}_\Delta - \mathbf{R}_0]\} \rangle = \langle \exp\{-i\mathbf{q} \cdot [\mathbf{R}_0 - \mathbf{R}_\Delta]\} \rangle \quad (3.230)$$

already mentioned in Sect. 1.1.2.²⁴ The displacement by self-diffusion in the interval Δ is $\mathbf{r}_{\text{self}} = \mathbf{R}_\Delta - \mathbf{R}_0$. At this point, it may be noteworthy that the ensemble average straightforwardly results in

²³ Here we tacitly anticipate *isotropic* diffusion so that it does not matter in which (gradient) direction we probe displacements. In cases where *anisotropic* displacements are expected due to microstructural constraints, NMR field gradient techniques can be generalized for the acquisition of the so-called *diffusion tensor* (see e.g., Ref. [46]).

²⁴ Since the propagator, with the aid of which the average is to be evaluated, is an *even* function of the displacement, the sign of the exponent does not matter.

$$\mathcal{G}_{\text{inc}}(\Delta) = \exp\left\{-\frac{1}{6}q^2\langle r_{\text{self}}^2 \rangle\right\} \quad (3.231)$$

in case a *Gaussian propagator*

$$P(r_{\text{self}}, \Delta) = \frac{1}{(4\pi D\Delta)^{3/2}} \exp\left\{-\frac{r_{\text{self}}^2}{4Dt}\right\} \quad (3.232)$$

applies according to Eq. (2.168) and is used for the evaluation. If the diffusion process is moreover normal, the linear *Einstein relation* for the mean square displacement during the effective diffusion time $t = \Delta$ applies, $\langle r_{\text{self}}^2 \rangle = 6Dt$, where D is the self-diffusion coefficient. Equation (3.231) thus takes the form

$$\mathcal{G}_{\text{inc}}(t) = \exp\{-q^2Dt\} \quad (3.233)$$

In real experiments, the width of the gradient pulses may be not short enough to neglect diffusion during these pulses. This however requires merely a simple *rescaling of the effective diffusion time* as will be demonstrated below. We will furthermore show that the impractical reversal of the gradient pulses can be replaced by suitable RF pulses applied in the course of the coherence evolution. The effect is the same as in the case of gradient reversal echoes: Local magnetizations are first dephased and then, after some delay, refocused. The echoes of interest in these cases are in particular the *Hahn echo* and the *stimulated echo* (see Fig. 3.25). In this frame, we will distinguish *pulsed-gradient spin-echo* (PGSE) from *steady-gradient spin-echo* (SGSE) techniques.

3.2.2 Field-Gradient Diffusometry with Hahn Echo and Stimulated-Echo Pulse Sequences

Let us now apply the principle outlined above to the standard RF pulses for field-gradient NMR diffusometry. Following the usual nomenclature in the literature, the width of field-gradient pulses (or effective field-gradient sections) will be denoted by δ as before and as indicated in Fig. 3.25. The distance from middle to middle between these pulses or sections will be represented by the symbol Δ . The field-gradient g is assumed to be spatially constant within the samples and aligned along the z direction. The two independent processes attenuating echoes irreversibly, namely, relaxation and diffusion, are characterized by attenuation factors a_{relax} and a_{diff} , respectively (see footnote 22). The magnitude of the relative echo amplitude at the echo time t_E is thus composed according to

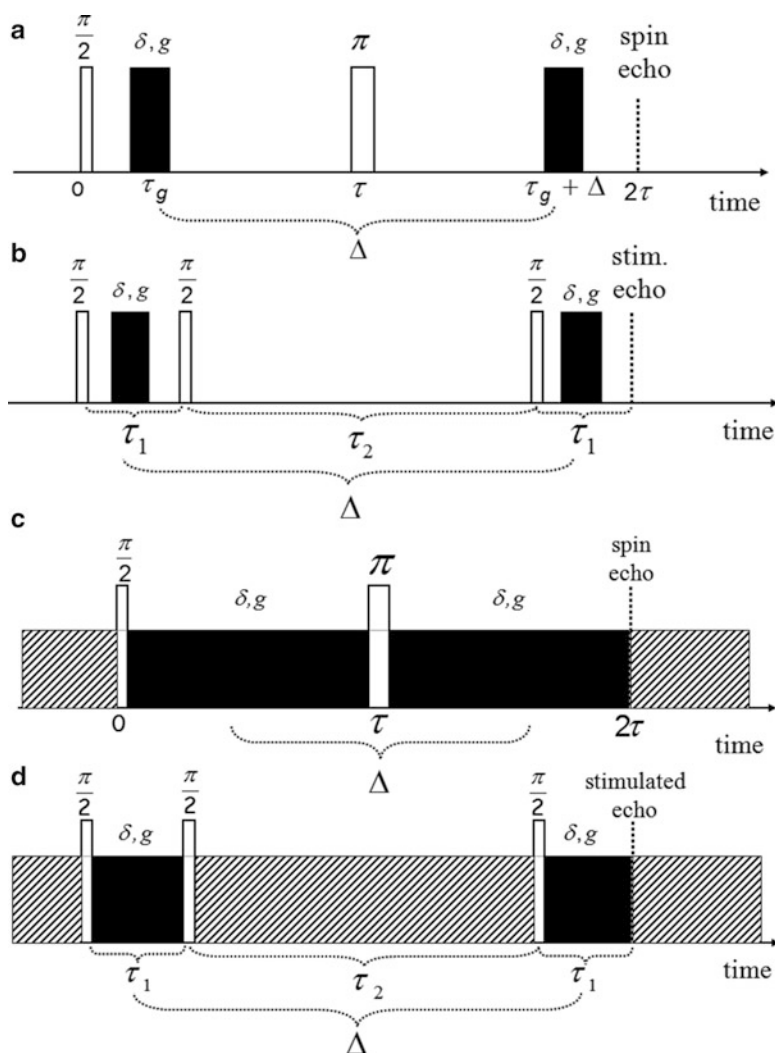


Fig. 3.25 Standard field-gradient and RF pulse sequences for PGSE and SGSE NMR diffusometry. Field-gradient pulses or intervals are represented by *black or hatched boxes*. δ is the width and g is the (spatially constant) magnitude of the magnetic-field gradient of the effective field-gradient pulses or sections. **(a)** Hahn spin-echo sequence consisting of a 90° and a 180° RF pulse with two identical field-gradient pulses in the intervals. **(b)** Stimulated-echo sequence consisting of three 90° RF pulses with identical field-gradient pulses in the first and third interval. **(c)** and **(d)** Hahn and stimulated spin-echo sequences, respectively, combined with steady field gradients. The *black boxes* represent the gradient sections relevant for echo attenuation by diffusion, whereas the *hatched areas* are irrelevant for diffusometry

$$a(t_E) \equiv \left\langle \frac{|m(t_E)|}{|m(0+)|} \right\rangle = a_{\text{relax}}(t_E) a_{\text{diff}}(t_E) \quad (3.234)$$

where $m(0+)$ is the complex transverse magnetization immediately after the first 90° RF pulse.

3.2.2.1 Hahn Spin Echo in the Short-Gradient Pulse Limit ($\delta \ll \Delta$)

The combined RF and field-gradient pulse sequence is shown in Fig. 3.25a. The short-gradient pulse limit, $\delta \ll \Delta$, ensures that diffusive displacements of the spin-bearing particles can be neglected during the gradient pulses. That is, all relevant displacements are assumed to take practically place in the central interval Δ . Coherence evolution in the presence of a field gradient winds the transverse magnetization up along the gradient direction in the form of a helix of pitch $2\pi/q$ as already illustrated in Fig. 3.24. The periodicity implied in this helix is characterized by the wave number

$$q = \gamma g \delta \quad (3.235)$$

Let us now refer to a selected spin ensemble defined by a location $z(\tau) \equiv z_1$ at the first gradient pulse and a position $z(\tau + \Delta) \equiv z_2$ at the second gradient pulse relative to the gradient direction. The respective precession phase shifts of this particular spin ensemble during the first and second gradient pulse will therefore be $\varphi_1 = qz_1$ and $\varphi_2 = qz_2$. Replacing the phase shifts φ_1 and φ_2 in Eq. (3.49) for the reduced density operator at the echo time $t_E = 2\tau$ by these expressions gives

$$\sigma(2\tau) = \frac{i}{\sqrt{2}} \left(I^{(-1)} e^{iq(z_1 - z_2)} + I^{(+1)} e^{-iq(z_1 - z_2)} \right) \quad (3.236)$$

The spherical spin operators $I^{(-1)}$ and $I^{(+1)}$ are defined in the context of Eq. (3.46).

The phase factors depend on the particle displacement $\zeta = z_1 - z_2$ which is distributed after the gradient pulse interval Δ according to the propagator $P(\zeta, \Delta)$. The ensemble average over all spin-bearing particles is given by

$$\begin{aligned} \langle \sigma(2\tau) \rangle &= \frac{i}{\sqrt{2}} \left(I^{(-1)} \langle e^{iq\zeta} \rangle + I^{(+1)} \langle e^{-iq\zeta} \rangle \right) \\ &= \frac{i}{\sqrt{2}} \left(I^{(-1)} + I^{(+1)} \right) \mathcal{G}_{\text{inc}}(\Delta) \end{aligned} \quad (3.237)$$

with the incoherent dynamic structure factor

$$\mathcal{G}_{\text{inc}}(\Delta) = \langle e^{\pm i q \zeta} \rangle = \int_{-\infty}^{+\infty} P(\zeta, \Delta) \exp\{\pm i q \zeta\} d\zeta = \int_{-\infty}^{+\infty} P(\zeta, \Delta) \cos\{q \zeta\} d\zeta \quad (3.238)$$

where we have anticipated that q is constant within the sample and that $P(\zeta, \Delta)$ is an even function of ζ . The imaginary part therefore cancels.

We thus have $a_{\text{diff}}(t_E) = \mathcal{G}_{\text{inc}}(\Delta)$ and, according to Eq. (3.51), $a_{\text{relax}}(t_E) = \exp\{-2\tau/T_2\}$. On this basis, the relative amplitude of the Hahn echo, Eq. (3.234), reads²⁵

$$a(2\tau, \Delta) \equiv \left\langle \frac{|m(2\tau)|}{|m(0+)|} \right\rangle = \exp\{-2\tau/T_2\} \mathcal{G}_{\text{inc}}(\Delta) \quad (3.239)$$

or

$$\begin{aligned} a(2\tau, \Delta) &= \exp\{-2\tau/T_2\} \exp\left\{-\frac{1}{6}q^2 \langle r_{\text{self}}^2 \rangle\right\} \\ &= \exp\{-2\tau/T_2\} \exp\{-q^2 D \Delta\} \end{aligned} \quad (3.240)$$

in terms of Eqs. (3.231) and (3.233) for a Gaussian propagator and normal, isotropic diffusion. The conversion step from the spin-operator level, Eq. (3.237), to the transverse magnetization $m(2\tau)$, that is, the expectation value rank, is performed with the aid of the trace operation we know already from the formalism in the context of Eq. (3.50).

3.2.2.2 Hahn Spin Echo for Long Gradient Pulses ($\delta \rightarrow \Delta/2$)

If the gradient pulse width δ in the scheme shown in Fig. 3.25a can no longer be neglected relative to the interval Δ , displacements during the gradient pulses need to be taken into account as well. For constant gradients along the z -axis, the phase shift during a pulse will be

$$\varphi_j(\delta) = \gamma g \int_0^\delta z_j(t') dt' \quad (3.241)$$

where the subscript $j = 1, 2$ indicates the first or the second gradient pulse. The phase factors $\langle \exp\{\pm i q \zeta\} \rangle$ in Eq. (3.237) must then be replaced by

$$\left\langle \exp\left\{\pm i \gamma g \left[\int_0^\delta z_1(t') dt' - \int_0^\delta z_2(t') dt' \right] \right\} \right\rangle \quad (3.242)$$

²⁵ Here we anticipate mono-exponential relaxation functions for simplicity. Note that in complex or very viscous systems, this is often not the case, especially as concerns transverse relaxation.

The analytical form of this attenuation function is best obtained by solving the *Bloch/Torrey equation* [47], that is, Bloch's equation for the complex transverse magnetization (see Eq. (3.11)) supplemented by a diffusion term according to

$$\frac{dm(z, t)}{dt} = -i\gamma g z m(z, t) - \frac{m(z, t)}{T_2} + D \frac{d^2}{dz^2} m(z, t) \quad (3.243)$$

Note that we are referring to a frame rotating with the *mean* Larmor frequency within the sample. Depending on the position z along the gradient direction, therefore a precession term, that is the first term on the right-hand side, arises relative to this rotating frame. The last term on the right-hand side corresponds to the one-dimensional version of the Fick's second law given in Eq. (2.167). Displacements in the other two dimensions do not matter since they are perpendicular to the field gradient.

The solution of the Bloch/Torrey equation for ordinary diffusion implies a Gaussian propagator and results in the diffusive attenuation factor

$$a_{\text{diff}}(\delta, \Delta) = \exp\{-q^2 D(\Delta - \delta/3)\} \quad (3.244)$$

so that the total echo-attenuation factor becomes

$$\begin{aligned} a(2\tau, \delta, \Delta) &\equiv \left\langle \frac{|m(2\tau)|}{|m(0+)|} \right\rangle \\ &= a_{\text{relax}}(t_E) a_{\text{diff}}(t_E) \exp\{-2\tau/T_2\} \exp\{-q^2 D(\Delta - \delta/3)\} \end{aligned} \quad (3.245)$$

(see footnote 25). That is, the incoherent dynamic structure factor $\mathcal{G}_{\text{inc}}(t_{\text{eff}})$ appears again but in rescaled form: The *effective* diffusion time is now

$$t_{\text{diff}} = \Delta - \frac{\delta}{3} \quad (3.246)$$

In the limit $\delta \ll \Delta$, the short-pulse limit Eq. (3.240) is reproduced.

3.2.2.3 Stimulated Echo

With this diffusometry variant, the attenuation factor $a_{\text{diff}}(\delta, \Delta)$ is the same as in the case of the Hahn echo although the pathway of the spin coherences is entirely different. The point is that diffusion of spin-bearing particles and coherence evolution are independent of each other (see footnote 22). As a consequence of the different coherence pathway, the attenuation factor by relaxation a_{relax} will also be modified. Let us first specify the pulse sequence and then detail the total echo-attenuation factor.

The stimulated echo can be produced with the aid of three 90° RF pulses as illustrated in Figs. 3.25b and 3.26a. The RF pulse intervals are τ_1 and τ_2 .

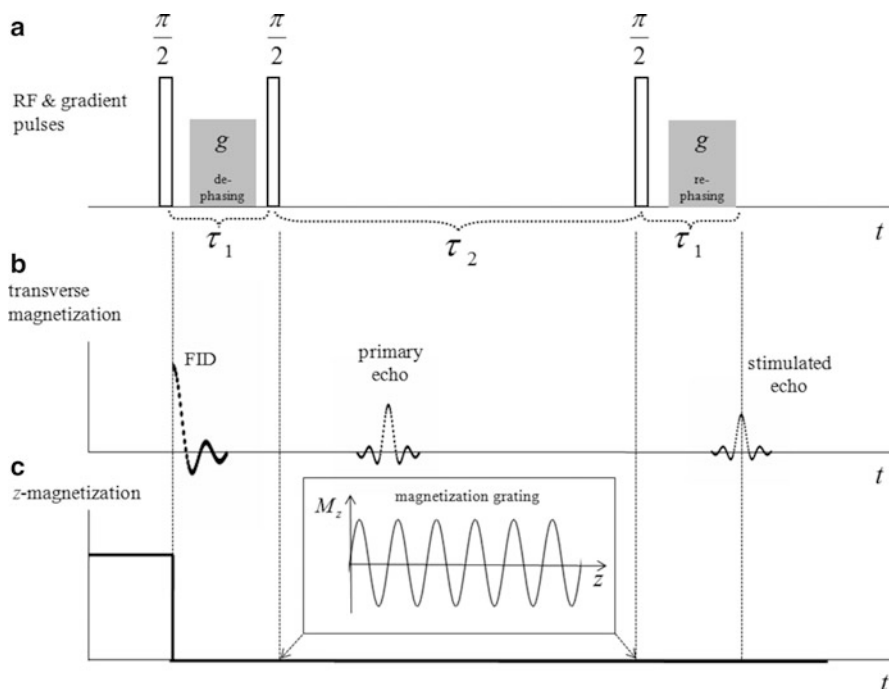


Fig. 3.26 Schematic representation of the formation of a *magnetization grating* (or *grid*) by the stimulated-echo sequence in combination with field gradients (see Fig. 3.25b, d). (a) RF and field gradient pulses. (b) *Average* transverse magnetization, that is, resultant of the x' and y' components in the rotating frame, as a function of time. (c) *Average* z component of the magnetization. The inset shows the distribution of the *local* magnetization along the direction of the gradient during the second RF pulse interval assuming a gradient aligned along the z -axis. The “wave” length of the grating is $\lambda = 2\pi/q$, where the wave number is given by $q = \gamma g \delta$. δ is the width and g is the (spatially constant) magnitude of the magnetic-field-gradient pulses. γ is the gyromagnetic ratio of the resonant spins. The magnetization grid is attenuated by spin–lattice relaxation and leveled by translational diffusion (not shown)

The maximum of the stimulated echo is achieved after a time $2\tau_1 + \tau_2$. A formal treatment of the pulse sequence can be found in Ref. [1], for example. The field-gradient pulses are placed in the first interval and after the third RF pulse prior to the stimulated echo. Diffusometry on this basis is particularly favorable if $\tau_1 \ll T_2 \ll T_1 > \tau_2$ since the effective diffusion time scale of the technique is restricted by T_1 rather than by T_2 . In viscous media, the values of both the transverse relaxation time and the diffusion coefficient tend to be very low so that an extension of the diffusion time scale is desirable [41]. This obvious advantage often overcompensates the signal loss by a factor $\frac{1}{2}$ relative to the Hahn echo.

In the first RF pulse interval, the spin coherences excited by the first 90° RF pulse evolve under the action of the magnetic-field gradient as in the case of the Hahn pulse sequence. The local magnetizations fan out in the transverse plane of a frame rotating with the mean Larmor frequency about the external magnetic flux density $\mathbf{B}_0$. Note that the term “local” is again used in the sense of footnote 21. The consequence will be the formation of a “helix” as discussed above.

The second 90° RF pulse “stores” half of the local magnetizations in z direction in spatially modulated form. That is, a so-called *magnetization grid* or *grating* is formed. Note that the *mean* magnetization (represented by the solid line in Fig. 3.26c) vanishes in the τ_2 interval, whereas the *local* magnetization is modulated along the z -axis as shown in the inset in Fig. 3.26c. The magnetization grating can be considered as the projection of the helix on a plane containing the z -axis. It has therefore a sinusoidal shape with a “wave” length

$$\lambda = \frac{2\pi}{q} \quad (3.247)$$

where $q = \gamma g \delta$ as before.

The other half of the local magnetizations remain in the transverse plane and will be refocused as the primary echo at the time $2\tau_1$ (see Fig. 3.26b). The primary echo is of minor interest for the present application and can usually be ignored in stimulated-echo diffusometry experiments. According to the short T_2 values we anticipate here, it will normally decay to zero in a time short relative to τ_2 .

The third 90° RF pulse finally converts the local z magnetizations surviving the τ_2 interval into transverse magnetizations which evolve then toward the stimulated echo at the time $t = 2\tau_1 + \tau_2$. Translational diffusion along the gradient direction tends to level the grating during the τ_2 interval more or less, so that the amplitude of the stimulated echo originating from the grating will be attenuated.²⁶

The coherence pathway from the first RF pulse interval to the stimulated echo consists of the sequence *transverse magnetization – longitudinal magnetization – transverse magnetization* for the three intervals $\tau_1 \cdots \tau_2 \cdots \tau_1$. The attenuation factor due to relaxation will consequently be

$$a_{\text{relax}} = \exp\left\{-\frac{2\tau_1}{T_2}\right\} \exp\left\{-\frac{\tau_2}{T_1}\right\} \quad (3.248)$$

(see footnote 25). Combining this with Eq. (3.244) valid for Gaussian propagators gives the total attenuation factor for the stimulated echo:

$$\begin{aligned} a(\tau_1, \tau_2, \delta, \Delta) &\equiv \left\langle \frac{|m(2\tau_1 + \tau_2)|}{|m(\tau_1 + \tau_2)|} \right\rangle = a_{\text{relax}} a_{\text{diff}} \\ &= \exp\left\{-\frac{2\tau_1}{T_2}\right\} \exp\left\{-\frac{\tau_2}{T_1}\right\} \exp\{-q^2 D(\Delta - \delta/3)\} \end{aligned} \quad (3.249)$$

²⁶ This leveling of the spatial modulation of excited states is interestingly entirely analogous to the optical *forced Rayleigh scattering* technique described in Ref. [48]. This is however to be rated as an *invasive* technique which would be beyond the scope of the present overview. The principle is that dye labels are chemically implemented in the sample. The modulation effect is then reached by periodic photobleaching of the dye labels by laser light.

with $q = \gamma g \delta$. The complex transverse magnetization immediately after the third RF pulse is designated by $m(\tau_1 + \tau_2 +)$. All time intervals are defined in Fig. 3.25b. The factor to be evaluated in diffusometry experiments is again the incoherent dynamic structure factor

$$\mathcal{G}_{\text{inc}}(t_{\text{eff}}) = \exp\{-q^2 D t_{\text{eff}}\} \quad (3.250)$$

for the effective diffusion time $t_{\text{eff}} = \Delta - \delta/3$ and a Gaussian propagator.

3.2.2.4 Spin Echoes and Steady B_0 Gradients

The efficiency of spatial encoding by field gradients depends on the wave number produced by the gradient pulses: $q = \gamma g \delta$. Pictorially, the “area” $g\delta$ of the gradient pulses should be as large as possible. To generate short and intense gradient pulses with extremely short rise and decay times is technically difficult and, even worse, is susceptible to motional artifacts due to pulsed magnetic forces on the gradient coil system and the (usually diamagnetic) sample. Eddy currents and mechanical ringing may also be a problem due to fast switching of gradients. For very short transverse relaxation times (which tend to be connected with slow translational diffusion), it may therefore be advisable to use *steady gradients* instead of the pulsed variants: Gradient switching is then avoided, and the gradient encoding efficiency in the coherence free-evolution intervals is optimal. Strong steady and stable gradients up to 10^2 T/m are readily available in the fringe field of superconducting magnets, for example, as illustrated in Fig. 3.27 [49].

Figure 3.25c shows the steady-gradient version for the Hahn echo method. The pulsed-gradient parameters δ and Δ defined in Fig. 3.25a now become identical and are equal to the RF pulse spacing,

$$\delta = \Delta = \tau \quad (3.251)$$

Equation (3.244) thus becomes

$$a_{\text{diff}}(\tau) = \exp\left\{-\frac{2}{3}q^2 D \tau\right\} = \mathcal{G}_{\text{inc}}(t_{\text{eff}}) \quad (3.252)$$

where we have anticipated a Gaussian propagator as before. The incoherent dynamic structure factor $\mathcal{G}_{\text{inc}}(t_{\text{eff}})$ is consequently rescaled by the effective diffusion time $t_{\text{diff}} = 2\tau/3$

The steady-gradient variant for the stimulated echo shown in Fig. 3.25d can be treated analogously. In this case, the pulsed-gradient parameters turn into $\delta = \tau_1$ and $\Delta = \tau_1 + \tau_2$ so that the diffusive attenuation factor for Gaussian propagators becomes

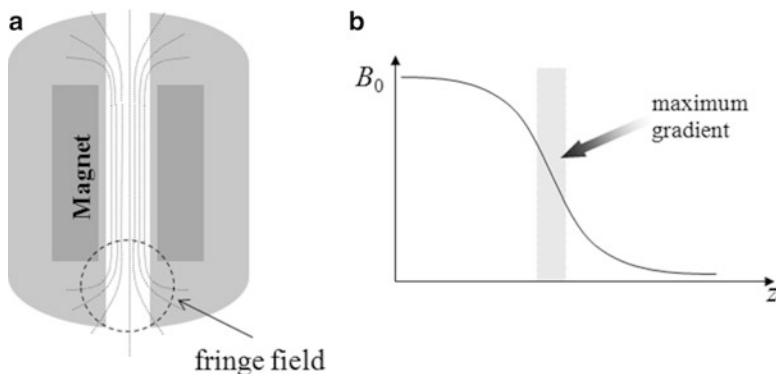


Fig. 3.27 (a) Schematic representation of the fringe field of a superconducting laboratory magnet. The sample and the probehead are placed in the area indicated by the *circle*. (b) Distribution of the magnetic flux density along the magnet axis. The field variation in a thin slice in the middle of the fringe-field decay is practically linear and therefore suitable for field-gradient NMR diffusometry. For a typical 9.4-T magnet with an 89 mm room temperature bore, the maximum gradient is 60 T/m at 4.7 T (corresponding to 200 MHz proton resonance frequency)

$$a_{\text{diff}}(\tau_1, \tau_2) = \exp \left\{ -q^2 D \left(\frac{2\tau_1}{3} + \tau_2 \right) \right\} = G_{\text{inc}}(t_{\text{eff}}) \quad (3.253)$$

where $q = \gamma g \tau_1$. In this case, the effective diffusion time is $t_{\text{eff}} = \tau_2 + 2\tau_1/3$.

3.2.2.5 Some Remarks on Practical Experimental Protocols

According to the above results, the incoherent dynamic structure factor can be probed by varying either the field gradients or the effective diffusion time. In order to discriminate diffusional and relaxational attenuation factors experimentally, it is however more favorable to keep all pulse intervals constant while the gradient strength g or the gradient pulse length δ is varied. The only source of signal attenuation in a series of PGSE signal acquisitions with incremented gradient pulses is then translational diffusion. A further advantage is that the diffusion time t_{eff} has a well-defined value in this case, and can be varied in subsequent experiments.

With SGSE diffusometry, it may be difficult to vary the gradient, especially if the fringe-field gradient of laboratory magnets is employed. That is, the attenuation factor by relaxation, a_{relax} , must either be determined separately, or its influence must be compensated in self-compensatory versions of the experiment. The former solution of the problem requires a second series of measurements in the absence of field gradients but otherwise under identical conditions (same RF pulse sequence, same frequency, etc.). The diffusive attenuation factor a_{diff} will then be equal to one, and a_{relax} can be evaluated for the correction of the data acquired in the presence of a gradient.

On the other hand, there are a number of self-compensatory protocols for stimulated-echo sequences regarding relaxation losses. In the simplest case, both

the stimulated and primary echo are recorded as indicated in Fig. 3.26b. For obvious reasons, the primary echo is subject to the reduced relaxational attenuation factor $\exp\{-2\tau_1/T_2\}$, whereas the stimulated echo is modified by $\exp\{-2\tau_1/T_2\} \exp\{-\tau_2/T_1\}$ as mentioned above. Forming the ratio of the stimulated and primary echo signals thus eliminates the transverse relaxation factor $\exp\{-2\tau_1/T_2\}$ while the remaining longitudinal counterpart $\exp\{-\tau_2/T_1\}$ can be kept constant by using fixed τ_2 intervals. In this way, the interval τ_1 can be varied for the determination of the diffusive attenuation factor a_{diff} given in Eq. (3.253). If moreover $\tau_2 \gg \tau_1$, a well-defined diffusion time $t_{\text{eff}} \approx \tau_2$ will be warranted at the same time [50]. A review of further techniques for the same purpose can be found in Ref. [51].

In samples with a heterogeneous distribution of the magnetic susceptibility, internal field gradients can arise that may interfere with field-gradient diffusometry protocols. Examples are porous media subjected to very high magnetic fields. Internal field gradients reveal themselves by faster dephasing of spin coherences than expected from the inhomogeneities intrinsic to the magnet. If the external field gradients cannot be made large enough to dominate these internal inhomogeneities, special RF pulse sequences or methods based on gradients of the RF amplitude can be used as a remedy. The MAGROFI technique will be described in Sect. 3.3.6 as an efficient example of the latter sort.

At this point, it should be noted that a second spin-displacement mechanism independent of molecular transport exists. This is the *spin diffusion* process in the narrower sense. It is based on immaterial spin migration by flip-flop spin transitions. Such transitions are produced by the operator terms containing products such as I^+S^- and I^-S^+ (see the analysis of dipolar coupling of like spins in Eq. (3.91)). In this way, “spin” in the sense of angular momentum is transported from nucleus to nucleus. The corresponding transport rate is however extremely small. For example, in Ref. [52], an immaterial spin diffusion coefficient of $10^{-15} \text{ m}^2/\text{s}$ was identified in polymer melts. The conclusion is that the smallest *molecular* diffusion coefficients that can be determined with the aid of field-gradient NMR diffusometry are physically limited by *immaterial* spin diffusion to values of the order $D > 10^{-15} \text{ m}^2/\text{s}$. We will get back to this problem in Sect. 5.4.6.7 in the frame of the discussion of the tube/reptation model of polymer dynamics.

3.2.3 Spin Echo Attenuation by Hydrodynamic Dispersion

Hydrodynamic dispersion is a phenomenon combining laminar flow and self-diffusion [53]. That is, displacements by *coherent* and *incoherent* transport are superimposed.²⁷ With flow, there is some correlation among the velocity vectors of the particles in a certain volume element. This is in contrast to self-diffusion where

²⁷ Coherent transport by flow is normally produced by pressure gradients. Another possibility is to exploit electroosmosis as demonstrated in Ref. [54] (see Sect. 3.3.5.1).

these vectors are randomized with respect to magnitude and/or direction. An application of this phenomenon will be described in Sect. 4.9.3.

Molecular displacements relative to a field gradient lead to precession phase shifts irrespective of whether the displacements are coherent or not. Nevertheless, an experimental distinction is possible by eliminating all precession phase shifts due to velocities that are *constant* in the measuring interval. Phase shifts produced by constant or even time-dependent accelerations can in principle also be compensated for, but are usually of minor importance [1]. The trick is to use gradient sequels $g(t)$ with vanishing zeroth, first, and, possibly, higher moments. The moments refer to the expansion of the particle trajectory into terms reflecting static position, constant velocity, constant acceleration, linear time-dependent acceleration, and so on. For example, if all z gradient pulses applied during the experimental free-evolution time t are adjusted in such a way that

$$\int_0^t g(t')(z + v_z t' + \dots) dt' = 0, \quad (3.254)$$

all precession phase shifts will vanish at the end of the interval. z is the initial position of the particle, and v_z is the initial velocity component along the z -axis. The zeroth moment (first sum term) compensates phase shifts of spins remaining at rest during t , the first moment (second sum term) accounts for phase shifts particles with constant velocities v_z experience, and so on. What remains within this approximation is phase-shift neither due to static spins nor arising from spins with constant velocities. That is, echo attenuation is indicative for motions incoherent *on this particular time scale*.

Figure 3.28a shows the principle of an RF and field-gradient pulse sequence for measurements of spin-echo attenuation by incoherent displacements in the presence of coherent contributions. For the analytical treatment, the short-gradient pulse limit is anticipated, that is, $\delta \ll \Delta_a, \Delta_b, \Delta_c$, where $\Delta_a, \Delta_b, \Delta_c$ are the gradient pulse intervals as defined in the figure. Apart from the gradient pulses, no inhomogeneity or spin coupling is assumed during the free-evolution intervals.

Let us now resume the reduced density operator treatment of pulse sequences started in Sect. 3.1.4.6. For the reduced density operator after the first gradient pulse, that is, in the time interval between $t = \tau_g +$ and $t = \tau_g + \Delta_a -$, the expression given in Eq. (3.47) can be taken:

$$\sigma(\tau_g +) = \sigma(\tau_g + \Delta_a -) = \frac{i}{\sqrt{2}} \left[I^{(+1)} e^{+i\varphi_1} + I^{(-1)} e^{-i\varphi_1} \right] \quad (3.255)$$

where $\varphi_1 = qz_1$, $q = \gamma g \delta$ and z_1 are the positions of the spin-bearing particle along the z -axis during the first gradient pulse. After the second gradient pulse, this expression becomes

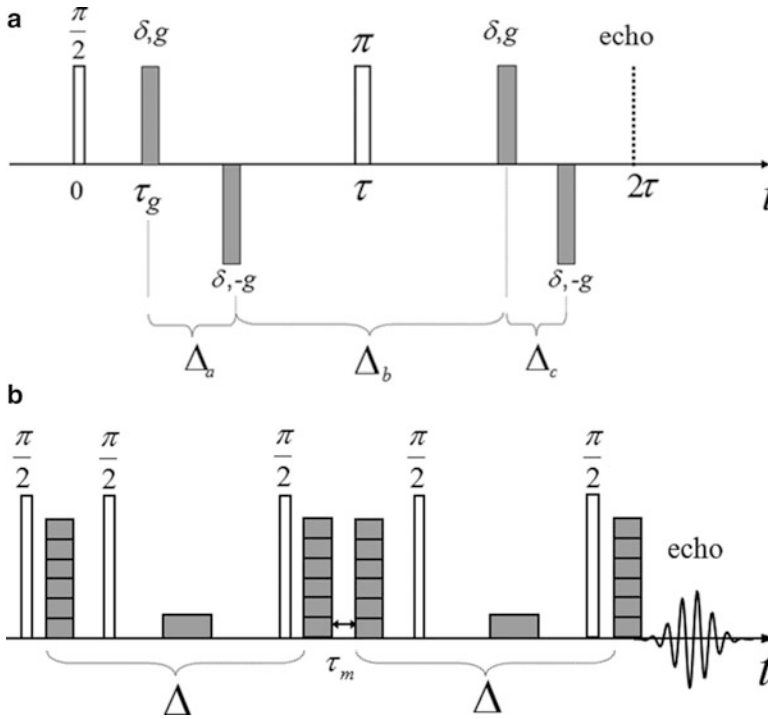


Fig. 3.28 Spin-echo RF pulse schemes are combined with magnetic-field-gradient pulses for diffusion or hydrodynamic-dispersion measurements while coherent-flow phase shifts are compensated on the time scale of the experiment. The gradient pulses are represented by gray-shaded boxes. (a) Bipolar gradient pulse sequence as treated in the text. (b) Version with unipolar gradient pulses [55] (Reproduced from Ref. [54] with kind permission of © Wiley-VCH 2009)

$$\sigma(\tau_g + \Delta_a +) = \sigma(\tau -) = \frac{i}{\sqrt{2}} \left[I^{(+1)} e^{+i\varphi_1} e^{-i\varphi_2} + I^{(-1)} e^{-i\varphi_1} e^{+i\varphi_2} \right] \quad (3.256)$$

The corresponding phase-shift angle is $\varphi_2 = qz_2$. z_2 is the position the particle has reached at the time of the second gradient pulse. The π pulse converts this into

$$\sigma(\tau +) = \sigma(\tau_g + \Delta_a + \Delta_b -) = \frac{i}{\sqrt{2}} \left[I^{(-1)} e^{+i\varphi_1} e^{-i\varphi_2} + I^{(+1)} e^{-i\varphi_1} e^{+i\varphi_2} \right] \quad (3.257)$$

The effect of the third gradient pulse is

$$\begin{aligned} \sigma(\tau_g + \Delta_a + \Delta_b +) &= \sigma(\tau_g + \Delta_a + \Delta_b + \Delta_c -) \\ &= \frac{i}{\sqrt{2}} \left[I^{(-1)} e^{+i\varphi_1} e^{-i\varphi_2} e^{-i\varphi_3} + I^{(+1)} e^{-i\varphi_1} e^{+i\varphi_2} e^{+i\varphi_3} \right] \end{aligned} \quad (3.258)$$

with $\varphi_3 = qz_3$. The position the particle has adopted when the third gradient pulse is applied is z_3 . Finally, after the fourth gradient pulse, the reduced density operator reads

$$\begin{aligned}\sigma(\tau_g + \Delta_a + \Delta_b + \Delta_c) &= \sigma(2\tau) \\ &= \frac{i}{\sqrt{2}} \left[I^{(-1)} e^{+i\varphi_1} e^{-i\varphi_2} e^{-i\varphi_3} e^{+i\varphi_4} + I^{(+1)} e^{-i\varphi_1} e^{+i\varphi_2} e^{+i\varphi_3} e^{-i\varphi_4} \right]\end{aligned}\quad (3.259)$$

In this case, the additional phase-shift angle is $\varphi_4 = qz_4$. z_4 is the position where the particle resides during the fourth gradient pulse.

The total phase-shift angles at the echo time $t_E = 2\tau$ implied in Eq. (3.259) are

$$\pm \varphi = \pm(\varphi_1 - \varphi_2 - \varphi_3 + \varphi_4) = \pm q[(z_1 - z_2) - (z_3 - z_4)] \quad (3.260)$$

$z_1 - z_2 \equiv \zeta_a$ and $z_3 - z_4 \equiv \zeta_c$ are the particle displacements along the z -axis in the gradient pulse intervals Δ_a and Δ_c , respectively. Actually, these intervals are adjusted to be equal, $\Delta_a = \Delta_c$. The reduced density operator at the echo time thus reads

$$\sigma(2\tau) = \frac{i}{\sqrt{2}} \left[I^{(-1)} e^{+iq(\zeta_a - \zeta_c)} + I^{(+1)} e^{-iq(\zeta_a - \zeta_c)} \right] \quad (3.261)$$

Completely coherent flow means that there is no random motion and that the z component of the velocity is constant, $v_z = \text{const}$. The displacements in the intervals $\Delta_a = \Delta_c$ are then equal, $\zeta_a = \zeta_c$. As a consequence, no phase shift remains at the echo time according to Eq. (3.260). There is no echo attenuation by coherent flow.

On the other hand, if the motion is completely incoherent as expected in the limit of pure self-diffusion, ζ_a and ζ_c will take uncorrelated values. Forming the ensemble average of the phase factors in Eq. (3.259) gives the diffusive attenuation factor

$$\begin{aligned}a_{\text{diff}} &= \left\langle e^{\pm iq(\zeta_a - \zeta_c)} \right\rangle = \left\langle e^{\pm iq\zeta_a} \right\rangle \left\langle e^{\mp iq\zeta_c} \right\rangle = \exp\{-2q^2 D \Delta_a\} \\ &= \exp\left\{-\frac{1}{3} q^2 \langle r^2 \rangle_{\Delta_a \text{ or } \Delta_c}\right\}\end{aligned}\quad (3.262)$$

where a Gaussian propagator has been assumed.

In the intermediate case, that is, for hydrodynamic dispersion in the proper sense, the correlation between the displacements ζ_a and ζ_c in the first and third gradient pulse intervals will be more or less strong. In this case, hydrodynamic dispersion comes into play with the echo-attenuation factor

$$a_{\text{disp}} = \left\langle e^{\pm iq(\zeta_a - \zeta_c)} \right\rangle \equiv \left\langle e^{\pm iq\zeta_{\text{eff}}} \right\rangle \quad (3.263)$$

$\zeta_{\text{eff}} \equiv \zeta_a - \zeta_c$ is the effective displacement. Anticipating a Gaussian distribution again, Eq. (3.263) can be evaluated for the following two limits:

$$a_{\text{disp}} = \begin{cases} \exp\{-q^2 D_{\text{disp}} \Delta_b\} & \text{for } \Delta_b \gg \Delta_a = \Delta_c \\ \exp\{-q^2 D_{\text{disp}} \Delta_a\} & \text{for } \Delta_b \ll \Delta_a = \Delta_c \end{cases} \quad (3.264)$$

In both cases, the dispersion coefficient D_{disp} is a function of the relevant and dominating displacement intervals, that is, Δ_b or Δ_a . This dependence reflects the loss of flow coherence with increasing displacement time.

If the distribution of the effective displacement ζ_{eff} is not a Gaussian function, an expansion of Eq. (3.263) can be performed. In the low wave-number limit, $q^2 \langle \zeta_{\text{eff}}^2 \rangle \ll 1$, the dispersion coefficient can be deduced from experimental data according to

$$a_{\text{disp}} = \langle e^{\pm i q \zeta_{\text{eff}}} \rangle \approx 1 - \frac{1}{2} q^2 \langle \zeta_{\text{eff}}^2 \rangle = \begin{cases} 1 - q^2 D_{\text{disp}} \Delta_b & \text{for } \Delta_b \gg \Delta_a = \Delta_c \\ 1 - q^2 D_{\text{disp}} \Delta_a & \text{for } \Delta_b \ll \Delta_a = \Delta_c \end{cases} \quad (3.265)$$

Under practical conditions, the generation of bipolar gradient pulses as they are proposed in the scheme Fig. 3.28a may be difficult. It is then more favorable to modify the pulse sequence according to Fig. 3.28b. The compensation effect on coherent flow is the same. Applications can be found in Refs. [54–56]. A combination with NMR microscopy for mapping purposes as it will be considered in the following section was reported in Ref. [57].

3.3 NMR Microscopy-Based Mapping Techniques

Magnetic resonance microscopy and *imaging* are rather unspecific terms usually associated with rendering morphologies of objects or organisms. The image contrasts reflect the effect of a combination of different experimental and material parameters such as echo and repetition times, relaxation times, spin density etc. This is certainly not what one is primarily aiming at when dealing with soft-matter dynamics. On the other hand, there is an entirely different application potential of magnetic resonance microscopy that is less well known. Variants of the RF and field-gradient pulse sequences used for magnetic resonance imaging permit quantitative *mapping* of various dynamic parameters with spatial resolutions as low as 20...50 μm in samples of a few millimeters diameter. In the following, a number of NMR methods for probing spatially resolved transport phenomena will be described. These include *spin-density mapping* as a tool for long-time,

long-distance isotopic interdiffusion studies, *velocity and acceleration mapping* in flowing liquids, and mapping of *hydrodynamic-dispersion* parameters.

3.3.1 Spin-Density Diffusometry

The principle of spin-density diffusometry corresponds to classical tracer methods: The sample is subdivided into two moieties among which interdiffusion of two different isotopes of the same element takes place. Initially the isotopes are separated in the two compartments. Typical examples of nuclear species suited for NMR studies are deuterated versus undeuterated materials or substances enriched with ^{13}C on the one hand versus the material with ^{13}C in natural abundance (which is roughly 1%). At time zero, the two moieties of the system are brought into contact with each other so that interdiffusion of the labeled compounds is initiated. The concentration profiles, that is, the profiles of the local spin density, $\rho(\mathbf{r})$, of the diffusing species are then recorded with the aid of magnetic resonance microscopy of the resonant isotope as a function of the diffusion time.

3.3.1.1 The Basis of Magnetic-Resonance Microscopy

Figure 3.29a and b show the RF and field-gradient pulse schemes for two- and three-dimensional magnetic resonance microscopy, respectively. An ordinary Hahn spin-echo RF pulse sequence is combined with a number of pulses of spatially constant field gradients

$$\mathbf{g} = \nabla B \quad (3.266)$$

serving the encoding of the spatial information. The gradient modifies the external magnetic flux density according to

$$\mathbf{B}(\mathbf{r}) \approx \begin{pmatrix} 0 \\ 0 \\ B(\mathbf{r}) \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ B_0 + \mathbf{g} \cdot \mathbf{r} \end{pmatrix} \quad (3.267)$$

Note that in terms of absolute values, the field changes caused by practical field gradients are so small that inclinations of the field vectors against the z direction can safely be neglected. The transformation to the frame rotating with the angular-frequency $\omega_0 = \gamma B_0$ gives the *effective* magnetic flux density

$$\mathbf{B}'(\mathbf{r}) = \begin{pmatrix} 0 \\ 0 \\ \mathbf{g} \cdot \mathbf{r} \end{pmatrix} \quad (3.268)$$

(compare the discussion in the context of the rotating-frame Bloch equations in Sect. 3.1.2).

In the presence of (spatially constant) field gradients, the Larmor frequency relative to the rotating frame becomes a (linear) function of the position, $\omega = \omega(\mathbf{r})$. The evolution of spin coherences relative to this reference frame consequently leads to position-dependent precession phase shifts, $\varphi = \varphi(\mathbf{r})$. The rotating-frame NMR signals per unit volume are thus a superposition of position-dependent Fourier components

$$s(\mathbf{r}, t) = s_0(\mathbf{r}) \sin[\omega(\mathbf{r})t + \varphi(\mathbf{r})] \quad (3.269)$$

where we ignore relaxation decays for the moment and for simplicity.

In this function, there are three independent parameters containing spatial information: the *local* amplitude $s_0(\mathbf{r})$, the *local* precession frequency offset $\omega(\mathbf{r})$, and the *local* precession phase-shift $\varphi(\mathbf{r})$. The amplitude is proportional to the local spin density, $s_0(\mathbf{r}) \propto \rho(\mathbf{r})$. This is the quantity to be mapped in the simplest case. The other two parameters serve the localization of the amplitude values by *phase* and *frequency encoding*.

The NMR signal to be recorded consists of contributions from all positions within the sample:

$$S(t) = \iiint_{\text{sample}} s(\mathbf{r}, t) d\mathbf{r} \quad (3.270)$$

This superposition of the functions Eq. (3.269) can be decoded by Fourier transformations with respect to the angular precession frequencies ω and the precession phase-shift φ relative to the rotating frame.

Frequency encoding of the amplitude information $s_0(x)$ refers to the first of the three space directions. In Fig. 3.29a and b, the so-called *reading* or *frequency-encoding gradient*, here arbitrarily assumed in x direction of the (notabene) laboratory frame, thus leads to offsets

$$\omega(x) = \gamma g_x x \quad (3.271)$$

where the effect of the field gradient is assumed to be much stronger than any spectral frequency shift by spin interactions. Spectroscopic offsets can consequently be neglected.

Equation (3.271) gives the angular-frequency offsets the rotating-frame induction signal will be composed of. Instead of angular frequencies, one often prefers to express the encoding variable in terms of the *wave-vector component*

$$k_x = \frac{t_{\text{rx}} \omega(x)}{x} = \gamma g_x t_{\text{rx}} \quad (3.272)$$

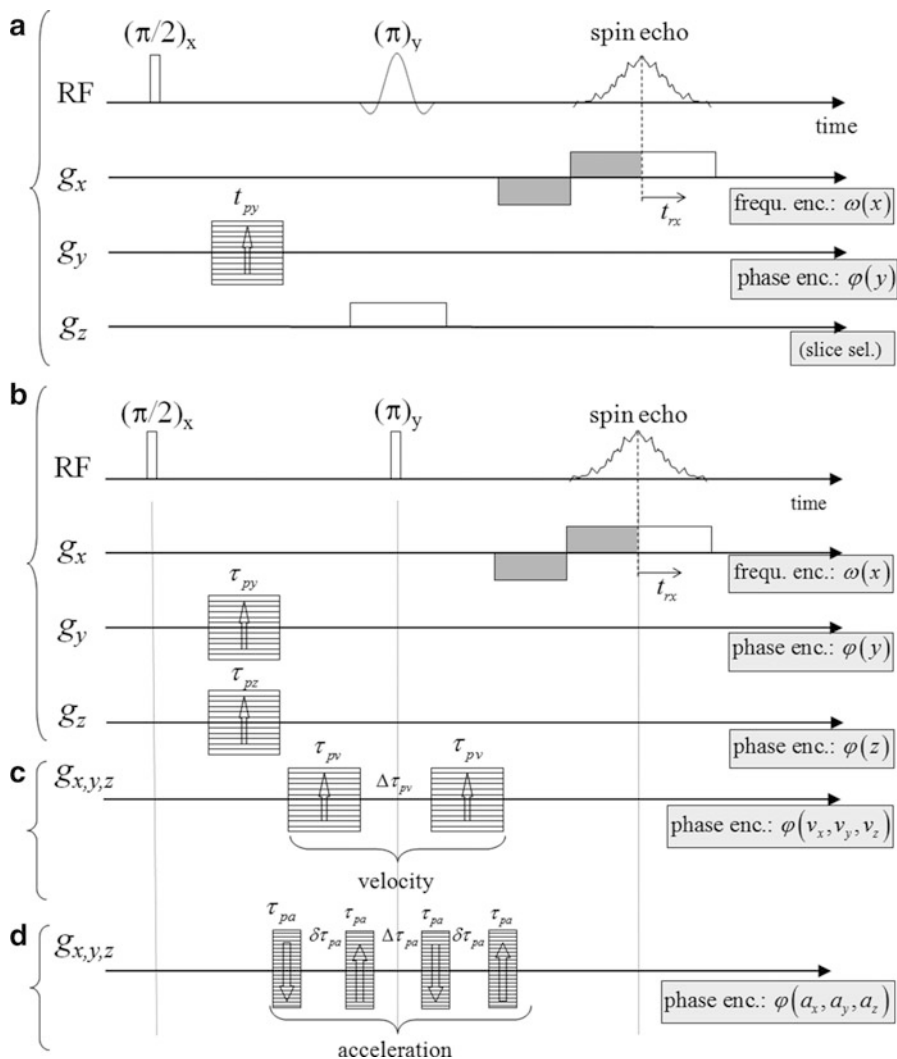


Fig. 3.29 Radio frequency (RF) and field-gradient (g_x , g_y , g_z) pulse sequences for mapping of material and transport parameters in two or three spatial dimensions. Spatial information is encoded by angular-frequency offsets ω and precession phase-shifts φ . Phase-encoding pulses are incremented in a series of subsequent transients as indicated by vertical arrows. In all cases, frequency encoding is achieved by acquiring the echo signal in the presence of a read-out gradient. (a) Two-dimensional imaging of a preselected slice of an object. (b) Three-dimensional imaging. (c) Supplementary gradient pulse train for additional phase encoding of velocity components (i.e., *velocity mapping*). (d) Supplementary gradient pulse train for additional phase encoding of acceleration components (i.e., *acceleration mapping*).

where t_{rx} is the period in which the spin coherences evolve in the presence of the reading gradient g_x along the x direction. The wave-vector component k_x is Fourier conjugate to the real-space coordinate x . With the aid of the relation $t_{rx} = k_x/(\gamma g_x)$, the time-domain NMR signal $S(t_{rx})$ can be expressed as the reciprocal-space function $S_k(k_x)$. This is the Fourier transform of the real-space distribution $\tilde{S}(x)$ containing the *image information* with respect to the x coordinate.

In order to refocus the coherences as a gradient reversal echo with a maximum in the middle of the proper frequency-encoding pulse, a negative gradient lobe is applied beforehand (compare the illustration in Fig. 3.24). To achieve this, the shaded sections of the gradient pulses in Fig. 3.29a and b are adjusted in such a way that the “areas,” that is, length times magnitude of the strength, are the same.

The information $s_0(y)$ along the y space direction can be *phase-encoded* with the aid of the rotating-frame precession phase angle

$$\varphi(y) = \gamma g_y t_{py} y = k_y y \quad (3.273)$$

generated by a phase encoding gradient pulse in y direction (Fig. 3.29a and b). τ_{py} is the length of the phase-encoding gradient pulse. The phase-shift $\varphi(y)$ can be interpreted as the y component of the wave vector:

$$k_y = \frac{\varphi(y)}{y} = \gamma g_y \tau_{py} \quad (3.274)$$

which is Fourier conjugate to the real-space variable y .

Likewise, phase encoding along the third space direction, that is, the z -axis, can be performed by adding a second phase-encoding gradient pulse as depicted in Fig. 3.29b. The phase shifts produced in this way are

$$\varphi(z) = \gamma g_z t_{pz} z = k_z z \quad (3.275)$$

τ_{pz} is the length of the phase-encoding pulse along the z direction. Analogously, the wave-vector component

$$k_z = \frac{\varphi(z)}{z} = \gamma g_z \tau_{pz} \quad (3.276)$$

is Fourier conjugate to the z coordinate of real space.

In order to cover the whole real-space region of interest, the phase-encoding pulses must be incremented independently in subsequent transients. In Fig. 3.29, the increments are represented by horizontal ladder lines. The arrows indicate the relative direction of the increments. The *repetition time* (or *recycle delay*) between subsequent phase-encoding steps should comply with $t_R \gg T_1$ to ensure equilibrium conditions at the beginning of the transients.

The combined frequency- and phase-encoded echo signal is $S_k = S_k(k_x, k_y)$ for two-dimensional imaging (Fig. 3.29a) and $S_k = S_k(k_x, k_y, k_z)$ in the three-dimensional case (Fig. 3.29b). These data sets are often called “holograms” in complete analogy to the optical phenomenon. The real-space information can be obtained on this basis via spatial Fourier transformation,

$$\tilde{S}(x, y) = \mathcal{F}_{k_x, k_y} \{S_k(k_x, k_y)\} \quad (3.277)$$

for two-dimensional imaging, and

$$\tilde{S}(x, y, z) = \mathcal{F}_{k_x, k_y, k_z} \{S_k(k_x, k_y, k_z)\} \quad (3.278)$$

for the three-dimensional case. As a consequence of the two- or three-dimensional Fourier transformation, the functions $\tilde{S}(x, y)$ and $\tilde{S}(x, y, z)$ are complex. The real-space image data are therefore rendered as the magnitude, that is, $s_0(x, y) \propto |\tilde{S}(x, y)|$ and $s_0(x, y, z) \propto |\tilde{S}(x, y, z)|$, respectively. If attenuation effects by relaxation or diffusion are negligible or enter as spatially constant factors not affecting the image reconstruction, the respective data sets represent the potentially time-dependent two- and three-dimensional *spin-density maps* $\rho(x, y, t) \propto s_0(x, y) \propto |\tilde{S}(x, y)|$ and $\rho(x, y, z, t) \propto s_0(x, y, z) \propto |\tilde{S}(x, y, z)|$.

In the two-dimensional version, Fig. 3.29a, phase encoding refers to only one space direction, here arbitrarily chosen as the y -axis. Encoding in the third direction is then replaced by a *slice-selection pulse* consisting of a *soft* (i.e. narrowband) RF pulses in the presence of a gradient in that particular space direction (here the z -axis).²⁸ Resonant excitation of the spins is then restricted to the desired slice region, while the outside space remains unaffected.

With the Hahn spin-echo sequence, slice selection can be based on the 90° or the 180° RF pulse (as shown in the scheme Fig. 3.29a) or on both RF pulses to ensure that signals selectively refer to the slice of interest across the object to be imaged. The selective echo formation thus ensures that only coherences of spins within the selected slice will be refocused in the form of an echo, and will hence contribute to the signal.

In the case of the pulse scheme Fig. 3.29a, the *digital resolutions* in x and y direction are given by

$$\Delta x = \frac{\pi}{\gamma g_x \tau_{rx}^{\max}} \quad \text{and} \quad \Delta y = \frac{\pi}{\gamma g_y \tau_{py}^{\max}} \quad (3.279)$$

²⁸ By contrast, a *hard* RF pulse is defined by an RF bandwidth large enough to excite the whole sample homogeneously irrespective of the offsets by field gradients or spin interactions. That is, the RF amplitude is correspondingly high and the pulse length short.

for frequency and phase encoding, respectively. $\tau_{rx}^{\max}$ is the longest reading interval compatible with a reasonable signal-to-noise ratio of the echoes. $g_y^{\max}$ is the maximum phase-encoding gradient reached at the end of the series of increments. Factors limiting the spatial resolution of magnetic resonance microscopy are (a) detection sensitivity, (b) strength of the magnetic-field-gradient pulses, and (c) filling factor of the RF coil relative to the voxels to be resolved. For more details, the reader is referred to Refs. [1, 3, 7], for instance.

The *fields of view* resulting from the settings of the pulse sequences are characterized by

$$-x_{\max} < \frac{\pi}{\gamma g_x \Delta \tau_r} < x_{\max} \quad \text{and} \quad -y_{\max} < \frac{\pi}{\gamma \Delta g_y \tau_{py}} < y_{\max} \quad (3.280)$$

$\Delta \tau_r$ is the so-called *dwell time*, that is, the digitization time per signal data point. Δg_y is the increment of the phase-encoding gradient between subsequent transients (i.e., the spacing of the “ladder rungs” in Fig. 3.29a).

3.3.1.2 An Interdiffusion Test Experiment

Figure 3.30 shows the results of a typical light/heavy water (or proton/deuteron) spin-density diffusometry experiment. The spin-density maps in (b) visualize interdiffusion in the course of time. The solution of the second Fick’s law, Eq. (2.171), for a stepwise, infinitely extended proton distribution at the beginning,

$$\rho(x, 0) = \begin{cases} \rho_0 & \text{for } x > x_0 \\ 0 & \text{for } x < x_0 \end{cases} \quad (3.281)$$

is given by [59]

$$\rho(x, t) = \frac{1}{2} \rho_0 \operatorname{erfc} \left(\frac{x_0 - x}{2\sqrt{Dt}} \right) \quad (3.282)$$

where the complementary error function is defined by $\operatorname{erfc}(\xi) = 2\pi^{-1/2} \int_{\xi}^{\infty} \exp\{-u^2\} du$. A similar test experiment based on interdiffusion between ^{13}C -labeled and unlabeled methanol in a polymer sample was reported in Ref. [60].

The time resolution of spin-density diffusometry depends on the time needed to record the data for one image. Typically it is much less than a minute. If only (one-dimensional) profiles are recorded, the time resolution will be much less. The propagation of the diffusion front, on the other hand, can be acquired over periods as long as acceptable in the frame of the investigation. Spatial resolution in the order of a few hundred μm can routinely be achieved with typical NMR microscopy systems.

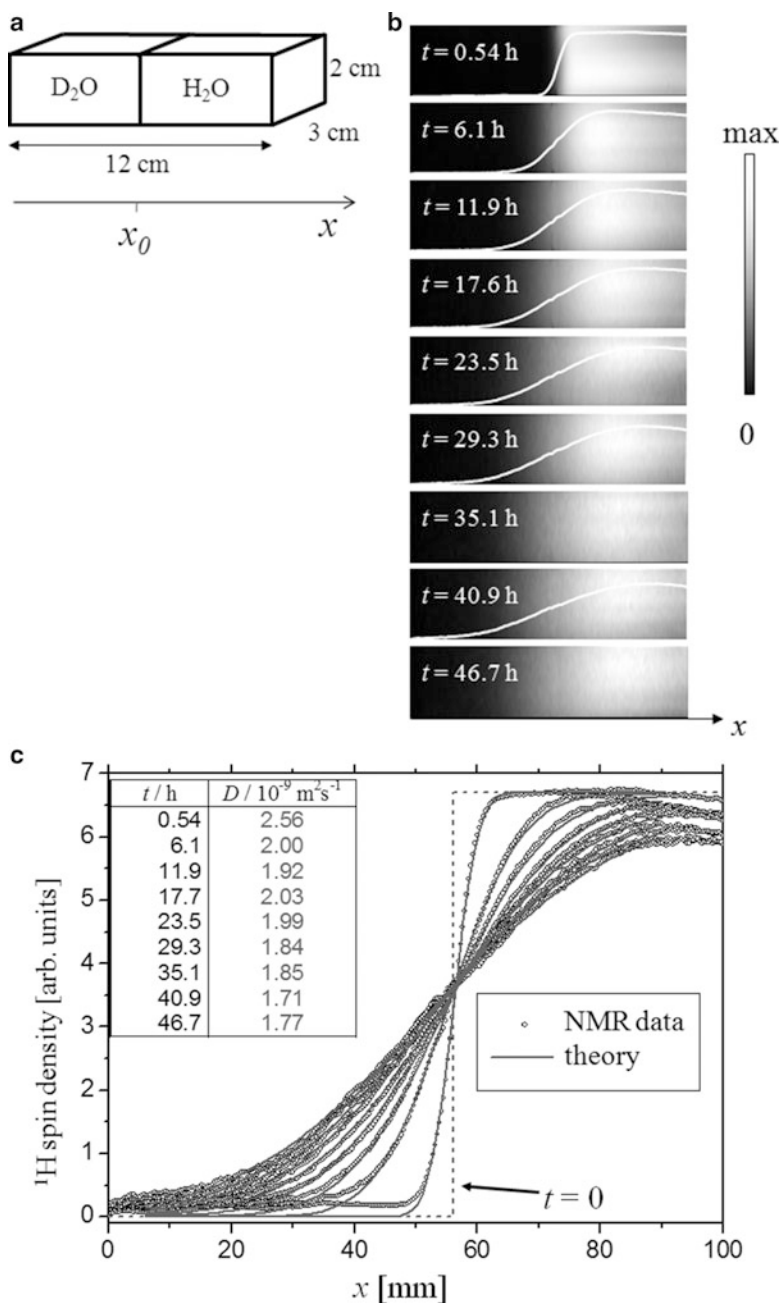


Fig. 3.30 Test experiment probing interdiffusion of water between two compartments with the aid of spin-density diffusometry. (a) Sample setup. The respective compartments contain water stabilized by gels and prepared with H_2O and D_2O . At time 0, the two moieties are contacted with each other. (b) Proton spin density maps after a number of different diffusion times. The white

3.3.2 Mapping of Self-Diffusion Coefficients

Soft-matter systems tend to be heterogeneous with respect to microstructure and composition. Maps of diffusion coefficients in such samples can therefore favorably employed for the characterization of local material properties.

The principle of the diffusometry technique described in the previous section is mapping of the *spin density* which – starting from a nonequilibrium isotope distribution – is subjected to interdiffusion phenomena and which is therefore a function of time and position. By contrast, the quantity of interest to be mapped in the experiments to be outlined now is the *self-diffusion coefficient* of the spin-bearing particles. The basis is field-gradient NMR diffusometry techniques already outlined above. These methods can conveniently be combined with the two- and three-dimensional imaging sequences shown in Fig. 3.29a and b in order to achieve spatial resolution.

If all pulse intervals of the pulse trains in Fig. 3.29a or b are kept constant, the echo amplitudes can be taken as a measure proportional to the initial magnetization prior to the first excitation pulse. The idea is now to produce diffusion (or hydrodynamic-dispersion) weighted maps by replacing the initial 90° RF pulse by any of the diffusometry pulse sequences outlined in Sect. 3.2. That is, the spin coherences produced by the 90° RF pulse in ordinary imaging sequences are replaced by the spin coherences resulting from precursor pulse sequences in the form of spin echoes. Precursor and imaging pulse sequences are combined in such a way that the precursor echo culminates to its maximum just at the time of the substituted 90° RF pulse [57]. Incrementing the field-gradient parameters of the precursor sequence and recording an image data set after each step permit one to evaluate maps of the diffusion coefficients with the desired spatial resolution.

Another point of interest to be mentioned in the present context is the unintentional influence of translational diffusion on contrasts in NMR microscopy. Depending on the system and the experimental settings, echo signals can be attenuated by diffusion in the presence of the spatial encoding gradients employed in the imaging process. The translational displacements responsible for this attenuation will however be restricted at any impermeable solid/liquid interfaces in the sample. That is, attenuation by diffusion will be less in voxels or pixels in the vicinity of such interfaces. The consequence is the so-called *edge enhancement* phenomenon [61]. It manifests itself as bright fringes along interface contours.



Fig. 3.30 (continued) lines represent the proton concentration profiles evaluated from the proton spin-density maps. (c) Proton concentration profiles after different diffusion times in comparison to the theoretical expectation for infinite compartment extension (Eq. 3.282). The diffusion coefficients fitted to the profiles are specified. Deviations from the known room temperature value of about $2 \times 10^{-9} \text{ m}^2/\text{s}$ at short and long times are due to imperfections of the sample in contrast to the assumptions of the theory. On the one hand, the initial $\text{H}_2\text{O}/\text{D}_2\text{O}$ distribution is not really stepwise as it should be ideally, and, on the other hand, the sample size is finite contrary to the theoretical premise (Reproduced from Ref. [58] with kind permission of © APS 2002)

3.3.3 Flow-Velocity NMR Mapping

The main subject of Chap. 4 will be fluid dynamics in complex environments. A particularly useful tool for studies of flowing systems is *velocity NMR mapping*. The principle of this technique is to supplement the two- or three-dimensional imaging pulse sequences shown in Fig. 3.29a and b by additional gradient pulse pairs for phase encoding of velocity components as illustrated in Fig. 3.29c. The velocity components are defined by the gradient directions of these pulse pairs. The supplementation of imaging pulse sequences by one, two, or even three such orthogonal gradient pulse pairs permits one to acquire maps of one, two or all three-flow velocity components, that is, two- or three-dimensional maps of either individual components or of the flow-velocity vector (or its magnitude).

As with spatial phase encoding, the strength of the velocity-encoding gradient pulse pair is incremented in additional transients (thick vertical arrows in Fig. 3.29c). Of course, the increments need to be *independent* of the increments of the position-encoding gradients. Depending on the velocity and spatial ranges to be probed, this can lead to excessive numbers of transients required for each mapping experiment. It is therefore advisable to keep the number of dimensions and the fields of view both for the spatial and the velocity variables as small as compatible with the information to be acquired.

The velocity-encoding gradient pulses are symmetrically arranged on either side of the 180° RF pulse of the Hahn echo sequence. The gradients of both pulses have the same sign, strength, and length. Any *spatial* phase encoding of the spin coherences by the first gradient pulse will thus be refocused by the second pulse after the 180° pulse. No net position-dependent phase shift will be left over from this pulse pair. However, a finite flow-velocity component along the gradient direction will give rise to a net phase shift proportional to the velocity component. That is, there will be a further Fourier domain for each velocity component in addition to the spatial Fourier domains. Multidimensional data sets acquired from correspondingly phase- and frequency-encoded NMR signals can then be processed with the objective to allocate a flow-velocity value to each voxel. On this basis, either maps of the velocity magnitude can be rendered or vectorial streamline representations can be constructed. This will be demonstrated in the following chapter.

To elucidate the principle of velocity phase encoding, let us consider displacements along the x -axis, for example. The trajectory of a particle, $\mathbf{r} = \mathbf{r}(t)$, can be analyzed in this direction by the expansion

$$x(t) = x_0 + v_{x0}t + \frac{1}{2}a_{x0}t^2 + \dots \quad (3.283)$$

where v_{x0} and a_{x0} are the initial particle velocity and acceleration components, respectively. We have considered this sort of analysis already in Eq. (3.254). In principle, higher-order terms may contribute as well. They vanish however if the flow field is stationary on the time scale of the NMR experiment, so that any

time-dependent accelerations can be neglected. The precession phase shift acquired by the velocity-encoding gradient pulse pair in Fig. 3.29c during the echo time t_E is

$$\varphi(x, t_E) = \gamma \int_0^{t_E} \Phi(t) g_x(t') x(t') dt' \quad (3.284)$$

$g_x(t')$ describes the temporal appearance of the gradient pulse pair, and the width of each gradient pulse be τ_{pv} . The gradient strength in the intervals τ_{pv} is $\hat{g}_x = \text{const}$ and zero outside. Since the 180° RF pulse is equivalent to the reversal of the gradient direction, the second gradient pulse must effectively be taken into account with the *opposite* sign of the first gradient pulse (see the description of the gradient reversal and Hahn echoes in Sect. 3.2). This is accounted for by the auxiliary function

$$\Phi(t) = \begin{cases} +1 & \text{before the } 180^\circ \text{ pulse} \\ -1 & \text{after the } 180^\circ \text{ pulse} \end{cases} \quad (3.285)$$

Inserting Eq. (3.283) into Eq. (3.284) gives the total phase shift the echo signal will be subjected to:

$$\begin{aligned} \varphi(t_E) = & -\gamma \hat{g}_x \left(\tau_{pv}^2 + \tau_{pv} \Delta \tau_{pv} \right) v_{x0} \\ & - \gamma \hat{g}_x \left(\tau_{pv}^3 + \frac{3}{2} \tau_{pv}^2 \Delta \tau_{pv} + \frac{1}{2} \tau_{pv} \Delta \tau_{pv}^2 \right) a_{x0} + \dots \end{aligned} \quad (3.286)$$

Obviously the dependence on x_0 has cancelled. The second expansion term depends on the initial acceleration. Higher-order terms refer to potentially time-dependent accelerations. Under stationary flow conditions, all these acceleration-dependent terms are irrelevant, so that we can restrict ourselves to the first term in Eq. (3.286). It predicts a phase shift proportional to the velocity component along the gradient direction. The NMR signal is thus encoded by the phase shift

$$\varphi(v_{x0}) = -\gamma \hat{g}_x \left(\tau_{pv}^2 + \tau_{pv} \Delta \tau_{pv} \right) v_{x0} \quad (3.287)$$

which depends *linearly* on the velocity component v_{x0} .

Fourier transformation of the phase-encoded signal data finally provides the velocity data to be allocated to the image pixels or voxels as a velocity map. In the limit $\tau_{pv} \gg \Delta \tau_{pv}$, the effective velocity phase-encoding shift, Eq. (3.287), can be approximated by

$$\varphi(v_{x0}) \approx -\gamma \hat{g}_x \tau_{pv}^2 v_{x0} \quad (3.288)$$

The *digital resolution* and the *velocity* “field-of-view,” that is, the range of velocities unambiguously covered by the settings of the pulse sequence, are then given by

$$\Delta v_x \approx \frac{\pi}{\gamma \tau_{pv}^2 g_x^{\max}} \quad (3.289)$$

and

$$-\frac{\pi}{\gamma \tau_{pv}^2 \Delta g_x} < v_x < \frac{\pi}{\gamma \tau_{pv}^2 \Delta g_x} \quad (3.290)$$

respectively. $g_x^{\max}$ is the maximum gradient strength and Δg_x the step by which the phase-encoding gradient is incremented.

3.3.4 Flow-Acceleration NMR Mapping

The versatility of NMR microscopy techniques for the characterization of flow phenomena is not exhausted with velocity mapping. The next variant of potential interest in this field is mapping of the local *flow acceleration*. In principle, local flow accelerations could also be deduced from velocity maps as derivations. However, the experimental accuracy would be very poor due to the discreteness of the voxel resolution. The direct measurement of the local accelerations is therefore preferable.

Phase encoding of an acceleration component is based on the gradient pulse train shown in Fig. 3.29d. Supplementing these pulses to the imaging pulse sequences Fig. 3.29a or b permits one to allocate accelerations to the image pixels or voxels. For this purpose, phase encoding is based on four gradient pulse lobes having the same duration and amplitude (magnitude), but different signs. The gradient pulses are arranged around the 180° RF pulse, two on each side. The first and the third lobe of this gradient pulse train have the same, the second and fourth lobe the opposite sign (see the vertical arrows indicating the direction of increments in subsequent transients). Using Eq. (3.284) with the definition Eq. (3.285) and referring to the x component of the acceleration, a_x , leads to the total precession phase shift produced by these pulses during the echo evolution time t_E

$$\begin{aligned} \varphi(t_E) &= \frac{1}{2} \gamma a_x \int_0^{t_E} \zeta(t) g_x(t') t'^2 dt' = \frac{1}{2} \gamma a_x \int_0^{4\tau_{pa} + 2\delta\tau_{pa} + \Delta\tau_{pa}} \zeta(t') g_x(t') t'^2 dt' \\ &= \frac{1}{2} \gamma a_x g_x (4\tau_{pa}^3 + 2\tau_{pa} \delta\tau_{pa}^2 + 6\tau_{pa}^2 \delta\tau_{pa} + 4\tau_{pa}^2 \Delta\tau_{pa} + 4\tau_{pa} \Delta\tau_{pa} \delta\tau_{pa}) \\ &\propto a_x \end{aligned} \quad (3.291)$$

The pulse intervals are defined in the scheme shown in Fig. 3.29.

The local precession phase shift generated by the gradient pulse quadruple in Fig. 3.29d is obviously proportional to the local acceleration, while any phase encodings of the spatial position and of the initial velocity cancel. Acquiring a set of echo signals phase encoded with the acceleration component along the gradient direction thus permits the evaluation of spatially resolved acceleration data via Fourier transformation [57, 62].

In the limit $\tau_{\text{pa}} \gg \Delta\tau_{\text{pa}}, \delta\tau_{\text{pa}}$, the acceleration-based phase shift, Eq. (3.291), is reduced to

$$\varphi(a_x) \approx 2\gamma g_x \tau_{\text{pa}}^3 a_x \quad (3.292)$$

In this case, the digital resolution and the acceleration “field-of-view” obey the approximate relations

$$\Delta a_x \approx \frac{\pi}{2\gamma \tau_{\text{pa}}^3 g_x^{\text{max}}} \quad (3.293)$$

and

$$-\frac{\pi}{2\gamma \tau_{\text{pa}}^3 \Delta g_x} < a_x < \frac{\pi}{2\gamma \tau_{\text{pa}}^3 \Delta g_x} \quad (3.294)$$

respectively. g_x^{max} and Δg_x have equivalent meanings as in Eqs. (3.289) and (3.290). A typical acceleration map acquired with this sort of experiment will be depicted in the next chapter in Fig. 4.11.

3.3.5 Mapping of Electric Transport Phenomena in Electrolyte Solutions

The following sections are devoted to transport mechanisms appearing to be somewhat out of place in the present context – at first sight. While electroosmotic flow, as the name suggests, is still related to hydrodynamic flow in a pressure gradient, ionic currents seem to belong to a totally different category. Comparisons between just these different transport species will nevertheless be drawn in Chap. 4. It will be shown that the laws governing the phenomena can be elucidated and discriminated from each other in a direct way on this basis. Let us therefore outline the experimental techniques needed for the acquisition of the corresponding transport parameters at this point.

3.3.5.1 Electroosmotic Flow

If an electrolytic system like the one described in Sect. 2.1.8 and illustrated in Fig. 2.12 is subjected to an external potential difference, the electrostatic forces on the ions of the double layer give rise to coherent *electroosmotic flow* (EOF) [63]. The flow velocity generated in this way can be mapped as already described above for pressure-induced flow. The RF, field-gradient, and current pulse sequences employed for (two-dimensional) spatial encoding are summarized in Fig. 3.31. The sequels (a) and (b) serve mapping of the flow velocity. These pulses are synchronized with the DC potential difference shown in (c) for the generation of electroosmotic flow as a consequence of ionic currents across the sample.

Prior to the proper phase-encoding experiment, the current pulse must be long enough on to ensure steady-state conditions [54]. A typical order of magnitude of this delay is $t^* \approx 10^{-2}$ s. One might suspect that the magnetic field produced by the ionic current interferes with the phase-encoding gradients serving the measurement of the flow velocity. However, there is no such problem since the ionic currents during the Hahn echo sequence are stationary and are *not incremented* in the course of the experiment in contrast to the gradients phase encoding the velocity.

3.3.5.2 Ionic Current Density

In contrast to the pulse sequence for mapping of the EOF velocity (Fig. 3.31a–c), the ionic current density is mapped with the aid of bipolar current pulses in the free-evolution intervals of the spin-echo pulse sequence. This is achieved with the combination of the sequels Fig. 3.31a and d. In this case, the phase shifts arising from the magnetic fields of the current distribution are intentionally not refocused. These phase shifts are just the source of the information on the local current density [64–66].

The principle of ionic current density (ICD) mapping is based on Maxwell's fourth equation for stationary electromagnetic fields,

$$\mathbf{j}(\mathbf{r}) = \frac{1}{\mu_0} \nabla \times \mathbf{B}(\mathbf{r}) \quad (3.295)$$

where $\mathbf{B}(\mathbf{r})$ is the magnetic flux density produced by the electric current density $\mathbf{j}(\mathbf{r})$ at the position $\mathbf{r}$. The quantity μ_0 is the magnetic-field constant. The curl operation depends on all three spatial derivatives of the flux density with respect to the spatial Cartesian coordinates. To probe all three components of the vector $\mathbf{j}(\mathbf{r})$, the sample needs to be rotated in 90° steps into the three space directions in subsequent experiments.

The protocol becomes much simpler if the current distribution is intrinsically two-dimensional so that it is practically invariant along one space direction, for example, the z -axis of the laboratory reference frame [66]. That is, the system under

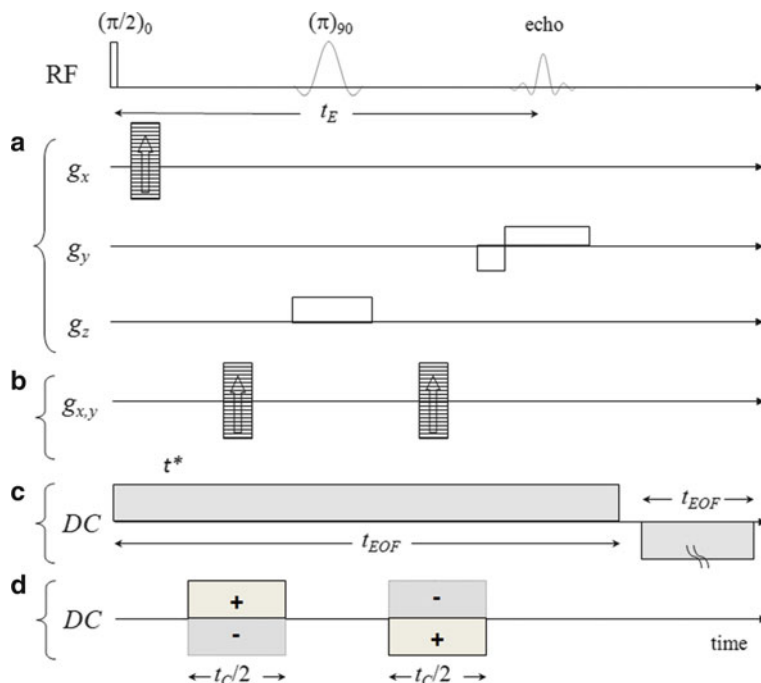


Fig. 3.31 Two-dimensional NMR mapping methods probing electric phenomena in electrolytic solutions. The sequences consist of radio frequency (RF), magnetic-field-gradient (g_x , g_y , g_z), and ionic current (DC) pulses. The signal acquired is a standard Hahn echo at the echo time t_E . The different pulse sequences (a)–(d) can be combined as needed. (a) Ordinary two-dimensional imaging sequence selecting a z slice. (b) Gradient pulses for phase encoding of a velocity component in the selected slice. Two independent pairs of such gradient pulses are necessary for the two space directions (x , y) under consideration. The vertical arrows indicate the direction of the increments in subsequent transients. Combining (a) + (b) in the form of two three-dimensional experiments, x, y, v_x and x, y, v_y , permits the record of maps of the velocity magnitude $v(x, y)$. (c) Electric current pulses for generating electro-osmotic flow (EOF) to be probed by velocity mapping. The delay time t^* serves the establishment of steady state conditions. $t_{EOF} > t_E$ is the total length of the current pulse. A current pulse of the same length but opposite polarity is applied during the recycle delay in order to reverse any chemical reactions at the electrodes. (d) Bipolar current pulse pairs producing phase shifts of the echo signal indicative for the local current density. Combining sequences (a) and (d) permits the evaluation of current density maps. In contrast to the EOF pulse scheme (c), the phase shifts induced by the current pulses before and after the 180° RF pulse do not cancel each other as a consequence of the bipolarity. Undesired offsets are eliminated by alternating the polarity of the current pulses in subsequent scans and subtracting the evaluated current densities from each other according to $j_{x,y} = (j_{x,y+} - j_{x,y-})/2$. $j_{x,y+}$ and $j_{x,y-}$ are the current densities evaluated for current pulses indicated by + and – signs, respectively (Reproduced from Ref. [54] with kind permission of © Wiley-VCH 2009)

investigation must be extended sufficiently in this direction to ensure uniform current density distributions in the space region probed in the experiments. The two-dimensionality of the current distribution requires that the current density in the third direction must be zero. In this case, only two components and two

derivatives in the transverse plane remain finite. Written in component form, Eq. (3.295) thus becomes

$$\begin{aligned} j_z(\mathbf{r}) &= 0 \\ j_x(\mathbf{r}) &= \frac{1}{\mu_0} \frac{\partial B_z}{\partial y} \\ j_y(\mathbf{r}) &= \frac{1}{\mu_0} \frac{\partial B_z}{\partial x} \end{aligned} \quad (3.296)$$

Since there are only in-plane components, no rotation of the sample is necessary.

The derivatives in Eq. (3.296) can numerically be evaluated from maps of the current-induced phase shifts of the echo signal. In order to account for the periodicity of the phase angles, *phase unwrapping* will be necessary. This is best done with the aid of *Goldstein's two-dimensional algorithm* [67]. Applications to porous media and comparisons with flow mapping experiments will be described in Sect. 4.9.6.

3.3.6 Magnetization Grid Rotating-Frame Imaging (MAGROFI)

In previous sections, two NMR methods probing diffusive displacements on very different time scales have been described: field-gradient NMR diffusometry (Sect. 3.2) and spin-density diffusometry (Sect. 3.3.1). A further, less general and less direct NMR method for the examination of translation displacements is based on the intermolecular contribution to spin–lattice relaxation as outlined in Sect. 3.1.9. There is a further NMR measuring principle that, in a sense, could be termed a hybrid technique between field-gradient and spin-density mapping diffusometry: The so-called **magnetization grid rotating-frame imaging** (MAGROFI) diffusometry [68–70] combines magnetization grating and imaging.

Figure 3.32 shows a schematic representation of the pulse sequence. Instead of using gradients of the main field B_0 , the required nonequilibrium distribution of the magnetization is now prepared with the aid of a gradient of the RF amplitude B_1 ,

$$g_1(x) = \left| \frac{\partial B_1(x)}{\partial x} \right| \quad (3.297)$$

In cases where the evolution of spin coherences is controlled by B_1 -based measures, one speaks of *rotating-frame techniques* in contrast to the more conventional laboratory-frame methods. Generally there are numerous rotating-frame counterparts equivalent to laboratory-frame pulse schemes. This in particular refers to rotating-frame echo phenomena [45].

For practical reasons, it is assumed that the B_1 -gradient is oriented perpendicular to the main magnetic field, for example, along the x -axis of the laboratory frame.

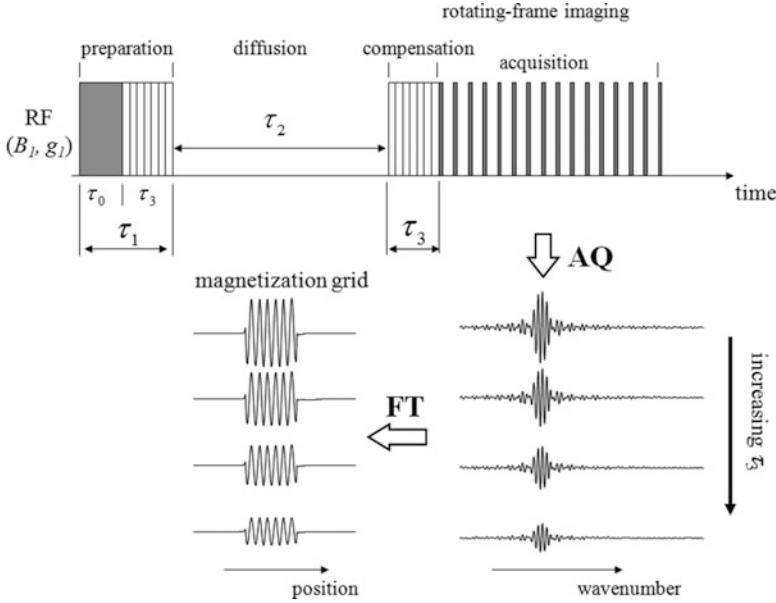


Fig. 3.32 Schematic representation of the MAGROFI technique for the measurement of diffusion coefficients with the aid of gradients of the amplitude B_1 of the RF field. The preparation pulse of variable length produces the z magnetization grid along the B_1 gradient direction. The wavelength of the grating is $\lambda = 2\pi/q_p$ where $q_p = \gamma g_1 \tau_1$. It varies with the total preparation pulse length τ_1 . After the diffusion time τ_2 , the magnetization grid is imaged with the aid of the rotating-frame technique using RF pulses subject to the same B_1 gradient as the preparation pulse. The purpose of the compensation pulse is to transform the wavelength of the image grating to the constant value $\lambda_0 = 2\pi/q_0$ where $q_0 = \gamma g_1 \tau_0$. This facilitates the evaluation of a diffusion coefficient at a certain position on the gradient axis. The primary data set is stroboscopically acquired in the acquisition (AQ) interval. The signal amplitude is thus recorded as a function of the cumulative length of the reading pulse. The magnetization grid more or less leveled by diffusion is then directly obtained by Fourier transformation (FT). The effective diffusion time can be defined by $t_{\text{diff}} = \tau_1/3 + \tau_2 + \tau_3/3 \approx \tau_2$, where the approximation represents the short-pulse limit $\tau_2 \gg \tau_1, \tau_3$, τ_3 is the width of the compensation pulse (Reproduced from Ref. [68] with kind permission of © Elsevier 2006)

All RF pulses in Fig. 3.32 are understood to be subject to the same B_1 gradient. The gradient is produced by a suitably shaped RF coil which is used both for transmitting the RF pulses and picking up the signal. As a favorable coil geometry, a conic design has been proposed as shown in Fig. 3.33 [68]. For the sake of simplicity of the treatment, we will assume in the following that the B_1 gradient is spatially constant within the sample, $g_1 = \text{const}$, that is,

$$B_1 = g_1 x \quad (3.298)$$

with a correspondingly chosen origin on the x -axis. It should however be mentioned at this point that constant B_1 gradients are not a stringent condition as demonstrated in Refs. [69, 70]. Merely, the treatment becomes somewhat more complicated for spatially varying gradients.

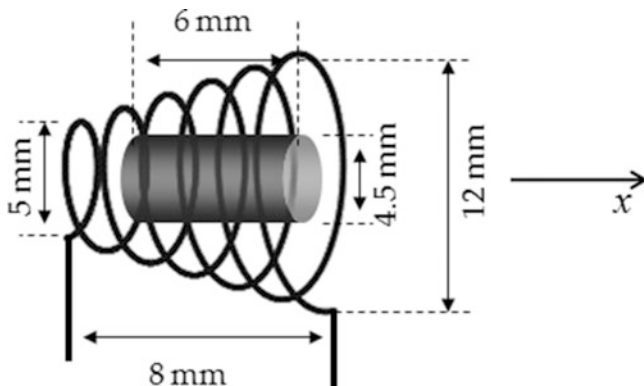


Fig. 3.33 Conic RF coil suitable for the generation of B_1 gradients [71]. The coil axis is assumed along the x direction of the laboratory frame of reference (Reproduced from Ref. [68] with kind permission of © Elsevier 2006)

The pulse sequence in Fig. 3.32 consists of three principal intervals: (1) *preparation* by an RF pulse generating the z magnetization grid along the x -axis of the laboratory frame, (2) *diffusion interval* allowing for leveling of the grid to some degree by translational diffusion, and (3) sequence for *imaging* of the grid with the aid of compensation and reading RF pulses.

For a treatment, the amplitude of the RF pulse B_1 is assumed to be aligned along the x' -axis of the frame rotating with the angular resonance frequency $\omega_0 = \gamma B_0$. All interactions among the spins are neglected during RF irradiation. It is also assumed that any gradients of the main magnetic-field B_0 of external or internal (i.e., susceptibility-induced) origin neither affect the excitation of the spins nor give rise to further diffusive signal attenuation in the imaging interval. This stipulates that all local offsets of the main magnetic field are negligible relative to the amplitude of the local RF field $B_1(\mathbf{r})$.

The first RF pulse of total length τ_1 rotates the equilibrium magnetization $\mathbf{M}_0$ out of the z direction. The so-called *nutaton (angular) frequency* about the x' -axis of the rotating frame is

$$\omega_1(x) = \gamma B_1(x) \quad (3.299)$$

Since the RF amplitude $B_1(x)$ is a (linear) function of the laboratory-frame coordinate x , the nutation frequency will depend on the x position as well. That is, the flip angle reached at the end of the preparation pulse after the period τ_1 ,

$$\alpha(x) = \gamma B_1(x) \tau_1 \quad (3.300)$$

is again a function of x . In other words, a magnetization helix about the gradient direction is established analogous to the illustration shown in Fig. 3.24.

The magnetization components generated by the preparation pulse can be calculated as solutions of the rotating-frame Bloch equations (3.22). The transverse components, that is, spin coherences, are spoiled in the diffusion interval by transverse relaxation and by B_0 inhomogeneities. The sole component that survives the interval τ_2 is z magnetization. In the limit of short and intense RF gradient pulses obeying $\tau_1 \ll T_2$ and $\omega_1 T_2 \gg 1$, the local z magnetization immediately after the preparation pulse at $t = \tau_1$ takes the form

$$M_z(x, \tau_1) = M_0 \cos[\gamma B_1(x) \tau_1] = M_0 \cos[\gamma g_1 \tau_1 x] = M_0 \cos(q_p x) \quad (3.301)$$

The wave number

$$q_p = \gamma g_1 \tau_1 \quad (3.302)$$

is determined by the gradient g_1 and the length $\tau_1 = \tau_0 + \tau_3$ of the preparation pulse. The cosine represents a magnetization grating we know already from the illustration in the inset of Fig. 3.26c.

In the course of the interval τ_2 , diffusive displacements of the molecules tend to level the z magnetization grid. Incrementing the preparation pulse length τ_1 in subsequent transients, that is, reducing the wavelength of the grating

$$\lambda = \frac{2\pi}{q_p} \quad (3.303)$$

results in increasing degrees of leveling.

Apart from diffusion, longitudinal relaxation as a second irreversible process modifies the magnetization grid. By tendency, a homogeneously distributed equilibrium magnetization is approached in the sample. Since relaxation is independent of diffusion, the total magnetization grating at the end of the diffusion interval τ_2 can be represented in factorized form as

$$\begin{aligned} M_z(x, \tau_1 + \tau_2) = & M_0 \cos(q_p x) \exp\left\{-D q_p^2 \tau_2\right\} \exp\left\{-\frac{\tau_2}{T_1}\right\} \\ & + M_0 \left(1 - \exp\left\{-\frac{\tau_2}{T_1}\right\}\right) \end{aligned} \quad (3.304)$$

where we have neglected displacements during the preparation interval τ_1 . This is justified by the assumption $\tau_2 \gg \tau_1$. In the derivation of Eq. (3.304), we have furthermore assumed that the diffusive displacement is distributed according to a Gaussian function as usual. D is the diffusion coefficient. The first term on the right-hand side thus represents the partially leveled magnetization grid. The second term refers to the fraction of magnetization recovered by longitudinal relaxation with the spin-lattice relaxation time T_1 .

Equation (3.304) represents the magnetization grid $\propto \cos(q_p x)$ to be imaged as a function of τ_1 and then evaluated with respect to the diffusion coefficient. All other parameters are kept constant. The same B_1 gradient that is used for the generation of the magnetization grid can also be used for one-dimensional imaging of the spatial magnetization distribution. The method is the so-called *rotating-frame imaging* technique [1, 3]. It is based on *nutaton-frequency-encoding*, $\omega_1 = \omega_1(x)$, of the spatial information instead of the conventional encoding measures, that is, phase encoding, $\varphi = \varphi(x)$, and precession frequency encoding, $\omega = \omega(x)$.

For imaging, the magnetization grating at the end of the τ_2 interval, Eq. (3.304), is subjected to a comb of short reading RF gradient pulses applied after a compensation pulse of variable length τ_3 (the function of the compensation pulse in this procedure is ignored for the moment and will be explained later). The spacings between the reading pulses are just long enough to permit the acquisition of one data point of each of the intermittent FIDs. This procedure is also referred to as *stroboscopic signal acquisition*. It implies the nutation-frequency encoded information on the magnetization grid. Instead of incrementing a single reading pulse in subsequent transients as proposed in the original rotating-frame imaging technique [72], the whole acquisition is performed in a single scan. This single-scan stroboscopic acquisition method is known as *rapid rotating frame-imaging* [73].

Each pulse of the comb corresponds to an increment of the width τ_r of the reading pulse in the original technique. With rapid rotating-frame imaging, the *effective* reading time thus is the sum of the widths of all preceding pulses in the comb. The local transverse magnetization stroboscopically produced by the reading-pulse comb as a function of the coordinate x and the cumulative pulse width τ_r is then found to be

$$M_y(x, t_r) = \left\{ M_0 \cos(q_p x) \exp\left\{-Dq_p^2 \tau_2\right\} \exp\left\{-\frac{\tau_2}{T_1}\right\} + M_0 \left(1 - \exp\left\{-\frac{\tau_2}{T_1}\right\}\right) \right\} \times \sin(q_r x) \quad (3.305)$$

where $t_r = \tau_1 + \tau_2 + \tau_r$. In this expression, we have introduced the wave number generated by the reading pulses:

$$q_r = \gamma g_1 \tau_r \quad (3.306)$$

The detected signal voltage $S(\tau_r)$ induced by the precessing magnetizations as a function of τ_r , the so-called *pseudo-FID*, is the superposition of the contributions from all positions in the sample:

$$S(\tau_r) = \int_{\text{sample}} f(x) \left\{ M_0 \cos(q_p x) \exp\left\{-Dq_p^2 \tau_2\right\} \exp\left\{-\frac{\tau_2}{T_1}\right\} + M_0 \left(1 - \exp\left\{-\frac{\tau_2}{T_1}\right\}\right) \right\} \sin(q_r x) dx \quad (3.307)$$

The factor $f(x)$ accounts for the (empirical or calculated) distribution of the voltage-induction sensitivity at different positions in the RF coil. Equation (3.307) represents a Fourier sine integral for the conjugate variable pair x and the reading wave number q_r . Fourier transformation of the pseudo-FID thus renders the desired distribution of the magnetization in real space as it existed at the end of the diffusion interval:

$$\tilde{S}(x, \tau_1) = A_0 \cos(q_p x) \exp\{-Dq_p^2 \tau_2\} \exp\left\{-\frac{\tau_2}{T_1}\right\} \quad (3.308)$$

where A_0 is a proportionality constant and where the limit $\tau_2 \gg \tau_1$ was assumed. This is the one-dimensional image that would be obtained if the compensation pulse indicated in Fig. 3.32 is disregarded.

Incrementing the preparation pulse length τ_1 in a series of transients of the pulse sequence increments the preparation wave number $q_p = \gamma g_1 \tau_1$ as well. That is, the wavelength of the magnetization grating, $\lambda = 2\pi/q_p$, decreases step by step. The consequence is that the leveling of the grating by diffusion becomes more and more efficient. On this basis, the diffusion coefficient can be evaluated from the diffusive attenuation factor $\exp\{-Dq_p^2 \tau_2\}$. Equation (3.308) was derived for the short-pulse limit $\tau_2 \gg \tau_1$. For longer preparation and reading-pulse intervals, the effective diffusion time is given by $t_{\text{diff}} = \tau_1/3 + \tau_2 + \tau_3/3$ instead of τ_2 [68].

Let us now resume the discussion of the compensation pulse interval τ_3 defined in Fig. 3.32. It is applied prior to the comb of reading pulses for practical reasons. The problem is that the grid wavelength $\lambda = 2\pi/(\gamma g_1 \tau_1)$ varies with the preparation pulse length τ_1 . According to Eq. (3.308), the diffusivity would have to be evaluated under such circumstances from a series of magnetization grid images with *different* wavelengths. This difficulty is remedied by the compensation pulse. It is incremented in the same way as the preparation pulse so that the *same* effective wavelength $\lambda_{\text{comp}} = 2\pi/(\gamma g_1 \tau_0)$ is rendered in the series of compensated images $\tilde{S}_{\text{comp}}(x, \tau_1)$:

$$\tilde{S}_{\text{comp}}(x, \tau_1) = A_0 \cos(q_p x) \exp\{-Dq_p^2 \tau_2\} \exp\left\{-\frac{\tau_2}{T_1}\right\} \quad (3.309)$$

The wave number $q_0 = \gamma g_1 \tau_0$ effective for the images thus becomes independent of the increment variable τ_1 . The fixed interval τ_0 is the starting width of the preparation pulse as indicated in Fig. 3.32. The diffusion coefficient can then conveniently be evaluated from a series of the compensated images at any position x chosen along the gradient. With Eq. (3.309), we thus have one more technique probing the *incoherent dynamic structure factor* $\mathcal{G}_{\text{inc}}(t_{\text{eff}})$ as a function of the effective diffusion time $t_{\text{eff}} \approx \tau_2$.

Although B_1 gradients can technically not be made as strong as B_0 gradients, there are a number of remarkable features making the MAGROFI technique superior to ordinary field-gradient diffusometry methods under certain

circumstances. According to Eq. (3.309), there is no dependence on transverse relaxation, which is a factor significantly limiting laboratory-frame techniques. Another most important advantage is the weak sensitivity to B_0 field gradients. That is, inhomogeneities due to magnetic-susceptibility distributions in heterogeneous samples as they often occur in soft-matter science do not matter.

3.4 Exchange NMR

Exchange NMR methods are of interest for systems where nuclei are embedded in a variety of distinct molecular *environments*. As synonymous expressions, “sites” and “pools” are occasionally in use (compare the discussion in Sect. 7.1.5). Local characteristics relevant in this context can be the resonance frequency and/or spin couplings and/or molecular mobility. The latter entails different relaxation times and diffusivities.

The resonance frequency can vary for example due to (1) different chemical shift, (2) molecular isomerism, (3) different magnetic susceptibility, (4) anisotropic spin interactions in combination with different orientations in solid-like materials, and (5) different positions in a field gradient. There is a large variety of mechanism that may contribute to the category *exchange*: chemical exchange of the spin-bearing particle, structural or isomeric fluctuations of the spin environment so that the resonance frequency becomes a fluctuating function of time, diffusion of the considered molecule in environments with varying magnetic-susceptibility, immaterial spin exchange by spin flip/flop processes (also known as spin diffusion or cross relaxation. See Sect. 3.2.2.5), and reorientations of molecules so that the secular terms of anisotropic spin interactions are modulated.

In the following, we will restrict ourselves to the treatment of a finite set of discrete spin environments between which random exchange can occur. We will first consider the effect of exchange on the evolution of spin states and coherences, and then turn to two- (or multiple-) dimensional exchange experiments.

3.4.1 Equation of Motion for Discrete Spin Environments

The network of potential exchange pathways is assumed to comprise N discrete unlike environments “ j ” of the spins. Relevant parameters are the angular resonance frequencies $\omega_{0,j}$, the longitudinal and transverse relaxation times $T_{1,j}$ and $T_{2,j}$, and in special cases the local diffusion coefficient and potentially the local flow velocity. Different resonance frequencies and different relaxation times are the most common scenarios of interest.

For each spin environment “ j ,” a complex transverse partial magnetization

$$m_j = M_{x',j} + iM_{y',j} \quad (3.310)$$

and a partial z magnetization $M_{z,j}$ with the equilibrium values $M_{0,j}$ can be defined where $j = 1 \dots N$. x' and y' are the transverse coordinate axes of the frame rotating with the basic Larmor frequency $\omega_0 = -\gamma \mathbf{B}_0$. These partial magnetizations can conveniently be represented by N -dimensional magnetization vectors,

$$\mathbf{m} = \begin{pmatrix} m_1 \\ \vdots \\ m_j \\ \vdots \\ m_N \end{pmatrix}; \quad \mathbf{M}_z = \begin{pmatrix} M_{z,1} \\ \vdots \\ M_{z,j} \\ \vdots \\ M_{z,N} \end{pmatrix}; \quad \mathbf{M}_0 = \begin{pmatrix} M_{0,1} \\ \vdots \\ M_{0,j} \\ \vdots \\ M_{0,N} \end{pmatrix} \quad (3.311)$$

the transverse and longitudinal *magnetization system vectors* to be distinguished from ordinary magnetization vectors. On this basis, the Bloch equations given in Eq. (3.11) can be extended by exchange terms. In matrix form

$$\begin{aligned} \frac{d\mathbf{m}(t)}{dt} &= \tilde{\ell} \mathbf{m}(t) \\ \frac{d\mathbf{M}_z(t)}{dt} &= \tilde{L} [\mathbf{M}_z(t) - \mathbf{M}_0] \end{aligned} \quad (3.312)$$

they are referred to as *Hahn/Maxwell/McConnell (HMM) equations* [74, 75] with the HMM matrices $\tilde{\ell}$ and $\tilde{L}$ as coefficients. The general solutions are²⁹

$$\begin{aligned} \mathbf{m}(t) &= \exp\left\{\tilde{\ell}t\right\} \mathbf{m}(0) \\ \mathbf{M}_z(t) &= \mathbf{M}_0 - \exp\left\{\tilde{L}t\right\} [\mathbf{M}_0 - \mathbf{M}_z(0)] \end{aligned} \quad (3.313)$$

As concerns transverse relaxation, the Bloch as well as the HMM equations stipulate that the motional-averaging condition is fulfilled (see Sect. 3.1.5.11).

The matrices $\tilde{\ell}$ and $\tilde{L}$ are defined by

$$\tilde{\ell} = i\tilde{\Omega} - \tilde{R}_2 + \tilde{K} \quad (3.314)$$

and

$$\tilde{L} = -\tilde{R}_1 + \tilde{K} \quad (3.315)$$

The matrix of the specific angular Larmor frequencies (relative to the rotating frame) is

²⁹ The analytical evaluation of matrices in exponents of exponential functions can be understood by replacing the exponential function by its expansion into a power series (see Eq. (3.325)). That is, one deals with powers of the matrices which can be evaluated as will be shown in Eq. (3.326).

$$\tilde{\Omega} = \begin{pmatrix} \omega_{0,1} & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & & & \cdot \\ \cdot & & \cdot & & \cdot \\ \cdot & & & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & \omega_{0,N} \end{pmatrix} \quad (3.316)$$

The longitudinal and transverse relaxation rate matrices

$$\begin{aligned} \tilde{R}_1 &= \begin{pmatrix} 1/T_{1,1} & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & & & \cdot \\ \cdot & & \cdot & & \cdot \\ \cdot & & & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & 1/T_{1,N} \end{pmatrix} \text{ and} \\ \tilde{R}_2 &= \begin{pmatrix} 1/T_{2,1} & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & & & \cdot \\ \cdot & & \cdot & & \cdot \\ \cdot & & & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & 1/T_{2,N} \end{pmatrix} \end{aligned} \quad (3.317)$$

represent the potential distribution of relaxation rates in the diverse environments. Finally, the exchange-kinetic matrix, which is of particular interest here, is defined as

$$\tilde{K} = \begin{pmatrix} k_{11} & \cdot & \cdot & \cdot & k_{1N} \\ \cdot & \cdot & & & \cdot \\ \cdot & & \cdot & & \cdot \\ \cdot & & & \cdot & \cdot \\ k_{N1} & \cdot & \cdot & \cdot & k_{NN} \end{pmatrix} \quad (3.318)$$

The elements k_{ji} are the transfer-rate constants from the environment “ i ” to environment “ j .” At equilibrium, the populations of the environments and, hence, all partial magnetizations are stationary. That is,

$$\frac{d}{dt} \begin{pmatrix} M_{0,1} \\ \cdot \\ \cdot \\ \cdot \\ M_{0,N} \end{pmatrix} = \begin{pmatrix} k_{11} & \cdot & \cdot & \cdot & k_{1N} \\ \cdot & \cdot & & & \cdot \\ \cdot & & \cdot & & \cdot \\ \cdot & & & \cdot & \cdot \\ k_{N1} & \cdot & \cdot & \cdot & k_{NN} \end{pmatrix} \begin{pmatrix} M_{0,1} \\ \cdot \\ \cdot \\ \cdot \\ M_{0,N} \end{pmatrix} = 0 \quad (3.319)$$

or

$$\sum_{i=1}^N k_{ji} M_{0,i} = 0 \quad (3.320)$$

Moreover, the principle of microscopic reversibility requires a detailed balance for the exchange paths. The transfer rates back and forth must be the same in each case:

$$k_{ij}M_{0,j} = k_{ji}M_{0,i} \quad (3.321)$$

Combining the conditions Eqs. (3.320) and (3.321) leads to

$$k_{ii} = - \sum_{j \neq i} k_{ij} \quad (3.322)$$

so that the exchange-kinetic matrix can be rewritten in the form

$$\tilde{K} = \begin{pmatrix} -\sum_{j \neq 1} k_{1j} & \cdot & \cdot & \cdot & k_{1N} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ k_{N1} & \cdot & \cdot & \cdot & -\sum_{j \neq N} k_{Nj} \end{pmatrix} \quad (3.323)$$

In terms of populations p_i , this result is equivalent to the familiar set of kinetic equations

$$\frac{dp_i}{dt} = \sum_{j=1}^N (k_{ij}p_j - k_{ji}p_i) \quad (3.324)$$

The positive sum terms represent the transfer rates *increasing* the population of environment “ i ,” whereas the minus sign indicates *depopulation*.

3.4.2 HMM Solutions in Terms of Eigenvalues³⁰

The general solutions of the two HMM equations, Eq. (3.313), contain exponential factors $\exp\{\tilde{P}t\}$ with $\tilde{P} = \tilde{\ell}$ and $\tilde{P} = \tilde{L}$, respectively. The exponential functions are interpreted by their expansions

$$e^{\tilde{P}t} = \sum_j \frac{1}{j!} \tilde{P}^j t^j \quad (3.325)$$

The power of the matrix $\tilde{P}$ is carried out by first diagonalizing the matrix and then applying the power according to the sandwich operation

³⁰ An introduction to matrix calculus can be found in Ref. [76], for instance.

$$\tilde{P}^j = \tilde{U} \tilde{\Lambda}^j \tilde{U}^{-1} \quad (3.326)$$

The matrix $\tilde{\Lambda}$ is the (diagonal) eigenvalue matrix of $\tilde{P}$. The transformation matrices are designated by $\tilde{U}$ and its inverse $\tilde{U}^{-1}$. The eigenvalue matrix is determined by the eigenvalues λ_k and has the form

$$\tilde{\Lambda} = \begin{pmatrix} \lambda_1 & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & & & \cdot \\ \cdot & & \cdot & & \cdot \\ \cdot & & & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & \lambda_N \end{pmatrix} \quad \text{so that} \quad \tilde{\Lambda}^j = \begin{pmatrix} \lambda_1^j & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & & & \cdot \\ \cdot & & \cdot & & \cdot \\ \cdot & & & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & \lambda_N^j \end{pmatrix} \quad (3.327)$$

The power series Eq. (3.325) can thus be analyzed as

$$\begin{aligned} e^{\tilde{P}t} &= \sum_j \frac{1}{j!} \tilde{U} \begin{pmatrix} \lambda_1^j & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & & & \cdot \\ \cdot & & \cdot & & \cdot \\ \cdot & & & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & \lambda_N^j \end{pmatrix} \tilde{U}^{-1} t^j \\ &= \tilde{U} \begin{pmatrix} e^{\lambda_1 t} & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & & & \cdot \\ \cdot & & \cdot & & \cdot \\ \cdot & & & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & e^{\lambda_N t} \end{pmatrix} \tilde{U}^{-1} \end{aligned} \quad (3.328)$$

Denoting the eigenvalues of $\tilde{\ell}$ by $\lambda_k^{(\ell)}$, and those of $\tilde{L}$ by $\lambda_k^{(L)}$, the general HMM solutions, Eq. (3.313), can finally be expressed by

$$\begin{aligned} \mathbf{m}(t) &= \tilde{U}_\ell \begin{pmatrix} e^{\lambda_1^{(\ell)} t} & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & & & \cdot \\ \cdot & & \cdot & & \cdot \\ \cdot & & & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & e^{\lambda_N^{(\ell)} t} \end{pmatrix} \tilde{U}_\ell^{-1} \mathbf{m}(0) \\ \mathbf{M}_z(t) &= \mathbf{M}_0 - \tilde{U}_L \begin{pmatrix} e^{\lambda_1^{(L)} t} & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & & & \cdot \\ \cdot & & \cdot & & \cdot \\ \cdot & & & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & e^{\lambda_N^{(L)} t} \end{pmatrix} \tilde{U}_L^{-1} [\mathbf{M}_0 - \mathbf{M}_z(0)] \end{aligned} \quad (3.329)$$

3.4.3 Two-Site Exchange Model

This is the simplest but nonetheless most relevant scenario of interest in the present context. We define two environments “1” and “2” between which exchange is to occur with rate constants k_{12} and k_{21} for the forward and backward exchange directions. The parameter sets specifying the two environments are

$$\begin{array}{ccc} \text{(environment "1")} & \begin{array}{c} T_{1,1}, T_{2,1}, \\ \dots, \omega_{0,1}, p_1 \end{array} & \begin{array}{c} \xrightarrow{k_{21}} \\ \xleftarrow{k_{12}} \end{array} & \begin{array}{c} T_{1,2}, T_{2,2}, \\ \dots, \omega_{0,2}, p_2 \end{array} & \text{(environment "2")} \end{array} \quad (3.330)$$

The populations obey the normalization relation $p_1 + p_2 = 1$. The dots indicate further relaxation times which, depending on the pulse sequence, might potentially play a role.

A typical example of such a situation is hydrogen atoms subject to exchange between OH groups and water molecules in an aqueous alcohol solution. The exchange can also be of a more physical nature such as water molecules exchanging between the hydration shells of macromolecules or polar pore surfaces and free water.

The matrices introduced above in the context of the HMM formalism now adopt the format 2×2 :

$$\begin{aligned} \tilde{\Omega} &= \begin{pmatrix} \omega_{0,1} & 0 \\ 0 & \omega_{0,2} \end{pmatrix}; & \tilde{K} &= \begin{pmatrix} -k_{21} & k_{12} \\ k_{21} & -k_{12} \end{pmatrix}; \\ \tilde{R}_1 &= \begin{pmatrix} 1/T_{1,1} & 0 \\ 0 & 1/T_{1,2} \end{pmatrix}; & \tilde{R}_2 &= \begin{pmatrix} 1/T_{2,1} & 0 \\ 0 & 1/T_{2,2} \end{pmatrix} \end{aligned} \quad (3.331)$$

The general HMM solutions Eq. (3.329), are thus reduced to

$$\begin{aligned} \mathbf{m}(t) &= \begin{pmatrix} m_1 \\ m_2 \end{pmatrix} = \tilde{U}_\ell \begin{pmatrix} e^{\lambda_1^{(\ell)} t} & 0 \\ 0 & e^{\lambda_2^{(\ell)} t} \end{pmatrix} \tilde{U}_\ell^{-1} \mathbf{m}(0) \\ \mathbf{M}_z(t) - \mathbf{M}_0 &= \begin{pmatrix} M_{z,1} \\ M_{z,2} \end{pmatrix} - \begin{pmatrix} M_{0,1} \\ M_{0,2} \end{pmatrix} = -\tilde{U}_L \begin{pmatrix} e^{\lambda_1^{(L)} t} & 0 \\ 0 & e^{\lambda_2^{(L)} t} \end{pmatrix} \tilde{U}_L^{-1} [\mathbf{M}_0 - \mathbf{M}_z(0)] \end{aligned} \quad (3.332)$$

In the following, we will distinguish two limits of these solutions with respect to the exchange rates.

3.4.3.1 Slow Exchange

In the limit $|k_{21}|, |k_{12}| \ll |T_{1,2}^{-1} - T_{1,1}^{-1}|$, the total longitudinal magnetization, $M_z(t) = M_{z,1}(t) + M_{z,2}(t)$, with the equilibrium value $M_0 = M_{0,1} + M_{0,2} = p_1 M_0 + p_2 M_0$ obeys

$$\frac{M_z(t) - M_0}{M_z(0) - M_0} = p_1 \exp\left\{-\left(\frac{1}{T_{1,1}} + k_{21}\right)t\right\} + (1 - p_1) \exp\left\{-\left(\frac{1}{T_{1,2}} + k_{12}\right)t\right\} \quad (3.333)$$

Likewise, we find the relation

$$\frac{m(t)}{m(0)} = p_1 \exp\left\{\left(i\omega_{0,1} - \frac{1}{T_{2,1}} - k_{21}\right)t\right\} + (1 - p_1) \exp\left\{\left(i\omega_{0,2} - \frac{1}{T_{2,2}} - k_{12}\right)t\right\} \quad (3.334)$$

for the total transverse magnetization $m(t) = m_1(t) + m_2(t)$ at very low exchange rates obeying $|k_{21}|, |k_{12}| \ll |\omega_{0,1} - \omega_{0,2}|, |T_{2,2}^{-1} - T_{2,1}^{-1}|$.

3.4.3.2 Fast Exchange

For high exchange rates, that is, $|k_{21}|, |k_{12}| \gg |T_{1,2}^{-1} - T_{1,1}^{-1}|$, the total longitudinal magnetization decays according to

$$\frac{M_z(t) - M_0}{M_z(0) - M_0} = \exp\left\{-\left(\frac{p_1}{T_{1,1}} + \frac{p_2}{T_{1,2}}\right)t\right\} \quad (3.335)$$

The total transverse magnetization, on the other hand, follows

$$\frac{m(t)}{m(0)} = \exp\left\{\left[i(p_1\omega_{0,1} + p_2\omega_{0,2}) - \frac{p_1}{T_{2,1}} - \frac{p_2}{T_{2,2}} - k_{12}\right]t\right\} \quad (3.336)$$

if $|k_{21}|, |k_{12}| \gg |\omega_{0,1} - \omega_{0,2}|, |T_{2,2}^{-1} - T_{2,1}^{-1}|$. The fast-exchange limit is thus ruled by mono-exponential relaxation curves and single-line resonances characterized by the effective parameters

$$\begin{aligned} \frac{1}{T_1} &= \frac{p_1}{T_{1,1}} + \frac{1 - p_1}{T_{1,2}} \\ \frac{1}{T_2} &= \frac{p_1}{T_{2,1}} + \frac{1 - p_1}{T_{2,2}} \\ \omega_0 &= p_1\omega_{0,1} + (1 - p_1)\omega_{0,2} \end{aligned} \quad (3.337)$$

Recall that this behavior stipulates *motional averaging* as concerns transverse relaxation. Note also that the above treatment is only valid for free evolution

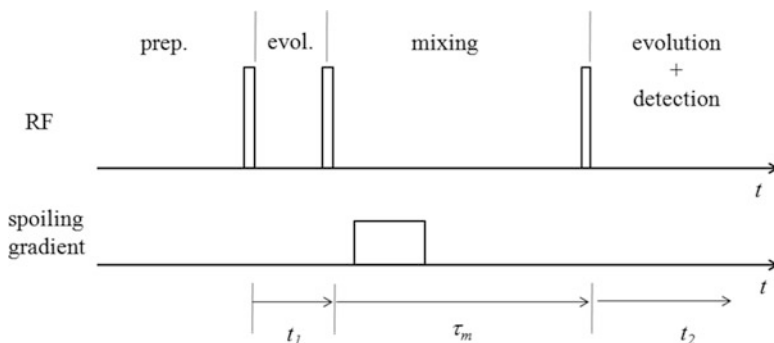


Fig. 3.34 RF pulse sequence for 2D exchange experiments. The sequence is based on three 90° RF pulses defining the intervals “preparation” (of the initial spin coherences), “evolution” (with different Larmor frequencies in different environments), “mixing” (of coherences by interchange of environments by exchange), and “detection” of the signal. Two (Fourier) time domains, t_1 and t_2 , are distinguished. They serve phase- and frequency encoding, respectively, of the spin coherences. The first evolution interval, t_1 , is incremented in subsequent transients, whereas the t_2 domain is probed by acquisition of the FID. The conjugated frequency domains, ω_1 and ω_2 , are interrelated to the two time domains by twofold Fourier transformation. Under normal circumstances, the mixing interval, τ_m , is much longer than t_1 and t_2 . Therefore, it is this interval that specifies the time scale of the exchange and relaxation processes to be detected via cross peaks. The (optional) spoiling gradient in the mixing interval is to randomize residual coherences in the mixing interval. Undesired signals originating from such coherences can also be eliminated with the aid of suitable phase cycles of the RF pulses

of the transverse magnetizations once excited at the beginning of the experiment. A different situation arises if a CPMG pulse train (see Sect. 3.1.4.7) is applied [77, 78].

3.4.4 Two-Dimensional Exchange Spectroscopy

The different resonance frequencies, exchange rates, and pathways between different spin environments can commonly be studied with the aid of *two-dimensional (2D) exchange spectroscopy* (EXSY) [2]. An RF pulse sequence suitable for this purpose is shown in Fig. 3.34. The principle is to *phase encode* the coherences of the isochromats for the different resonances in the *evolution interval* of length t_1 . The *frequency-encoded* signal is recorded in the detection interval on a time axis t_2 . Between the evolution and detection intervals, the *mixing interval* of length τ_m is sandwiched. There is a certain analogy to the two-dimensional imaging technique described in Sect. 3.3.1. In principle, the same encoding measures are employed. The main difference is that no encoding gradients are involved so that the information to be acquired is of a spectroscopic nature instead of a spatial one.

The treatment of the pulse scheme in Fig. 3.34 is simplified if a number of conditions are fulfilled. The spins under consideration are assumed to have different resonance frequencies in different environments, but are not coupled by spin interactions. There is therefore no need to consider multiple-quantum coherences and spin-order phenomena as competing processes [1, 2]. The exchange is supposed to be slow enough so that coalescence of the resonances can be excluded.

The pulse sequence starts with the spin system in thermal equilibrium. The transverse and longitudinal magnetization system vectors (see Eq. (3.311)) at time $t = 0 -$ are

$$\begin{aligned} \mathbf{m}(0-) &= 0 \\ \mathbf{M}_z(0-) &= \mathbf{M}_0 \end{aligned} \quad (3.338)$$

As in previous sections, minus and plus signs indicate that the respective moments *just before* and *immediately after* the RF pulse under consideration are meant. The first 90° RF pulse is applied along the y' -axis of the frame rotating with the carrier frequency centered in the spectrum. The magnetization system vectors after the pulse are thus flipped to

$$\begin{aligned} \mathbf{m}(0+) &= -\mathbf{M}_0 \\ \mathbf{M}_z(0+) &= 0 \end{aligned} \quad (3.339)$$

In the following free-evolution period, the magnetization components are subject to relaxation and precession with the rotating-frame Larmor frequencies $\omega_{0,k}$ for the respective environments. According to Eq. (3.313), the magnetization system vectors before the second RF pulse thus evolve to

$$\begin{aligned} \mathbf{m}(t_1-) &= \exp\{(i\tilde{\Omega} - \tilde{R}_2 + \tilde{K})t_1\}\mathbf{m}(0+) \\ \mathbf{M}_z(t_1-) &= \mathbf{M}_0 - \exp\{(-\tilde{R}_1 + \tilde{K})t_1\}[\mathbf{M}_0 - \mathbf{M}_z(0+)] \end{aligned} \quad (3.340)$$

where the matrices $\tilde{\Omega}$, $\tilde{R}_1$, $\tilde{R}_2$, and $\tilde{K}$ for the frequencies, relaxation and exchange rates are defined in Eqs. (3.316), (3.317), and (3.318).

The second 90° RF pulse with the rotating-frame phase direction y' transfers the x' components of the transverse magnetizations into the z' direction, whereas the components along the y' direction are left untouched. The magnetization system vectors at the beginning of the mixing interval thus take the form

$$\begin{aligned} \mathbf{m}(t_1+) &= -\mathbf{M}_z(t_1-) + i\Im\{\mathbf{m}(t_1-)\} \\ \mathbf{M}_z(t_1+) &= \Re\{\mathbf{m}(t_1-)\} \end{aligned} \quad (3.341)$$

where the symbols $\Im\{\dots\}$ and $\Re\{\dots\}$ refer to the imaginary and real part, respectively. The *homospoil* field-gradient pulse in the mixing interval (see Fig. 3.34) dephases all remaining coherences completely so that their evolution can no longer lead to contributions to the final signal. The transverse magnetization

can therefore be set zero, while the longitudinal magnetizations are subject to exchange and spin–lattice relaxation. At the end of the mixing interval, we thus have

$$\begin{aligned} m(t_1 + \tau_m -) &= 0 \\ \mathbf{M}_z(t_1 + \tau_m -) &= \mathbf{M}_0 - \exp\left\{(-\tilde{R}_1 + \tilde{K})\tau_m\right\}[\mathbf{M}_0 - \mathbf{M}_z(t_1 +)] \end{aligned} \quad (3.342)$$

The third 90° RF pulse having again a phase direction y' converts the z' magnetizations into transverse magnetizations according to

$$\begin{aligned} m(t_1 + \tau_m +) &= -\mathbf{M}_z(t_1 + \tau_m -) \\ \mathbf{M}_z(t_1 + \tau_m +) &= 0 \end{aligned} \quad (3.343)$$

The evolution in the detection interval produces the complex transverse magnetization

$$m(t_1 + \tau_m + t_2) = -\exp\left\{(i\tilde{\Omega} - \tilde{R}_2 + \tilde{K})t_2\right\}\mathbf{M}_z(t_1 + \tau_m -) \quad (3.344)$$

Substituting step by step all magnetization terms by the expressions for the preceding intervals gives

$$\begin{aligned} m(t_1 + \tau_m + t_2) &= -\exp\left\{(i\tilde{\Omega} - \tilde{R}_2 + \tilde{K})t_2\right\} \\ &\times \left[1 - \exp\left\{(-\tilde{R}_1 + \tilde{K})\tau_m\right\}\left(1 + \Re\left\{\exp\left\{(i\tilde{\Omega} - \tilde{R}_2 + \tilde{K})t_1\right\}\right\}\right)\right]\mathbf{M}_0 \end{aligned} \quad (3.345)$$

All terms not depending on t_1 give rise to *axial peaks* (see below) which are of no further interest here. The figures 1 in the above expression can therefore be discarded. Furthermore, the treatment can be simplified in the following by neglecting the influence of relaxation and exchange during the evolution periods t_1 and t_2 . That is, we anticipate the limit $t_1, t_2 \ll T_{2j}, k_{ij}^{-1}$:

$$m(t_1 + \tau_m + t_2) \approx \exp\left\{i\tilde{\Omega}t_2\right\}\exp\left\{(-\tilde{R}_1 + \tilde{K})\tau_m\right\}\Re\left\{\exp\left\{i\tilde{\Omega}t_1\right\}\right\}\mathbf{M}_0 \quad (3.346)$$

The complex transverse magnetization Eq. (3.346), now considered as a function $m = m(t_1, t_2)$ of the two independent variables t_1 and t_2 , is the quantity to be acquired and to be processed as a two-dimensional spectrum $\tilde{S}(\omega_1, \omega_2, \tau_m)$. Before discussing the results, let us first explain the specific detection technology required for this purpose.

For a given interval t_1 , the signal can be recorded as a function of t_2 in *quadrature*: In NMR spectroscopy, the signal component *in phase* with the reference phase of the phase-sensitive detector is defined as the real part of the complex signal. The imaginary part is then in quadrature to this signal, that is, 90° out of the

reference phase. Both parts can be acquired at a time with the aid of a two-channel phase-sensitive receiver with the reference phases in quadrature. The two data sets obtained in this way permit the complex Fourier transformation from the time scale t_2 to the frequency domain ω_2 .

What about the t_1 variable? Equation (3.346) obviously provides only the real part for the particular pulse phases assumed in the above derivation. The problem is, that, as before, both the real and the imaginary parts are needed if the time domain t_1 is to be Fourier transformed to the conjugate frequency domain ω_1 . The remedy is to mimic quadrature detection by alternately choosing the phase directions of the second RF pulse along the y' - and x' -axes in subsequent transients [79]. That is, two data sets are recorded for the real and imaginary part. They can be represented by the expressions

$$\begin{aligned} \mathbf{m}(t_1 + \tau_m + t_2)|_{y'} &= \exp\{i\tilde{\Omega}t_2\} \exp\{(-\tilde{R}_1 + \tilde{K})\tau_m\} \Re\left\{\exp\{i\tilde{\Omega}t_1\} \mathbf{M}_0\right\} \\ \mathbf{m}(t_1 + \tau_m + t_2)|_{x'} &= i \exp\{i\tilde{\Omega}t_2\} \exp\{(-\tilde{R}_1 + \tilde{K})\tau_m\} \Im\left\{\exp\{i\tilde{\Omega}t_1\} \mathbf{M}_0\right\} \end{aligned} \quad (3.347)$$

Combining the two separately acquired signals finally yields the complex transverse magnetization

$$\mathbf{m}(t_1 + \tau_m + t_2) = \exp\{i\tilde{\Omega}t_2\} \exp\{(-\tilde{R}_1 + \tilde{K})\tau_m\} \exp\{i\tilde{\Omega}t_1\} \mathbf{M}_0 \quad (3.348)$$

needed for the twofold complex Fourier transformation from the time domains t_1 and t_2 to the respective angular-frequency domains ω_1 and ω_2 . The result of this operation will be a complex function again. As a quantity that can conveniently be plotted in the form of two-dimensional spectra, one usually calculates the magnitude of $\mathbf{m}(t_1 + \tau_m + t_2)$.

Further evaluation of the general result Eq. (3.348) requires the specification of a certain exchange network. An example is exchange between two-spin environments as represented by the scheme in Eq. (3.330). For the sake of simplicity, let us assume that the transfer-rate constants and the spin-lattice relaxation times are equal in each case, that is, $k_{12} = k_{21} = k$ and $T_{1,1} = T_{1,2} = T_1$. The mean residence time in each of the environments is consequently $\tau = 1/k$.

Under these assumptions, the exponential functions on the right-hand side of Eq. (3.348) can be expressed by

$$\begin{aligned} \exp\{i\tilde{\Omega}t_n\} &= \sum_j \frac{1}{j!} \tilde{\Omega}^j t_n^j \\ &= \sum_j \frac{1}{j!} \begin{pmatrix} \omega_{0,1} & 0 \\ 0 & \omega_{0,2} \end{pmatrix}^j (it_n)^j = \begin{pmatrix} \exp\{i\omega_{0,1}t_n\} & 0 \\ 0 & \exp\{i\omega_{0,2}t_n\} \end{pmatrix} \end{aligned} \quad (3.349)$$

and

$$\begin{aligned}
 \exp\{(-R_1 + K)\tau_m\} &= \sum_j \frac{1}{j!} \begin{pmatrix} -1/T_1 - k & k \\ k & -1/T_1 - k \end{pmatrix}^j \tau_m^j \\
 &= \frac{1}{2} \begin{pmatrix} 1 + \exp\{-2k\tau_m\} & 1 - \exp\{-2k\tau_m\} \\ 1 - \exp\{-2k\tau_m\} & 1 + \exp\{-2k\tau_m\} \end{pmatrix} \exp\left\{-\frac{\tau_m}{T_1}\right\}
 \end{aligned} \tag{3.350}$$

where $n = 1$ or 2 . Replacing the exponential functions in Eq. (3.348) and representing the transverse magnetization system vector in component form lead to

$$\begin{aligned}
 &\begin{pmatrix} m_1(t = t_1 + \tau_m + t_2) \\ m_2(t = t_1 + \tau_m + t_2) \end{pmatrix} \\
 &= \frac{1}{2} \exp\left\{-\frac{\tau_m}{T_1}\right\} \\
 &\times \begin{pmatrix} [1 + \exp\{-2k\tau_m\}] \exp\{i\omega_{0,1}(t_1 + t_2)\} & [1 - \exp\{-2k\tau_m\}] \exp\{i(\omega_{0,1}t_2 + \omega_{0,2}t_1)\} \\ [1 - \exp\{-2k\tau_m\}] \exp\{i(\omega_{0,2}t_2 + \omega_{0,1}t_1)\} & [1 + \exp\{-2k\tau_m\}] \exp\{i\omega_{0,2}(t_1 + t_2)\} \end{pmatrix} \begin{pmatrix} M_{0,1} \\ M_{0,2} \end{pmatrix} \\
 &= \frac{1}{2} \exp\left\{-\frac{\tau_m}{T_1}\right\} \\
 &\times \begin{pmatrix} [1 + \exp\{-2k\tau_m\}] \exp\{i\omega_{0,1}(t_1 + t_2)\} M_{0,1} + [1 - \exp\{-2k\tau_m\}] \exp\{i(\omega_{0,1}t_2 + \omega_{0,2}t_1)\} M_{0,2} \\ [1 - \exp\{-2k\tau_m\}] \exp\{i(\omega_{0,2}t_2 + \omega_{0,1}t_1)\} M_{0,1} + [1 + \exp\{-2k\tau_m\}] \exp\{i\omega_{0,2}(t_1 + t_2)\} M_{0,2} \end{pmatrix}
 \end{aligned} \tag{3.351}$$

The signals detected in experiments are proportional to the sum of the partial transverse magnetizations

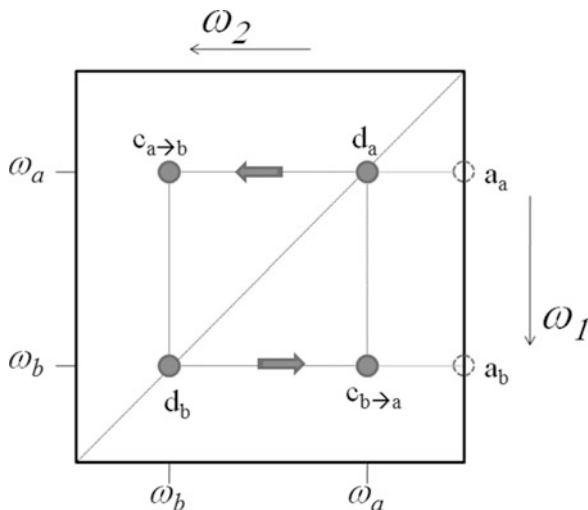
$$S(t_1, t_2, \tau_m) \propto m_1(t = t_1 + \tau_m + t_2) + m_2(t = t_1 + \tau_m + t_2) \tag{3.352}$$

The twofold Fourier transformation with respect to the time domains t_1 and t_2 gives the two-dimensional spectrum $\tilde{S}(\omega_1, \omega_2, \tau_m)$ with the mixing time τ_m as an experimental parameter. Taking the magnitude $|\tilde{S}(\omega_1, \omega_2, \tau_m)|$ and plotting this function in two-dimensional representation versus ω_1 and ω_2 gives the desired spectrum as schematically illustrated in Fig. 3.35.

The spectrum in principle consists of *diagonal*, *cross*, and *axial* peaks labeled with the letters d, c, and a. The diagonal peaks represent spins having suffered either no exchange or a cyclic one. Exchange among sites with different resonance frequencies gives rise to cross peaks which are therefore indicative for the process of interest in the present context. Axial peaks eventually appear because of incomplete excitation by the pulses or owing to spin-lattice relaxation in the mixing interval.

The intensities of the diagonal peaks at the positions $\omega_{0,1}, \omega_{0,1}$ and $\omega_{0,2}, \omega_{0,2}$ are proportional to $\frac{1}{2}[1 + \exp\{-2k\tau_m\}] \exp\{-\tau_m/T_1\} M_{0,1}$ and $\frac{1}{2}[1 + \exp\{-2k\tau_m\}] \exp\{-\tau_m/T_1\} M_{0,2}$, respectively. The cross peaks are located at the positions $\omega_{0,1}, \omega_{0,2}$ and $\omega_{0,2}, \omega_{0,1}$. Their respective intensities are proportional to

Fig. 3.35 Schematic *top-view* representation of a two-dimensional exchange spectrum for a sample containing two different spin environments “a” and “b,” that is, two different (angular) resonance frequencies ω_a and ω_b , respectively. The peak locations are indicated by circles. The two diagonal peaks are labeled by d_a and d_b , the cross peaks as $c_{a \rightarrow b}$ and $c_{b \rightarrow a}$, and the axial peaks as a_a and a_b . The *thick arrows* indicate the spectral exchange pathways leading to cross peaks



$\frac{1}{2}[1 - \exp\{-2k\tau_m\}] \exp\{-\tau_m/T_1\}M_{0,1}$ and $\frac{1}{2}[1 - \exp\{-2k\tau_m\}] \exp\{-\tau_m/T_1\}M_{0,2}$. For vanishing exchange rate constant, that is, $k = 0$, consequently no cross peaks are expected. The maximum cross-peak intensity is achieved if the mixing time obeys the condition $\tau_m = \frac{1}{2k} \ln(2kT_1 + 1)$. These relations may give an idea how detailed the dynamic exchange parameters of an exchange network can be elucidated with the aid of two-dimensional exchange NMR spectroscopy.

3.4.5 Two-Dimensional Spin Relaxation and Diffusion Correlation Maps

The NMR relaxometry and diffusometry techniques described in this chapter refer altogether to particle *ensembles*. When applied to *heterogeneous* media, the results must consequently be decomposed into distinct components contributing to the acquired signals. In systems consisting of different, more or less distinct “pools,” that is, compartmented heterogeneities of structure and dynamics, that are associated with different spin-relaxation times and diffusion coefficients, exchange correlation experiments can be carried out even if no spectroscopic distinction of the pools is possible.

In this case, correlation maps do not refer to intensities of different resonance lines but to amplitude factors of different relaxation or echo-attenuation components [80, 81]. It is anticipated that the corresponding NMR signals are proportional to superpositions of distributions of the type $1 - \sum_j a_j \exp\{-t/T_1^{(j)}\}$, $\sum_j b_j \exp\{-t/T_2^{(j)}\}$, and $\sum_j c_j \exp\{-q^2 t D_j\}$, where a_j, b_j, c_j are the respective

amplitude factors and $T_1^{(j)}, T_2^{(j)}, D_j$ are the respective pool spin-relaxation times and diffusion coefficients. q is the field-gradient wave number defined in Eq. (3.225).

In principle, the RF pulse and field-gradient pulse sequences employed for the acquisition of two-dimensional spin relaxation and diffusion correlation maps are analogous to that employed for two-dimensional exchange spectroscopy (see Fig. 3.34): Apart from preparation of the desired initial nonequilibrium magnetization, they consist of two *evolution* intervals possibly separated by a *mixing* interval. In the present case, the term “evolution” by contrast does not refer to precession with different Larmor frequencies, but to attenuation by spin relaxation or diffusive displacements in the presence of field gradients. That is, the evolution intervals imply elements typical for relaxometry and diffusometry as described in Sects. 3.1.4 and 3.2. Examples are inversion–recovery and CPMG RF pulse sequels and field-gradient pulse pairs. The first evolution interval needs to be incremented in subsequent transients in order to cover the desired time range. It may also be necessary to increment the second evolution unless complete relaxation curves are detected at a time as it is the case with CPMG sequels.

Instead of the data processing known from two-dimensional exchange spectroscopy, that is, Fourier transformation of the two-dimensional time dependence of the acquired signal data set, two-dimensional spin relaxation or diffusion correlation maps are evaluated with the aid of the *inverse Laplace transform* procedure [82, 83]. The signal amplitudes S can thus be determined as functions of the spin-relaxation times or the diffusion coefficient. In principle, any combination of the measurands accessible by relaxometry and diffusometry techniques can be correlated in this way. Typical examples are maps $S(T_2, T_2)$ [84–86], $S(T_1, T_2)$ [87], $S(D, T_2)$ [88], $S(T_1, D)$ [89], and $S(D, D)$ [90–92]. In each case, cross peaks indicate exchange between the pools during the pulse sequence.

Numerous applications are reported in the references cited above. Experiments of this sort may be powerful tools for rough assessments of exchange features in practical systems. A word of caution should nevertheless be added at this point: The techniques work only unambiguously if (1) the system consists of a *finite* (and small) number of pools with really *distinct* relaxation or diffusion parameters and (2) the pool relaxation and echo-attenuation curves must be *mono-exponential* as anticipated above. The latter condition is often violated in complex systems where diffusion tends to be anomalous (see Sect. 2.5.1.3) and where transverse relaxation curves can be influenced by residual spin couplings (see the subsequent section).

3.5 The Dipolar-Correlation Effect

Field-cycling NMR relaxometry and studies of residual dipolar couplings based on the Anderson/Weiss theory are methods sensitive to relatively slow molecular dynamics. This category is supplemented by the *dipolar-correlation effect* arising in systems where dipolar couplings are not or only incompletely averaged [93, 94].

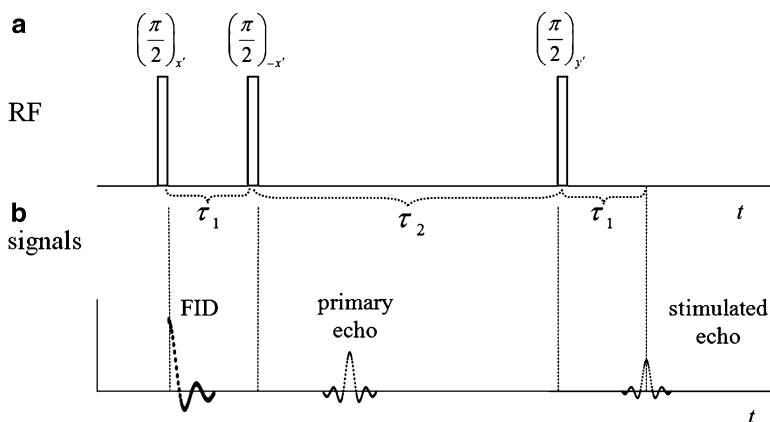


Fig. 3.36 Stimulated-echo RF pulse sequence for measuring the dipolar-correlation effect

The relevant time scale starts typically at about 10^{-4} s, that is, in the limit where the motional-averaging condition, $\Omega_{\text{rl}}\tau_c \ll 1$, which relates the correlation time of the fluctuating spin interactions, τ_c , and the rigid-lattice linewidth, Ω_{rl} , is no longer warranted. Applications of the dipolar-correlation effect include the case where the motional-averaging condition is fulfilled only for a spatially restricted component of molecular reorientations, whereas it is violated otherwise. Typical examples of this sort are liquid crystals or polymers. Under such circumstances, motional averaging tends to be restricted to rotational diffusion and reorientations about the molecular long axis.

The experimental technique is based on a sequence of three 90° RF pulses, the versatility of which has already been demonstrated in the context of field-gradient NMR diffusometry and two-dimensional exchange spectroscopy. In the present case, the peculiar point is that no gradient is employed apart from the inhomogeneities intrinsic to the magnet. The signals to be acquired are the *primary* and the *stimulated echo* as specified in Fig. 3.36. As will be explained in more detail below, these signals appear at times $t = 2\tau_1$ and $t = 2\tau_1 + \tau_2$, respectively, where the time intervals are defined in the figure.³¹ The respective complex transverse magnetizations inducing the maximum echo signals will be designated by $m(2\tau_1)$ and $m(2\tau_1 + \tau_2)$. With the usual definition of the times immediately after the first RF pulse, $t = 0+$, and immediately after the third RF pulse, $t = \tau_1 + \tau_2 +$, the attenuation factors of the primary echo

$$a_{\text{pr}}(2\tau_1) \equiv \frac{|m(2\tau_1)|}{|m(0+)|} a_{\text{r2}}(2\tau_1) a_{\text{dc}}(2\tau_1) \quad (3.353)$$

³¹ Note that the particular choice of the rotating-frame pulse phases and of the flip angles specified in Fig. 3.36 prevents the occurrence of a so-called *dipolar-order transfer echo* (see Ref. [1], for instance) which otherwise would be superimposed to the stimulated echo and, hence, would complicate the treatment.

and of the stimulated echo

$$a_{\text{st}}(2\tau_1 + \tau_2) \equiv \frac{|m(2\tau_1 + \tau_2)|}{|m(\tau_1 + \tau_2)|} a_{r2}(2\tau_1) a_{r1}(\tau_2) a_{\text{dc}}(2\tau_1 + \tau_2) \quad (3.354)$$

can be expressed by the familiar contributions by transverse relaxation, $a_{r2}(2\tau_1)$, and spin–lattice relaxation, $a_{r1}(\tau_2)$, which we know already from the complete motional-averaging case. In addition, $a_{\text{dc}}(2\tau_1)$ and $a_{\text{dc}}(2\tau_1 + \tau_2)$ are introduced as new factors accounting for attenuation by fluctuating residual dipolar couplings. The examination of the latter phenomenon is referred to as *dipolar-correlation effect*.

The experimental technique specified so far for the record of the dipolar-correlation effect and the subsequent theoretical treatment anticipate that the evolution of spin coherences is exclusively affected by (residual) dipolar couplings and (external) field gradients. However, in complex systems, *spin exchange* between sites of different chemical-shift and susceptibility-induced offsets may give rise to superimposed undulations of the echo-attenuation curves possibly concealing the proper dipolar-correlation effect. This problem can be remedied by modifying the pulse sequence by additional 180° RF pulses in the free-evolution intervals. A detailed description can be found in Ref. [95]. In the present treatise, we will restrict ourselves to the discussion of the basic stimulated-echo pulse sequence.

3.5.1 The Residual Dipolar-Coupling Constant

In the following, we will refer to an ensemble of systems each consisting of two equivalent spins $1/2$. The spin vector operators are denoted by $\mathbf{I}_k$ and $\mathbf{I}_l$. According to the expansion of the dipolar Hamiltonian specified in Eqs. (3.88), (3.89), (3.90), and (3.91), the combined secular terms can be expressed in the form of the *truncated Hamiltonian*

$$\mathcal{H}_{\text{d}}^{(0)} = \frac{\mu_0}{4\pi} \gamma^2 \hbar^2 \frac{1 - 3 \cos^2 \vartheta_{kl}}{r_{kl}^3} \frac{1}{2} \{3I_{kz}I_{lz} - \mathbf{I}_k \cdot \mathbf{I}_l\} \quad (3.355)$$

where r_{kl} and ϑ_{kl} are the magnitude and the polar angle (relative to the external magnetic flux density $\mathbf{B}_0$) of the internuclear distance vector. In quantum-mechanical terms, the two-spin systems under consideration are composed of *indistinguishable* particles. It is then appropriate to consider the total spin

$$\mathbf{F} = \mathbf{I}_k + \mathbf{I}_l \quad (3.356)$$

On this basis, the scalar product on the right-hand side of Eq. (3.355) can be replaced by

$$\mathbf{I}_k \cdot \mathbf{I}_l = \frac{1}{2} (\mathbf{F}^2 - \mathbf{I}_k^2 - \mathbf{I}_l^2) = \frac{1}{2} [F(F+1) - I_k(I_k+1) - I_l(I_l+1)] \quad (3.357)$$

where F, I_k, I_l represent the respective spin quantum numbers.

In the present case of 2-spin- $\frac{1}{2}$ systems, the two possible quantum numbers of the total spin are $F = \frac{1}{2} - \frac{1}{2} = 0$ (*singlet state*) and $F = \frac{1}{2} + \frac{1}{2} = 1$ (*triplet state*). The singlet state does not reveal itself in NMR experiments. For the triplet state the scalar product is equal to $1/4$ and can be dropped from the Hamilton operator because it does not influence the evolution of the density operator. It merely reduces all triplet energy eigenvalues by a constant amount $-\frac{\mu_0}{4\pi} \frac{1}{8} \frac{\gamma^2 \hbar^2}{r_{kl}^3} (1 - 3 \cos^2 \vartheta_{kl})$ where the constants $\mu_0, \gamma, \hbar$ have the usual meaning. The remaining Hamiltonian effective for the evolution of equivalent two-spin $\frac{1}{2}$ coherences is thus reduced to³²

$$\mathcal{H}_d^{(\text{ev})} = \frac{\mu_0}{4\pi} \frac{3}{2} \frac{\gamma^2 \hbar^2}{r_{kl}^3} (1 - 3 \cos^2 \vartheta_{kl}) I_{kz} I_{lz} \quad (3.358)$$

With the definition of the dipolar-coupling constant (in angular-frequency units)

$$\Omega_d = \frac{3\mu_0 \gamma^2 \hbar (1 - 3 \cos^2 \vartheta_{kl})}{8\pi r_{kl}^3} \quad (3.359)$$

the effective Hamiltonian reads

$$\mathcal{H}_d^{(\text{ev})} = \hbar \Omega_d I_{kz} I_{lz} \quad (3.360)$$

For typical applications, the secular dipolar interactions are assumed to be *partially* averaged by molecular reorientations that are fast but restricted with respect to the solid-angle range of the internuclear vector. The correlation time of this contribution, τ_f , thus obeys the motional-averaging condition $\Omega_{rl} \tau_f \ll 1$, where Ω_{rl} is the rigid-lattice linewidth. For protons, this limit typically means $\tau_f \ll 10^{-5}$ s, whereas the experimental time scale defined by the spacings in the pulse sequence Fig. 3.36 is much longer, that is, $\tau_f \ll \tau_1, \tau_2$. The *residual dipolar-coupling constant* is then defined as the average $\bar{\Omega}_d$ formed over the time scale of this fast component of molecular reorientations. For instance, the addition theorem of spherical harmonics suggests

$$\bar{\Omega}_d = \frac{3\mu_0 \gamma^2 \hbar}{16\pi r_{kl}^3} (1 - 3 \cos^2 \alpha) (3 \cos^2 \beta_{kl} - 1) \quad (3.361)$$

³² At this point, it should be noted that this version of the dipolar Hamilton operator is solely introduced for the treatment of the *evolution* of spin coherences, but is not suitable for the calculation of dipolar spectra [1].

for fast rotation about a fixed axis, where α is the polar angle of the rotation axis relative to $\mathbf{B}_0$ and β_{kl} is the angle spanned by the internuclear vector and the rotation axis.³³

It is now of crucial importance to note that the residual dipolar-coupling constant $\bar{\Omega}_d$ is reduced but not necessarily stationary. It can rather fluctuate as a consequence of slow dynamic processes with time constants τ_s complying with the condition $\Omega_{rl}\tau_s > 1$. In the case of rotational diffusion about an axis exemplified in Eq. (3.361), this means that the rotation axis and, hence, the angle α tumble slowly with a rate not leading to further motional averaging. In this sense, the attribute “secular” of the dipolar interactions has the meaning of “very slowly varying” relative to a fluctuation rate corresponding to the rigid-lattice linewidth Ω_{rl} .

Monitoring such slow fluctuations $\bar{\Omega}_d = \bar{\Omega}_d(t)$ with the aid of the pulse sequence shown in Fig. 3.36 requires that the experimental time scale defined by the pulse spacings is of the order $\tau_1, \tau_2 \approx \tau_s < T_1$. Spin coherences can only be refocused in the form of echoes as far as the residual dipolar couplings are *correlated* in the whole echo-formation process. Actually, this is the realm of dynamics to be studied by the technique to be outlined in the following.

3.5.2 Echo-Attenuation Functions Due to Residual Dipolar Couplings

During the pulse sequence depicted in Fig. 3.36, the evolution of the coherences of two-spin $\frac{1}{2}$ systems with vector operators $\mathbf{I}_k$ and $\mathbf{I}_l$ starts in thermal equilibrium. The corresponding (reduced) density operator prior to the first RF pulse therefore reads³⁴

$$\sigma(0-) = I_{kz} + I_{lz} \quad (3.362)$$

According to the convention introduced above, the minus sign indicates a time just before the first RF pulse. The effect of the initial $(\pi/2)_x$ pulse is

$$\sigma(0+) = I_{ky} + I_{ly} \quad (3.363)$$

where the time 0+ refers to the instant immediately after the RF pulse. During the first pulse interval, the spin coherences represented by the operators in

³³ In the case of powder distributions, the final result of the treatment must be averaged over all angles ϑ' between the rotation axis and the external magnetic flux density.

³⁴ For a definition of density operators and their reduced form, see footnote 8 and the references cited there. A good introduction to the treatment of coherence evolution with the aid of reduced density operators can also be found in Ref. [21].

Eq. (3.363) evolve in the rotating frame under the influence of offsets Ω_g arising from magnetic-field inhomogeneities, and offsets due to the residual dipolar-coupling constant $\bar{\Omega}_d$. The resulting density operator is

$$\begin{aligned} \sigma(\tau_1-) = & \left[(I_{ky} + I_{ly}) \cos \varphi_{d1} - 2(I_{kx}I_{lz} + I_{lx}I_{kz}) \sin \varphi_{d1} \right] \cos \varphi_{g1} \\ & + \left[(I_{kx} + I_{lx}) \cos \varphi_{d1} + 2(I_{ky}I_{lz} + I_{ly}I_{kz}) \sin \varphi_{d1} \right] \sin \varphi_{g1} \end{aligned} \quad (3.364)$$

where the respective precession phase shifts are

$$\varphi_{g1} = \int_0^{\tau_1} \Omega_g(t') dt' \quad (3.365)$$

and

$$\varphi_{d1} = \frac{1}{2} \int_0^{\tau_1} \bar{\Omega}_d(t') dt' \quad (3.366)$$

For simplicity, it is assumed here that the magnet-inhomogeneity offset Ω_g originates from a spatially constant gradient $\mathbf{g}$ according to $\Omega_g = \gamma \mathbf{g} \cdot \mathbf{r}$, where $\mathbf{r}$ is the position of the spin system relative to the gradient.

The second RF pulse, $(\pi/2)_{-x}$, converts Eq. (3.364) into

$$\begin{aligned} \sigma(\tau_1+) = & \left[(I_{kz} + I_{lz}) \cos \varphi_{d1} + 2(I_{kx}I_{ly} + I_{lx}I_{ky}) \sin \varphi_{d1} \right] \cos \varphi_{g1} \\ & + \left[(I_{kx} + I_{lx}) \cos \varphi_{d1} + 2(I_{kz}I_{ly} + I_{lz}I_{ky}) \sin \varphi_{d1} \right] \sin \varphi_{g1} \end{aligned} \quad (3.367)$$

The term $2(I_{kx}I_{ly} + I_{lx}I_{ky}) \sin \varphi_{d1}$ represents zero- and double-quantum coherences in the τ_2 interval [1, 21]. These coherence species can be disregarded in the further treatment since they will not contribute to the primary and the stimulated echo under the envisaged conditions. As concerns the stimulated echo, spin coherences of any order are expected to fade away in the τ_2 interval by transverse relaxation in view of the residual dipolar couplings anticipated in this sort of experiment.

The remaining part of Eq. (3.367) can be split into two terms according to

$$\sigma(\tau_1+) = \sigma_{st}(\tau_1+) + \sigma_{pr}(\tau_1+) \quad (3.368)$$

The first contribution,

$$\sigma_{st}(\tau_1+) = (I_{kz} + I_{lz}) \cos \varphi_{d1} \cos \varphi_{g1} \quad (3.369)$$

eventually leads to the stimulated echo modified by residual dipolar couplings. The evolution of the second term,

$$\sigma_{\text{pr}}(\tau_1+) = [(I_{kx} + I_{lx}) \cos \varphi_{d1} - 2(I_{kz}I_{ly} + I_{lz}I_{ky}) \sin \varphi_{d1}] \sin \varphi_{g1} \quad (3.370)$$

results in the likewise modified primary echo which reaches its maximum at the time $t = 2\tau_1$.

3.5.2.1 The Modified Primary Echo

After the second RF pulse, the reduced density operator Eq. (3.370) evolves further and reaches the effective expression

$$\begin{aligned} \sigma_{\text{pr}}(2\tau_1) = & \frac{1}{2} \left\{ (I_{kx} + I_{lx}) \left[\sin(\varphi_{g2} + \varphi_{g1}) - \sin(\varphi_{g2} - \varphi_{g1}) \right] \right. \\ & \left. + (I_{ky} + I_{ly}) \left[\cos(\varphi_{g2} + \varphi_{g1}) - \cos(\varphi_{g2} - \varphi_{g1}) \right] \right\} \cos(\varphi_{d2} - \varphi_{d1}) + \sigma_{\text{ap}}(2\tau_1) \end{aligned} \quad (3.371)$$

at the time $t = 2\tau_1$ corresponding to the maximum of the modified primary echo. The antiphase-coherence terms $\sigma_{\text{ap}}(2\tau_1)$ need not be specified and can be discarded at this point. They do not contribute to the echo formation. The precession phase shifts accumulated during the evolution interval $\tau_1 \dots 2\tau_1$ are

$$\varphi_{g2} = \int_{\tau_1}^{2\tau_1} \Omega_g(t') dt' \quad (3.372)$$

and

$$\varphi_{d2} = \frac{1}{2} \int_{\tau_1}^{2\tau_1} \bar{\Omega}_d(t') dt' \quad (3.373)$$

The attenuation factor of the primary echo, Eq. (3.353), can now be calculated as a quantity proportional to the complex transverse magnetization at the echo time $t = 2\tau_1$,

$$m(2\tau_1) = M_{x'} + iM_{y'} \quad (3.374)$$

which in turn is proportional to the expectation value of the total transverse spin operators $(I_{kx} + I_{lx}) + i(I_{ky} + I_{ly})$. The expectation value is obtained as the trace of the product of the spin operators with the reduced density operator

Eq. (3.371) (see footnote 8), so that the attenuation factor Eq. (3.353) obeys the proportionality

$$a_{\text{pr}}(2\tau_1) = a_{r2}(2\tau_1)a_{\text{dc}}(2\tau_1) \\ \propto \langle \text{Tr} \{ [(I_{kx} + I_{lx}) + i(I_{ky} + I_{ly})] \sigma_{\text{pr}}(2\tau_1) \} \rangle a_{2r}(2\tau_1) \quad (3.375)$$

Attenuation by transverse relaxation, that is, the factor $a_{2r}(2\tau_1)$, is not affected by this operation since the fast fluctuations to which this process refers can be considered to be *independent* of the slow fluctuations of the secular contributions. The angle brackets indicate the ensemble average with respect to the phase shifts φ_{g1} , φ_{g2} , φ_{d1} , and φ_{d2} . Evaluating the trace $\text{Tr}\{\dots\}$ in Eq. (3.375) with the aid of the reduced density operator Eq. (3.371) and taking into account that the phase shifts induced by gradients and dipolar interaction are independent of each other lead to

$$a_{\text{pr}}(2\tau_1) \propto \frac{1}{2} \left[\langle \sin(\varphi_{g2} + \varphi_{g1}) \rangle - \langle \sin(\varphi_{g2} - \varphi_{g1}) \rangle \right. \\ \left. + i \langle \cos(\varphi_{g2} + \varphi_{g1}) \rangle - i \langle \cos(\varphi_{g2} - \varphi_{g1}) \rangle \right] \langle \cos(\varphi_{d2} - \varphi_{d1}) \rangle a_{2r}(2\tau_1) \quad (3.376)$$

Let us now assume that the inhomogeneity-induced phase shifts in the pulse intervals are equally distributed over a broad range. The phase-shift sums in the arguments of the sine and cosine functions are then widely distributed as well. The superposition of these trigonometric functions is therefore destructive, and the averages vanish: $\langle \sin(\varphi_{g2} + \varphi_{g1}) \rangle \approx \langle \cos(\varphi_{g2} + \varphi_{g1}) \rangle \approx 0$. On the other hand, $\langle \cos(\varphi_{g2} - \varphi_{g1}) \rangle = 1$ remains finite because the inhomogeneity-induced phase shifts cancel in the echo-formation process.³⁵ Equation (3.376) is thus reduced to

$$a_{\text{pr}}(2\tau_1) \propto -\frac{i}{2} \langle \cos(\varphi_{d2} - \varphi_{d1}) \rangle a_{2r}(2\tau_1) \quad (3.377)$$

By contrast, the average $\langle \cos(\varphi_{d2} - \varphi_{d1}) \rangle$ does not vanish since the dipolar phase shifts φ_{d1} , φ_{d2} are *correlated* on the experimental time scale, that is, the pulse spacings. Exploiting the fact that $\langle \sin(\varphi_{d2} - \varphi_{d1}) \rangle = 0$ for an even distribution of the dipolar phase shifts and replacing the cosine by a complex exponential function finally gives

³⁵ The field gradients inherent to the magnetic-field inhomogeneity may be assumed to be too weak to cause any perceptible attenuation by translational diffusion.

$$a_{\text{pr}}(2\tau_1) \propto -\frac{i}{2} \langle \exp\{-i(\varphi_{\text{d}2} - \varphi_{\text{d}1})\} \rangle a_{\text{r}2}(2\tau_1) \quad (3.378)$$

for the total attenuation factor of the primary echo.³⁶

3.5.2.2 The Modified Stimulated Echo

The stimulated echo originates from the z magnetization in the τ_2 interval. The corresponding reduced density operator consequently depends only on the z components of the spin operators which are not subject to any evolution. At the end of the τ_2 interval, the reduced density operator therefore retains the form of Eq. (3.369),

$$\sigma_{\text{st}}(\tau_1 + \tau_2 -) = (I_{kz} + I_{lz}) \cos \varphi_{\text{d}1} \cos \varphi_{\text{g}1} \quad (3.379)$$

The third RF pulse specified in the scheme Fig. 3.36 as $(\pi/2)_y$, converts this into

$$\sigma_{\text{st}}(\tau_1 + \tau_2 +) = -(I_{kx} + I_{lx}) \cos \varphi_{\text{d}1} \cos \varphi_{\text{g}1} \quad (3.380)$$

The respective coherences reestablished in this way evolve in the interval after the third RF pulse and produce the stimulated echo with its maximum at $t = 2\tau_1 + \tau_2$. The reduced density operator at this instant reads

$$\begin{aligned} \sigma_{\text{st}}(2\tau_1 + \tau_2) = & -\frac{1}{4} (I_{kx} + I_{lx}) [\cos(\varphi_{\text{d}3} - \varphi_{\text{d}1}) + \cos(\varphi_{\text{d}3} + \varphi_{\text{d}1})] \\ & [\cos(\varphi_{\text{g}3} - \varphi_{\text{g}1}) + \cos(\varphi_{\text{g}3} + \varphi_{\text{g}1})] \\ & -\frac{1}{4} (I_{ky} + I_{ly}) [\cos(\varphi_{\text{d}3} - \varphi_{\text{d}1}) + \cos(\varphi_{\text{d}3} + \varphi_{\text{d}1})] \\ & [\cos(\varphi_{\text{g}3} - \varphi_{\text{g}1}) + \cos(\varphi_{\text{g}3} + \varphi_{\text{g}1})] \end{aligned} \quad (3.381)$$

where

$$\varphi_{\text{g}3} = \int_{\tau_1 + \tau_2}^{2\tau_1 + \tau_2} \Omega_{\text{g}}(t') dt' \quad (3.382)$$

³⁶ Note that the echo formation implies the refocusing of a dipolar contribution although the phases of the first two RF pulses are not in quadrature. At first sight, this is unexpected since no *solid echo* should arise under such conditions (see, e.g., Refs. [1, 4]). However, the relatively strong influence of the field gradients spoils any sensitivity to the relative phase of the second RF pulse so that part of the spin ensemble fulfills the quadrature requirement anyway. Otherwise, the density operator Eq. (3.371) would vanish identically.

and

$$\varphi_{d3} = \frac{1}{2} \int_{\tau_1 + \tau_2}^{2\tau_1 + \tau_2} \bar{\Omega}_d(t') dt' \quad (3.383)$$

In analogy to Eq. (3.375), the attenuation factor of the modified stimulated echo obeys the proportionality

$$a_{st} \propto \langle \text{Tr} \{ [(I_{kx} + I_{lx}) + i(I_{ky} + I_{ly})] \sigma_{st}(2\tau_1 + \tau_2) \} \rangle a_{r2}(2\tau_1) a_{r1}(\tau_2) \quad (3.384)$$

The loss factors $a_{r1}(\tau_2)$ and $a_{r2}(2\tau_1)$ are due to spin–lattice relaxation in the τ_2 interval and transverse relaxation in the first and last τ_1 free-evolution intervals. Since spin relaxation is the consequence of fast fluctuations of spin interactions as specified above, these factors are *independent* of the slow secular fluctuations which are of main concern in the present context. The angle brackets indicate the ensemble average with respect to the phase shifts φ_{g1} , φ_{g3} , φ_{d1} and φ_{d3} .

Carrying out the trace $\text{Tr}\{\dots\}$ with the aid of the reduced density operator Eq. (3.381) leads to

$$\begin{aligned} a_{st} \propto & -\frac{1}{4} [\langle \cos(\varphi_{d3} - \varphi_{d1}) \rangle + \langle \cos(\varphi_{d3} + \varphi_{d1}) \rangle] \left[\langle \cos(\varphi_{g3} - \varphi_{g1}) \rangle + \langle \cos(\varphi_{g3} + \varphi_{g1}) \rangle \right] \\ & - \frac{i}{4} [\langle \cos(\varphi_{d3} - \varphi_{d1}) \rangle + \langle \cos(\varphi_{d3} + \varphi_{d1}) \rangle] \left[\langle \sin(\varphi_{g3} - \varphi_{g1}) \rangle + \langle \sin(\varphi_{g3} + \varphi_{g1}) \rangle \right] \\ & a_{r2}(2\tau_1) a_{r1}(\tau_2) \end{aligned} \quad (3.385)$$

Since $\langle \sin(\varphi_{g3} + \varphi_{g1}) \rangle \approx \langle \cos(\varphi_{g3} + \varphi_{g1}) \rangle \approx 0$, $\langle \sin(\varphi_{g3} - \varphi_{g1}) \rangle = 0$, and $\langle \cos(\varphi_{g3} - \varphi_{g1}) \rangle = 1$ in analogy to the treatment of the primary echo, the amplitude of the modified stimulated echo is predicted to be proportional to

$$a_{st}(2\tau_1 + \tau_2) \propto \frac{1}{2} (\langle \exp\{-i(\varphi_{d3} - \varphi_{d1})\} \rangle + \langle \exp\{-i(\varphi_{d3} + \varphi_{d1})\} \rangle) a_{r2}(2\tau_1) a_{r1}(\tau_2) \quad (3.386)$$

where the cosine terms have been replaced by exponential functions as before. Note that the dipolar phase shifts vanish in the case of complete motional averaging on the time scales of the first and last τ_1 intervals as expected for ordinary stimulated-echo experiments.

3.5.3 The Dipolar-Correlation Quotient

After having determined the attenuation factors of the primary and stimulated echoes, $a_{\text{pr}}(2\tau_1)$ (Eq. (3.353)) and $a_{\text{st}}(2\tau_1 + \tau_2)$ (Eq. (3.354)), respectively, the quotient

$$Q = \frac{a_{\text{st}}(2\tau_1 + \tau_2)}{a_{\text{pr}}(2\tau_1)} = a_{\text{r1}}(\tau_2)Q_{\text{dc}} \quad (3.387)$$

can be formed. The attenuation factor due to transverse relaxation, $a_{\text{r2}}(2\tau_1)$, is common to both echoes and cancels therefore. The attenuation factor by spin–lattice relaxation, $a_{\text{r1}}(\tau_2)$, can be kept constant by leaving the interval τ_2 fixed while τ_1 is varied in the course of experiments. In this way, the *dipolar-correlation quotient* Q_{dc} can be evaluated. According to the above formalism, it is defined by

$$\begin{aligned} Q_{\text{dc}} &\equiv \frac{a_{\text{dc}}(2\tau_1 + \tau_2)}{a_{\text{dc}}(2\tau_1)} \\ &= \frac{1}{2} \left(\frac{\langle \exp\{-i(\varphi_{\text{d3}} - \varphi_{\text{d1}})\} \rangle + \langle \exp\{-i(\varphi_{\text{d3}} + \varphi_{\text{d1}})\} \rangle}{\langle \exp\{-i(\varphi_{\text{d2}} - \varphi_{\text{d1}})\} \rangle} \right) \end{aligned} \quad (3.388)$$

The dipolar phase shifts φ_{d1} , φ_{d2} , and φ_{d3} in the three intervals of the pulse sequence can be split into a stationary part and a contribution fluctuating on the time scale of the experiment. The residual dipolar-coupling constant is accordingly analyzed as

$$\bar{\Omega}_{\text{d}}(t) = \langle \bar{\Omega}_{\text{d}} \rangle + \delta\bar{\Omega}_{\text{d}}(t) \quad (3.389)$$

where $\langle \delta\bar{\Omega}_{\text{d}}(t) \rangle = 0$. The *effective* residual dipolar-coupling constant $\langle \bar{\Omega}_{\text{d}} \rangle_{\text{d}}$ remains constant on the experimental time scale, whereas $\delta\bar{\Omega}_{\text{d}}(t)$ fluctuates with rates smaller than Ω_{rl} .³⁷ The phase shifts in Eq. (3.388) can thus be expressed in an analogous manner by

³⁷ Recall that all faster fluctuations have already been taken into account by the partial motional averaging process resulting in the residual dipolar-coupling constant. In terms of echo attenuation, they are reflected by a_{r1} and a_{r2} .

$$\begin{aligned}
\varphi_{d1} &= \frac{1}{2} \left[\langle \bar{\Omega}_d \rangle \tau_1 + \int_0^{\tau_1} \delta \bar{\Omega}_d(t') dt' \right] = \langle \varphi_{d1} \rangle + \delta \varphi_{d1} \\
\varphi_{d2} &= \frac{1}{2} \left[\langle \bar{\Omega}_d \rangle \tau_1 + \int_{\tau_1}^{2\tau_1} \delta \bar{\Omega}_d(t') dt' \right] = \langle \varphi_{d1} \rangle + \delta \varphi_{d2} \\
\varphi_{d3} &= \frac{1}{2} \left[\langle \bar{\Omega}_d \rangle \tau_1 + \int_{\tau_1+\tau_2}^{2\tau_1+\tau_2} \delta \bar{\Omega}_d(t') dt' \right] = \langle \varphi_{d1} \rangle + \delta \varphi_{d3}
\end{aligned} \tag{3.390}$$

Inserting these relations into Eq. (3.388) gives

$$Q_{dc} = \frac{\langle e^{-i(\delta\varphi_{d3}-\delta\varphi_{d1})} \rangle + \cos(2\langle \varphi_{d1} \rangle) \langle e^{-i(\delta\varphi_{d3}+\delta\varphi_{d1})} \rangle}{2\langle e^{-i(\delta\varphi_{d2}-\delta\varphi_{d1})} \rangle} \tag{3.391}$$

Assuming a Gaussian distribution of the phase shifts permits the evaluation of the ensemble averages in Eq. (3.391). The result is

$$\begin{aligned}
Q_{dc} &= \frac{\exp\left\{-\frac{1}{2}\langle (\delta\varphi_{d3}-\delta\varphi_{d1})^2 \rangle\right\} + \cos(2\langle \varphi_{d1} \rangle) \exp\left\{-\frac{1}{2}\langle (\delta\varphi_{d3}+\delta\varphi_{d1})^2 \rangle\right\}}{2\exp\left\{-\frac{1}{2}\langle (\delta\varphi_{d2}-\delta\varphi_{d1})^2 \rangle\right\}} \\
&= \frac{1}{2} \exp\{\langle \delta\varphi_{d1}\delta\varphi_{d3} \rangle - \langle \delta\varphi_{d1}\delta\varphi_{d2} \rangle\} (1 + \cos(\langle \bar{\Omega}_d \rangle \tau_1) \exp\{-2\langle \delta\varphi_{d1}\delta\varphi_{d3} \rangle\})
\end{aligned} \tag{3.392}$$

where $\langle \bar{\Omega}_d \rangle \tau_1 = 2\langle \varphi_{d1} \rangle = 2\langle \varphi_{d3} \rangle$ according to Eqs. (3.373) and (3.383) in combination with Eq. (3.389). The particular distribution function assumed here is a consequence of the *central-limit theorem* [28] stating that the accumulative sum of a sufficiently large number of random contributions is distributed according to a Gauss function irrespective of how the contributions themselves are distributed.

3.5.4 The Phase-Shift Correlation Functions

In the following, the quantity of interest will be the correlation function of the fluctuating part of the residual dipolar-coupling constant,

$$G_d(\tau) \equiv \langle \delta \bar{\Omega}_d(t') \delta \bar{\Omega}_d(t'') \rangle = \langle \delta \bar{\Omega}_d^2 \rangle G_d(\tau) \tag{3.393}$$

This is the basic function that reflects the characteristics of molecular dynamics. The stationarity condition of stochastic processes ensures that the time dependence solely refers to the difference interval $\tau = t'' - t'$, but not on the absolute time. As usual, the normalized correlation function is represented by the calligraphic

symbol $G_d(\tau)$. It obeys the conditions $G_d(0) = 1$ and $G_d(\tau) = G_d(-\tau)$. In the following, the objective will be to express the phase-shift correlation functions $\langle \delta\varphi_{d1} \delta\varphi_{d3} \rangle$ and $\langle \delta\varphi_{d1} \delta\varphi_{d2} \rangle$ in Eq. (3.392) in terms of $G_d(\tau)$ or $\bar{G}_d(\tau)$. Making use of the implicit definitions given in Eq. (3.390), we may write

$$\begin{aligned} \langle \delta\varphi_{d1} \delta\varphi_{d3} \rangle &= \frac{1}{4} \left\langle \int_0^{\tau_1} \delta\bar{\Omega}_d(t') dt' \int_{\tau_1+\tau_2}^{2\tau_1+\tau_2} \delta\bar{\Omega}_d(t'') dt'' \right\rangle \\ &= \frac{1}{4} \langle \delta\bar{\Omega}_d^2 \rangle \int_0^{\tau_1} dt' \int_{\tau_1+\tau_2}^{2\tau_1+\tau_2} dt'' G_d(t'' - t') \end{aligned} \quad (3.394)$$

and

$$\begin{aligned} \langle \delta\varphi_{d1} \delta\varphi_{d2} \rangle &= \frac{1}{4} \left\langle \int_0^{\tau_1} \delta\bar{\Omega}_d(t') dt' \int_{\tau_1}^{2\tau_1} \delta\bar{\Omega}_d(t'') dt'' \right\rangle \\ &= \frac{1}{4} \langle \delta\bar{\Omega}_d^2 \rangle \int_0^{\tau_1} dt' \int_{\tau_1}^{2\tau_1} dt'' G_d(t'' - t') \end{aligned} \quad (3.395)$$

Analogous to the variable substitution treatment of the effect of residual dipolar couplings on free-induction decays delineated in Sect. 3.1.6, these expressions can straightforwardly be converted into

$$\begin{aligned} \langle \delta\varphi_{d1} \delta\varphi_{d3} \rangle &= \frac{1}{4} \langle \delta\bar{\Omega}_d^2 \rangle \\ &\times \left[\int_0^{\tau_1} d\tau (\tau_1 - \tau) G_d(\tau_1 + \tau_2 - \tau) + \int_0^{\tau_1} d\tau (\tau_1 - \tau) G_d(\tau_1 + \tau_2 + \tau) \right] \end{aligned} \quad (3.396)$$

and

$$\begin{aligned} \langle \delta\varphi_{d1} \delta\varphi_{d2} \rangle &= \frac{1}{4} \langle \delta\bar{\Omega}_d^2 \rangle \\ &\times \left[\int_0^{\tau_1} d\tau (\tau_1 - \tau) G_d(\tau_1 + \tau) + \int_0^{\tau_1} d\tau (\tau_1 - \tau) G_d(\tau_1 - \tau) \right] \end{aligned} \quad (3.397)$$

respectively.

As an example, let us now assume an exponential decay of the correlation function,

$$G_d(\tau) = \exp\left\{-\frac{|\tau|}{\tau_c}\right\} \quad (3.398)$$

where τ_c is the correlation time. One cannot expect that such an elementary function accounts for typical dynamic scenarios that might be relevant in soft-matter dynamics (see, e.g., Sect. 6.6). It is however a good basis for the discussion of dynamic principles in this context. Inserting Eq. (3.398) into Eqs. (3.396) and (3.397) gives

$$\begin{aligned} \langle \delta\varphi_{d1} \delta\varphi_{d3} \rangle &= \langle \delta\varphi_{d1} \delta\varphi_{d2} \rangle \exp\left\{-\frac{\tau_2}{\tau_c}\right\} \\ \langle \delta\varphi_{d1} \delta\varphi_{d2} \rangle &= \frac{1}{4} \langle \delta\bar{\Omega}_d^2 \rangle \tau_c^2 \exp\left\{-\frac{\tau_1}{\tau_c}\right\} \left[\exp\left\{-\frac{\tau_1}{\tau_c}\right\} + \exp\left\{\frac{\tau_1}{\tau_c}\right\} - 2 \right] \end{aligned} \quad (3.399)$$

For exponential correlation functions, the dipolar-correlation quotient Eq. (3.392) thus takes the form

$$Q_{dc} = \frac{1}{2} \exp\left\{-\frac{1}{4} \langle \delta\bar{\Omega}_d^2 \rangle C_1\right\} \left(1 + \cos(\langle \bar{\Omega}_d \rangle \tau_1) \exp\left\{-\frac{1}{2} \langle \delta\bar{\Omega}_d^2 \rangle C_2\right\}\right) \quad (3.400)$$

with the coefficients

$$\begin{aligned} C_1 &= \tau_c^2 \left(\exp\left\{-\frac{2\tau_1}{\tau_c}\right\} - 2 \exp\left\{-\frac{\tau_1}{\tau_c}\right\} + 1 \right) \left(1 - \exp\left\{-\frac{\tau_2}{\tau_c}\right\} \right) \\ C_2 &= \tau_c^2 \left(\exp\left\{-\frac{2\tau_1}{\tau_c}\right\} - 2 \exp\left\{-\frac{\tau_1}{\tau_c}\right\} + 1 \right) \exp\left\{-\frac{\tau_2}{\tau_c}\right\} \end{aligned} \quad (3.401)$$

Figure 3.37 shows a plot of Eq. (3.400) as a function of the experimental parameter τ_1 , that is, the spacing of the first two RF pulses, and of the system parameter $\langle \delta\bar{\Omega}_d^2 \rangle$, the mean square fluctuation of the residual dipolar-coupling constant. The undulation along the τ_1 axis indicates the term $\cos(\langle \bar{\Omega}_d \rangle \tau_1)$ oscillating with the effective residual dipolar-coupling constant. Actually, this oscillation is an indication of macroscopic order in the system as will be demonstrated in Sect. 6.6 in the context of liquid crystals. The decay along the $\langle \delta\bar{\Omega}_d^2 \rangle$ axis reflects the influence of the fluctuating part of the residual dipolar-coupling constant.

Let us summarize: The dipolar-correlation quotient Eq. (3.392) is the product of in principle three averaging processes on different time scales: (1) *Fast* components of molecular motions complying to the motional condition $\Omega_n \tau_c \ll 1$ reduce the dipolar-coupling constant Ω_d (Eq. (3.359)) to the *residual dipolar-coupling constant* $\bar{\Omega}_d$ (see, e.g., Eq. (3.361)). (2) *Slow* molecular motions taking place on the time

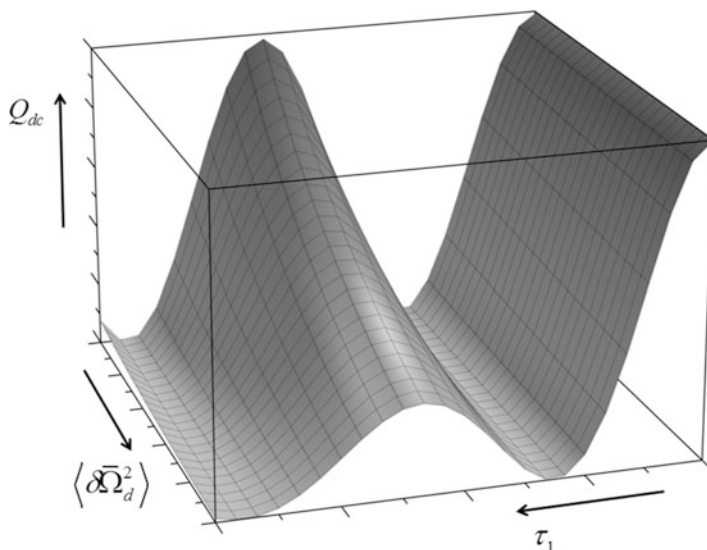


Fig. 3.37 Plot of the dipolar-correlation quotient Q_{dc} as a function of the RF pulse interval τ_1 and the mean square fluctuation of the residual dipolar-coupling constant $\langle \delta \bar{\Omega}_d^2 \rangle$ according to Eq. (3.400)

scale of the RF pulse sequence cause slow fluctuations $\delta \bar{\Omega}_d(t)$ of the residual dipolar-coupling constant $\bar{\Omega}_d$ and reduce it further to the *effective residual dipolar-coupling constant* $\langle \bar{\Omega}_d \rangle$ (see Eq. 3.389). (3) Finally, the dipolar-correlation quotient Q_{dc} resulting from all these motions must be averaged over a potential *powder distribution* of the axes about which the anisotropic molecular motions occur (this powder average has not yet been specified in the above treatment). We will get back to the dipolar-correlation effect in Sect. 6.6 where applications to nematic liquid crystals will be discussed.

3.6 Quasi-Elastic Neutron Scattering

In the following sections, we will turn to a number of non-NMR techniques suitable for extending and supplementing the experimental time, wave number, and frequency scales of interest in soft-matter science. As the first technique widely used in this field, we will consider quasi-elastic neutron scattering. In a sense, there are close similarities to various dynamic NMR techniques described in the previous sections. Apart from the common and partially identical correlation function background for diffusometry applications, the nuclei probed are typically protons and deuterons acting as scattering centers on the one hand and resonant spin-bearing nuclei on the other. The complementary use of both techniques therefore suggests itself.

Table 3.1 Coherent and incoherent scattering cross-sections characteristic for a number of abundant isotopes typically relevant in soft matter

Isotopes	Spin quantum number	$\sigma_{\text{coh}} (10^{-28} \text{m}^2)$	$\sigma_{\text{inc}} (10^{-28} \text{m}^2)$
^1H	$\frac{1}{2}$	1.8	79.9
^2H	1	5.6	2.0
^{12}C	0	5.6	0
^{14}N	1	11.0	0.5
^{16}O	0	4.2	0

Note that under natural abundance conditions minor admixtures of other isotopes to these elements exist so that the effective mean values are slightly different

3.6.1 Overview and Terminology

In general, neutron scattering experiments with condensed-matter samples can serve very different objectives. This implies studies of structure, lattice dynamics, molecular vibrations, and diffusive displacements [96–100]. Applications of the latter sort are of particular interest in the present context. Corresponding reviews can be found in Refs. [101–104].

Depending on the processes to be probed, neutron scattering is classified by attributes such as *coherent*, *incoherent*, *elastic* (or *quasi-elastic*), and *inelastic*. *Coherent* means that neutrons scattered at different nuclei can interfere *constructively* via their de Broglie wave properties in analogy to laser light interference. The crucial feature of this sort of experiment is the predetermined phase relation between waves scattered at different nuclei.

The coherence of the scattered waves tends to be spoiled if different isotopes contribute and if the nuclear spin of the scattering centers is finite, so that the phases of the scattered waves will be fluctuating. Under such circumstances, a significant or even dominating part of neutron scattering will be *incoherent*: There is no fixed phase relation anymore between neutron waves scattered at different nuclei. The scattering events at the target nuclei will be coherent with a certain probability and incoherent with the complementary probability. As a consequence, no structure-dependent, constructive interference of the neutron waves can arise. Scattering properties of typical isotopes are listed in Table 3.1.

In contrast to *inelastic* processes, the *elastic* peak of the neutron energy distribution after scattering represents the fraction which is not connected with any energy transfer to or from quantum-mechanical states of vibrations or rotations (not to speak of excited states of the nuclei themselves). The elastic peak can however be broadened by exchange of (much smaller) amounts of thermal energy of the *translational* degrees of freedom of the scattering centers. Due to thermal motions, the interaction between neutrons and target nuclei fluctuates randomly as a function of time. The fluctuations in particular refer to diffusive molecular displacements while the neutron (taken as a de Broglie wave packet) interacts with the scattering center upon crossing the target. One speaks then of *quasi-elastic* scattering which is of particular interest in the present context as a probe of molecular dynamics.

At this point, an important note appears to be adequate: The width of the wave packet of a traveling particle is often characterized by its *coherence length* which in

the present context is definitely much longer than the sample dimension. The term *coherence* used in this sense must however not be confused with the scattering attributes *coherent* or *incoherent*. These have nothing much to do with wave packet properties. They rather indicate whether waves scattered at different scattering centers can interfere constructively with each other or not. A more detailed discussion of this topic can be found in Ref. [105].

Quasi-elastic neutron scattering experiments in soft matter predominantly refer to light and heavy hydrogen nuclei usually quoted somewhat loosely as *protons* and *deuterons*, respectively. The scattering cross-section, that is, the scattering efficiency, of ^1H nuclei is at least one order of magnitude larger than with other nuclear species and therefore offers a sufficiently large contrast to the background. Since ^1H nuclei possess a spin $1/2$, the nature of the scattering process is mainly incoherent. ^2H nuclei on the other hand are more likely scattered coherently than incoherently as suggested by the respective scattering cross-sections. Using samples with isotopes in natural abundance or synthetically enriched with deuterons thus permits one to establish experimental protocols for the elucidation of either purely incoherent or purely coherent scattering.

3.6.2 The Experiment

The scattering geometry of neutron experiments is schematically shown in Fig. 3.38. An – as far as possible – monodisperse and collimated neutron beam is directed on the sample. The flux of the incident beam, that is the number of neutrons per unit time and unit area, is denoted by Φ . The kinetic energy of the incident neutrons is given by the free-particle expression

$$E_k = \frac{\hbar^2 k^2}{2m} \quad (3.402)$$

m is the neutron rest mass. The momentum is $\mathbf{p} = \hbar \mathbf{k}$ with $\mathbf{k}$ the wave vector of the incident neutrons. The magnitude of $\mathbf{k}$, that is, $k = 2\pi/\lambda$, is determined by the de Broglie wave length λ . The wave-length is related to the energy of free neutrons, E_k , according to³⁸

$$\lambda = \frac{2\pi}{k} = \frac{h}{p} = \frac{h}{mv} = \frac{h}{\sqrt{2mE_k}} \quad (3.403)$$

where v is the neutron velocity.

³⁸ Relative to light velocity in vacuum, $c_0 \approx 3 \times 10^8 \text{ m s}^{-1}$, the range of neutron velocities of interest in the present context covers extremely low values, $\leq 10^{-5} c_0$. Neutrons can therefore be treated here as *nonrelativistic* particles. The neutron rest mass is $m \approx 1.67 \times 10^{-27} \text{ kg}$. Planck's quantum of action is $h \approx 6.63 \times 10^{-34} \text{ J s}$.

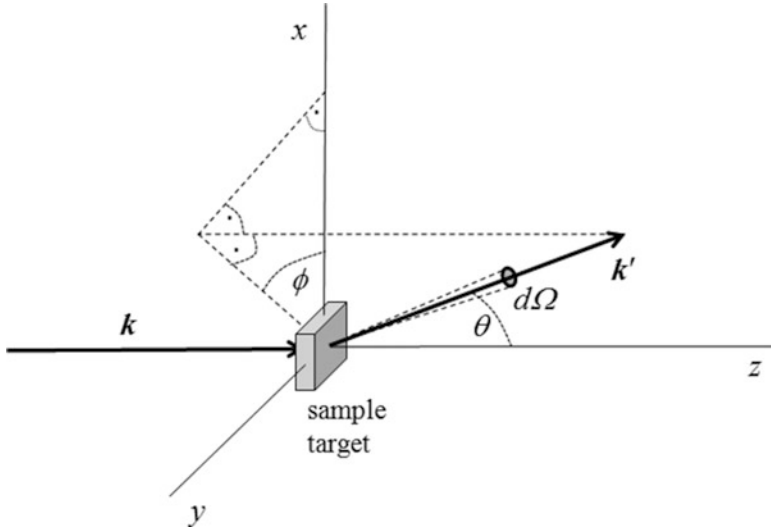


Fig. 3.38 Principle of neutron scattering experiments: Incident (monodisperse and collimated) neutrons of momentum $\hbar k$ are scattered in directions defined by the polar and azimuthal angles θ and ϕ , respectively. The energy-resolving neutron detector counts the scattered neutrons with a certain solid-angle resolution $d\Omega$. The momentum of the scattered neutrons is $\hbar k'$

Neutrons scattered at the target nuclei adopt the wave vectors k' in directions defined by the polar and azimuthal angles θ and ϕ , respectively, as illustrated in Fig. 3.38. After the scattering process, the neutrons are free again so that their energy can be represented by

$$E_{k'} = \frac{\hbar^2 k'^2}{2m} \quad (3.404)$$

analogous to Eq. (3.402).

Relative to typical wave lengths of neutrons, the extension of the scattering centers is negligible. The target nuclei can therefore be considered as point-like objects. Any angular structure of the scattering distribution does not matter. One speaks of *s-wave scattering* producing waves of spherical symmetry, whereas incident neutrons are treated as plane de Broglie waves (see Fig. 3.39).

Because of the spherical angular distribution, the flux of scattered neutrons varies with the distance ℓ' from the scattering centers according to $\Phi' \propto \ell'^{-2}$. In order to have a measurand independent of the experimental setup, one therefore refers to a solid-angle element $d\Omega$ defined by the aperture of the detector device. The cross-sectional area probed in a distance ℓ' from the sample is then $\ell'^2 d\Omega$. The detected number of neutrons per unit time thus is

$$dI_d = \Phi' \ell'^2 d\Omega = \text{const} \quad (3.405)$$

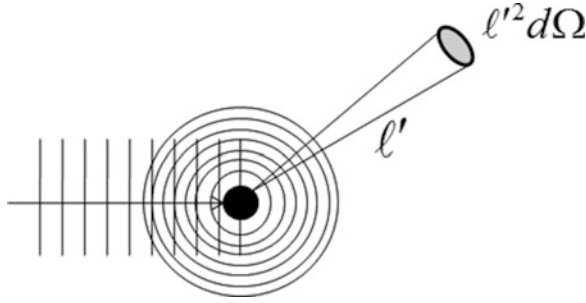


Fig. 3.39 Schematic representation of the scattering process in terms of de Broglie waves. The incident neutrons arrive from the left as plane waves with the wave vector $\mathbf{k}$. After the scattering event in the target (*black dot*), they propagate as spherical waves probed in the solid-angle element $d\Omega$ about the direction of the wave vector $\mathbf{k}'$

The *detection rate* is thus independent of the distance from the target. Note that Eq. (3.405) anticipates that all scattered neutrons in the selected solid-angle and energy intervals are counted indeed. Practically, this number will however be reduced due to instrumental factors which we will not consider further here.

The deflected neutrons are counted in $d\Omega$ about the direction of $\mathbf{k}'$. One of the primary quantities to be evaluated from the incoming and outgoing fluxes, Φ and Φ' , respectively, is

$$d\sigma = \frac{dI_d}{\Phi} = \frac{\Phi' \ell'^2}{\Phi'} d\Omega \quad (3.406)$$

That is, Eq. (3.405) divided by Φ . On this basis, one defines the *differential scattering cross-section*

$$\frac{d\sigma}{d\Omega} = \frac{\Phi' \ell'^2}{\Phi} = \frac{dI_d}{\Phi d\Omega} \quad (3.407)$$

A remarkable feature of $d\sigma/d\Omega$ is that it is practically independent of the geometry of the experimental setup. On the other hand, subtraction of background counts and correction for systematic instrumental imperfections will possibly be needed before analyzing the differential cross-section. It may also be necessary to correct the detection rate with respect to multiple scattering and self-screening in the sample.

The detection rate can furthermore be determined energy selectively with the aid of multichannel analyzers. The counts refer then to an interval between $E_{k'}$ and $E_{k'} + dE_{k'}$. Forming the derivative of Eq. (3.406) by $dE_{k'}$ leads to the *partial (or double) differential cross-section*

$$\frac{d^2\sigma}{d\Omega dE_{k'}} = \frac{d^2I_d}{\Phi d\Omega dE_{k'}} \quad (3.408)$$

This is the basic measurand of quasi-elastic neutron scattering: The double-differential cross-section is the rate of counts relative to the incoming flux, the solid-angle aperture, and the energy resolution of the system.

The primary objective of the following treatment will be to relate Eq. (3.408) with molecular dynamics in the target. Integrating this expression once or twice gives the differential cross-section without energy resolution

$$\frac{\partial \sigma}{\partial \Omega} = \int_0^{\infty} \left(\frac{\partial^2 \sigma}{\partial \Omega \partial E_{k'}} \right) dE_{k'} \quad (3.409)$$

and the *total scattering cross-section*

$$\sigma = \int \left(\frac{\partial \sigma}{\partial \Omega} \right) d\Omega = \int_0^{\pi} \frac{\partial \sigma}{\partial \Omega} 2\pi \sin \theta d\theta \quad (3.410)$$

implying all scattering directions. The dimension of cross-sections is [area] with the unit *barn* ($1 \text{ b} = 10^{-28} \text{ m}^2$). Cross-sections are properties specific for the interaction between the incident neutrons and the target nuclei. The probability that an incident particle interacts with a target nucleus is given by $P_{\text{int}} = \sigma N_t / A$, where the ratio N_t / A is the number of target nuclei, N_t , per target area, A .

Neutron beams suitable for experimental purposes can be produced with the aid of high-flux nuclear fission reactors, spallation neutron sources, and electron linear accelerators [100]. After generation in the source, neutrons are usually *moderated*, that is, thermalized via multiple inelastic scattering events in a suitable medium containing a large fraction of light nuclei such as hydrogen. In this preparative process, neutrons adopt thermal energies $E_k \approx E_{\text{thermal}} = 3k_B T / 2$ corresponding to the three translational degrees of freedom of a free particle, where k_B is Boltzmann's constant.

For probing quasi-elastic scattering, that is, the broadening of the elastic peak by thermal motions, a *relative* energy resolution $\Delta E_{k'} / E_{k'}$ as good as possible is desirable. One therefore uses *cold* neutrons moderated at particularly low temperatures. The moderating medium may be liquid hydrogen or deuterium with temperatures in the range 20–25 K. The mean thermal energy at $T = 20 \text{ K}$ is $E_{\text{thermal}}(T = 20 \text{ K}) \approx 2.6 \text{ meV} \approx 4 \times 10^{-22} \text{ J}$ compared to the room temperature thermal energy at $T = 300 \text{ K}$ amounting to $E_{\text{thermal}}(T = 300 \text{ K}) \approx 38.8 \text{ meV} \approx 6 \times 10^{-21} \text{ J}$. According to Eq. (3.403), these thermal-energy values correspond to wave lengths $\lambda(20 \text{ K}) \approx 5.7 \times 10^{-10} \text{ m} = 57 \text{ nm}$ and $\lambda(300 \text{ K}) \approx 1.48 \times 10^{-10} \text{ m} = 14.8 \text{ nm}$, respectively. Likewise, the respective velocities related to these wave lengths are $v(20 \text{ K}) \approx 694 \text{ m/s}$ and $v(300 \text{ K}) \approx 2674 \text{ m/s}$. Relative energy resolutions technically achievable with cold neutrons are in the range $\Delta E_{k'} / E_{k'} = 10^{-5} \dots 10^{-3}$.

Three different experimental setups are in use and can be combined in studies if necessary. The operation principles are specified as *time-of-flight*, *backscattering*,

and *spin echo* [98, 100]. The time scales probed by such instruments range from ps to 100 ns in this sequence. Soft matter is often composed of relatively large molecules and tends to form rather viscous systems. It is therefore important to be able to probe slow processes. The neutron spin-echo scattering method with its superior relative energy resolution of $\Delta E_k/E_k \approx 10^{-5}$ is therefore of particular interest.

3.6.3 Theory of the Double-Differential Cross-Section

The objective in the following will be to relate the neutron scattering measurand, that is, the double-differential cross-section $\partial^2\sigma/\partial\Omega\partial E_k$, with parameters of molecular dynamics such as fluctuation time constants and diffusion coefficients. During the scattering process, the neutron interacts with a target nucleus and temporarily forms a system subject to certain quantum-mechanical states. The neutron changes its initial state $|\mathbf{k}\rangle$ with the wave vector $\mathbf{k}$ to the final state $|\mathbf{k}'\rangle$ with the wave vector $\mathbf{k}'$. Simultaneously, the nuclear states are transferred from $|\varphi\rangle$ to $|\varphi'\rangle$. Since the states of the neutron and of the nucleus are independent of each other, the states of the scattering system before and after the scattering event can be expressed by products of the above kets, that is, $|\mathbf{k}, \varphi\rangle = |\mathbf{k}\rangle|\varphi\rangle$ and $|\mathbf{k}', \varphi'\rangle = |\mathbf{k}'\rangle|\varphi'\rangle$, respectively.

The initial and final neutron states, $|\mathbf{k}\rangle$ and $|\mathbf{k}'\rangle$, can be characterized by plane-wave functions $\Psi \propto \exp\{i\mathbf{k} \cdot \boldsymbol{\ell}\}$ and $\Psi' \propto \exp\{i\mathbf{k}' \cdot \boldsymbol{\ell}'\}$, respectively, where $\boldsymbol{\ell}$ and $\boldsymbol{\ell}'$ are the path vectors along which the neutrons propagate before and after scattering. At first sight, the plane-wave description appears to conflict with the s-wave scattering scenario depicted in Fig. 3.39. According to that representation, the scattered neutron wave should be rather of a spherical nature, $\Psi' \propto \ell'^{-1} \exp\{i\mathbf{k}' \cdot \boldsymbol{\ell}'\}$. That is, the probability densities before and after scattering are expected to be $|\Psi|^2 = \text{const}$ and $|\Psi'|^2 \propto \ell'^{-2}$, respectively. However, as outlined above, it must be kept in mind that the scattered neutrons are detected in a narrow cone with the angular aperture $d\Omega$ about the wave-vector $\mathbf{k}'$. The sensitive detector area therefore is $\ell'^2 d\Omega$, so that the inverse square dependence of the final probability density on the distance from the target cancels in the counting process. The detection rate is consequently independent of the target-detector distance, and the scattered neutrons can therefore be described in the detection cone as a plane de Broglie wave $\Psi' \propto \exp\{i\mathbf{k}' \cdot \boldsymbol{\ell}'\}$ in good approximation. Apart from that, the experimental setup implies that the target-detector distance is much greater than any internuclear distance in the sample. Therefore, both target and detector can be considered as point-like objects connected by the distance vector $\boldsymbol{\ell}'$.

Since individual nuclear states cannot be identified in experiments, the average over all possible initial and final states of the nucleus must be taken. This will be done after having established the formalism for transitions between a given initial and a given final state. The further strategy will be in the following to express

the double-differential cross-section first by the probability per unit time that a transition $|\mathbf{k}\rangle|\varphi\rangle \rightarrow |\mathbf{k}'\rangle|\varphi'\rangle$ takes place. This probability will then be related with correlation functions representing molecular fluctuations. Finally, the correlation functions will be exemplified for simple molecular motions.

For the derivation of the double-differential cross-section, let us start with the total scattering cross-section σ . The number of neutrons scattered into all directions per unit time is $\Phi\sigma$, where Φ is the incident neutron flux. The number of neutrons of state $|\mathbf{k}\rangle$ hitting the target per unit time be N . The target nuclei are assumed in the state $|\varphi\rangle$. The probability per unit time $W_{k,\varphi \rightarrow k',\varphi'}$ that the scattering system is transferred from the state $|\mathbf{k}, \varphi\rangle = |\mathbf{k}\rangle|\varphi\rangle$ to $|\mathbf{k}', \varphi'\rangle = |\mathbf{k}'\rangle|\varphi'\rangle$ is then

$$\Phi\sigma_{\varphi \rightarrow \varphi'} = N \sum_{\text{all directions}} W_{k,\varphi \rightarrow k',\varphi'} = C_n N \int_{k' \text{ space}} W_{k,\varphi \rightarrow k',\varphi'} d^3 k' \quad (3.411)$$

The subscript of the cross-section $\sigma_{\varphi \rightarrow \varphi'}$ indicates the particular transition of the target nucleus from state $|\varphi\rangle$ to $|\varphi'\rangle$. The probability per unit time $W_{k,\varphi \rightarrow k',\varphi'}$ refers to the same transition while the neutron is scattered from state $|\mathbf{k}\rangle$ to $|\mathbf{k}'\rangle$. The integral covers the whole k' space, so that the normalization constant C_n is equal to the inverse k' space volume.

According to the so-called *box normalization* of plane waves, a cubic box volume L^3 is attributed to each neutron in which it is formally considered to reside.³⁹ The total k' space volume is consequently $(2\pi/L)^3$, so that $C_n = (L/2\pi)^3$. The total number of neutrons scattered into any direction per unit time is thus given by

$$\Phi\sigma_{\varphi \rightarrow \varphi'} = \frac{NL^3}{(2\pi)^3} \int_{k' \text{ space}} W_{k,\varphi \rightarrow k',\varphi'} d^3 k' \quad (3.412)$$

As illustrated in Fig. 3.40, the k' -space “volume” element $d^3 k'$ can be expressed by

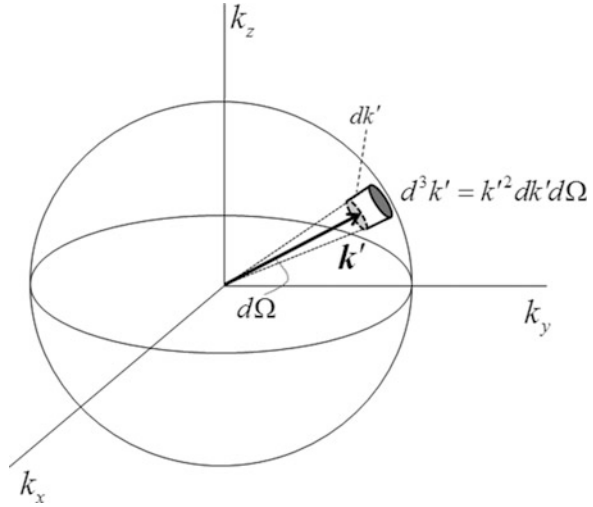
$$d^3 k' = k'^2 dk' d\Omega \quad (3.413)$$

After the scattering event, the energy of the neutron (which can then be considered to be free) is related to its momentum p' and, hence, to the square of its wave vector according to

$$E_{k'} = \frac{p'^2}{2m} = \frac{\hbar^2 k'^2}{2m} \quad (3.414)$$

³⁹ In the *box normalization formalism*, the dimension L of the box attributed to a neutron appears to be arbitrary. The justification is that the L dependence eventually cancels due to other terms arising in the course of the theory. A more extended discussion of plane waves and box normalization can be found in textbooks on quantum mechanics such as Ref. [106], for example.

Fig. 3.40 k' -space “volume” element cut out of the spherical shell between k' and $k'+dk'$ by a $d\Omega$ cone about the k' direction



The derivation of this expression leads to

$$dk' = \frac{m}{\hbar^2 k'} dE_{k'} \quad (3.415)$$

Inserting Eq. (3.415) in Eq. (3.413) and the result in Eq. (3.412) gives

$$\Phi \sigma_{\varphi \rightarrow \varphi'} = \frac{NL^3}{(2\pi)^3} \frac{m}{\hbar^2} \iint W_{k, \varphi \rightarrow k', \varphi'} k' dE_{k'} d\Omega \quad (3.416)$$

This relation is to be compared with the definition

$$\Phi \sigma_{\varphi \rightarrow \varphi'} = \Phi \iint \frac{\partial^2 \sigma_{\varphi \rightarrow \varphi'}}{\partial \Omega \partial E_{k'}} dE_{k'} d\Omega \quad (3.417)$$

suggesting the relation

$$\frac{\partial^2 \sigma_{\varphi \rightarrow \varphi'}}{\partial \Omega \partial E_{k'}} = \Phi^{-1} \frac{NL^3}{(2\pi)^3} \frac{m}{\hbar^2} k' W_{k, \varphi \rightarrow k', \varphi'} \quad (3.418)$$

between the double-differential scattering cross-section and the transition probability per unit time.

In the frame of first-order perturbation theory (called *Born approximation* in the context of scattering), the probability per unit time that the wave vector $\mathbf{k}$ of the incident neutron is transferred to $\mathbf{k}'$ upon interaction with a target nucleus is given by the well-known *golden rule*

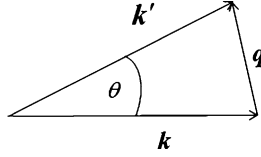


Fig. 3.41 Graphical representation of Eq. (3.420) for the scattering vector q . With quasi-elastic neutron scattering experiments, that is, $k \approx k'$, different scattering vectors can be probed by adjusting the polar angle θ in the experimental detection set-up accordingly

$$W_{k,\varphi \rightarrow k',\varphi'} = \frac{2\pi}{\hbar} |\langle k', \varphi' | V | k, \varphi \rangle|^2 \delta(E_k + E_\varphi - E_{k'} - E_{\varphi'}) \quad (3.419)$$

The Dirac's delta function $\delta(E_k + E_\varphi - E_{k'} - E_{\varphi'})$ in this expression accounts for the conservation of the energy of the scattering system. The energies of the target nucleus before and after the scattering event are E_φ and $E_{\varphi'}$, respectively. Likewise, E_k and $E_{k'}$ are the energies of the incident and scattered neutron. Multiple scattering is neglected as it is justified for accordingly thin targets. V is the operator of the interaction potential between neutrons and target nuclei.

Quasi-elastic scattering means that the energies of the incident and scattered neutrons are practically the same, $E_k \approx E_{k'}$. According to Eqs. (3.402) and (3.404), this means that the magnitudes of the initial and final wave vectors are also about the same, $k \approx k'$. However, the vector directions may be different as illustrated in Fig. 3.41. The difference

$$q = k - k' \quad (3.420)$$

is called the *scattering vector*. With $k = k' = 2\pi/\lambda$, the magnitude of the scattering vector obeys

$$q \approx (4\pi/\lambda) \sin \theta/2 \quad (3.421)$$

as illustrated in Fig. 3.41.

The matrix element $\langle k', \varphi' | V | k, \varphi \rangle$ in Eq. (3.419) links the incident and scattered states of the neutron. The operator of the interaction potential V the neutron experiences in the scattering event can be specified as a *Fermi pseudo-potential*: The interaction of an incident neutron with the target nuclei is governed by the *strong interaction* between nucleons. Relative to atomistic or molecular length scales and relative to the wave length of the incident neutrons, it decays extremely fast on a distance of the order 10^{-15} m = 1 fm. The potential of this point-like interaction can therefore be represented by a distance distribution according to a Dirac's delta function:

$$V(\ell) = \frac{2\pi\hbar^2}{m} \sum_{j=1}^{N_t} b_j \delta(\ell - R_j) \quad (3.422)$$

The sum covers all target nuclei numbered from 1 to N_t . The factor b_j is the so-called *scattering length* of nucleus j characterizing the scattering efficiency of this particular nuclide. The order of magnitude of the scattering length corresponds to the dimension of the nucleus, that is, femtometers. The instantaneous position vectors of the neutron and the target nucleus j are denoted by ℓ and $\mathbf{R}_j$, respectively.

Three remarks appear to be appropriate at this point: (1) The three-dimensional Dirac's delta function in the Fermi pseudo-potential obeys the property $\int_{\text{all space}} \delta(\mathbf{R}) d^3R = 1$. That is, the dimension of the Dirac's delta function is $[\text{length}]^{-3}$. (2) The potential V implies couplings of any sort between neutron and nucleus. In principle, it also includes spin interactions if the nucleus possesses a finite spin. Since only coinciding positions are considered, the spin-coupling contribution is represented by the *Fermi contact interaction* which is proportional to the scalar product $(\mathbf{I} \cdot \mathbf{S})$, where the vector operators $\mathbf{I}$ and $\mathbf{S}$ refer to the nuclear and neutron spins, respectively. (3) All nuclear specifics such as isotope and spin which are relevant for the scattering properties are commonly represented by the scattering length b_j . As a consequence, no spin state quantum number appears in the formalism. Numerical values of the scattering length of diverse atomic species and their isotopes can be found at Ref. [107], for instance.

The effect of the Dirac's delta function in Eq. (3.422) is that the interaction potential becomes infinite if the positions coincide, that is, for $\ell - \mathbf{R}_j = 0$, and vanishes otherwise. This reflects the extreme short range effective for neutron/nucleus interactions. The weighting factors $2\pi\hbar^2 b_j/m$ are chosen in such a way that the Fermi pseudo-potential is consistent with the condition that scattering at a single fixed nucleus must be of spherical symmetry while the structure of the scattering centers is irrelevant for (elastic) neutron scattering. A straightforward derivation of this factor can be found in Ref. [97], for example.

The golden rule Eq. (3.419) postulates that the perturbation represented by the potential V is *weak* relative to the energy of the unperturbed system. Since we are considering thermal neutrons and nuclei in their ground states, this condition means that the expectation value of the interaction potential V should be much weaker than thermal energy. At first sight, this appears to conflict with the delta function character of the Fermi pseudo-potential which even diverges at the position of the nucleus. However, the point-like extension of the interaction range ensures in the integral sense that the neutron–nucleus impact is of the so-called *weak-collision* type. Relative to thermal energy of the system, the scattering event is a minor perturbation. This is validated by the fact that scattering can actually be purely elastic or – as it is of interest in the present context – quasi-elastic.

Inserting the Fermi pseudo-potential Eq. (3.422) in the golden-rule formula Eq. (3.419) and this into the expression for the double-differential cross-section Eq. (3.418) leads to

$$\frac{\partial^2 \sigma_{\varphi \rightarrow \varphi'}}{\partial \Omega \partial E_{k'}} = \Phi^{-1} N L^3 \frac{\hbar}{m} k' \left| \left\langle \mathbf{k}', \varphi' \left| \sum_{j=1}^{N_t} b_j \delta(\ell - \mathbf{R}_j) \right| \mathbf{k}, \varphi \right\rangle \right|^2 \delta(E_k + E_\varphi - E_{k'} - E_{\varphi'}) \quad (3.423)$$

The total number N of incident neutrons in the plane-wave state $|\mathbf{k}\rangle$ can be expressed by the incident flux and the wave number. The velocity of the incident neutrons is

$$v = \frac{\Phi L^3}{N} \quad (3.424)$$

where L^3 is the mean (“box normalization”) volume per neutron. On the other hand,

$$v = \frac{p}{m} = \frac{\hbar k}{m} \quad (3.425)$$

Combining both expressions gives

$$N = \frac{\Phi L^3 m}{\hbar k} \quad (3.426)$$

so that Eq. (3.423) can be rewritten as

$$\frac{\partial^2 \sigma_{\varphi \rightarrow \varphi'}}{\partial \Omega \partial E_{k'}} = L^6 \frac{k'}{k} \left| \left\langle \mathbf{k}', \varphi' \left| \sum_{j=1}^{N_t} b_j \delta(\boldsymbol{\ell} - \mathbf{R}_j) \right| \mathbf{k}, \varphi \right\rangle \right|^2 \delta(E_k + E_\varphi - E_{k'} - E_{\varphi'}) \quad (3.427)$$

Let us now proceed in three further steps. At first we will employ the plane-wave neutron eigenfunctions for the derivation of the scattering vector. Then it will be shown that the energy-conserving delta function can be expressed by its Fourier transform which means that a time integral comes into play. Finally we will show how the fluctuating positions of the target nuclei can be taken into account.

Expressed as wave functions, that is, as the box-normalized eigenfunctions of the momentum operator $-i\hbar\nabla$, the plane-wave neutron states are

$$\psi_k(\boldsymbol{\ell}) = L^{-3/2} \exp\{i\mathbf{k} \cdot \boldsymbol{\ell}\} \quad \text{and} \quad \psi_{k'}(\boldsymbol{\ell}) = L^{-3/2} \exp\{i\mathbf{k}' \cdot \boldsymbol{\ell}\} \quad (3.428)$$

where $\boldsymbol{\ell}$ is the instantaneous position vector of the neutron. On this basis, the matrix element in Eq. (3.427) can be modified as

$$\begin{aligned} \left\langle \mathbf{k}', \varphi' \left| \sum_{j=1}^{N_t} b_j \delta(\boldsymbol{\ell} - \mathbf{R}_j) \right| \mathbf{k}, \varphi \right\rangle &= L^{-3} \left\langle \varphi' \left| \sum_{j=1}^{N_t} b_j e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{R}_j} \right| \varphi \right\rangle \\ &= L^{-3} \left\langle \varphi' \left| \sum_{j=1}^{N_t} b_j e^{i\mathbf{q} \cdot \mathbf{R}_j} \right| \varphi \right\rangle \end{aligned} \quad (3.429)$$

The squared magnitude of this expression contains a factor L^{-6} which cancels the factor L^6 in Eq. (3.427) (as predicted in footnote 39).

The important result of Eq. (3.429) is that the dependence of the matrix element on the scattering vector $\mathbf{q}$ becomes evident in this way. Equation (3.427) for the double-differential cross-section can thus be rewritten as⁴⁰

$$\begin{aligned}\frac{\partial^2 \sigma_{\varphi \rightarrow \varphi'}}{\partial \Omega \partial E_{k'}} &= \frac{k'}{k} \left| \sum_{j=1}^{N_t} b_j \langle \varphi' | e^{i\mathbf{q} \cdot \mathbf{R}_j} | \varphi \rangle \right|^2 \delta(E_k + E_\varphi - E_{k'} - E_{\varphi'}) \\ &= \frac{k'}{k} \sum_{j,l=1}^{N_t} b_j b_l \langle \varphi' | e^{i\mathbf{q} \cdot \mathbf{R}_j} | \varphi \rangle^* \langle \varphi' | e^{i\mathbf{q} \cdot \mathbf{R}_l} | \varphi \rangle \delta(E_k + E_\varphi - E_{k'} - E_{\varphi'}) \\ &= \frac{k'}{k} \sum_{j,l=1}^{N_t} b_j b_l \langle \varphi | e^{-i\mathbf{q} \cdot \mathbf{R}_j} | \varphi' \rangle \langle \varphi' | e^{i\mathbf{q} \cdot \mathbf{R}_l} | \varphi \rangle \delta(E_k + E_\varphi - E_{k'} - E_{\varphi'}) \quad (3.430)\end{aligned}$$

The energy-conserving delta function $\delta(E_k + E_\varphi - E_{k'} - E_{\varphi'})$ can be replaced by the Fourier relation⁴¹

$$\begin{aligned}\delta(E_k + E_\varphi - E_{k'} - E_{\varphi'}) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp\left\{i(E_k + E_\varphi - E_{k'} - E_{\varphi'}) \frac{t}{\hbar}\right\} d\left(\frac{t}{\hbar}\right) \\ &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \exp\left\{\frac{i}{\hbar}(E_\varphi - E_{\varphi'})t\right\} \exp(-i\omega t) dt \quad (3.431)\end{aligned}$$

where $\omega = (E_{k'} - E_k)/\hbar$. After some rearrangement, Eq. (3.430), last line, thus becomes

$$\begin{aligned}\frac{\partial^2 \sigma_{\varphi \rightarrow \varphi'}}{\partial \Omega \partial E_{k'}} &= \frac{1}{2\pi\hbar} \frac{k'}{k} \sum_{j,l=1}^{N_t} b_j b_l \langle \varphi | e^{-i\mathbf{q} \cdot \mathbf{R}_j} | \varphi' \rangle \langle \varphi' | e^{i\mathbf{q} \cdot \mathbf{R}_l} | \varphi \rangle \int_{-\infty}^{\infty} e^{-i\omega t} e^{-iE_{\varphi'} t/\hbar} e^{iE_\varphi t/\hbar} dt \\ &= \frac{1}{2\pi\hbar} \frac{k'}{k} \sum_{j,l=1}^{N_t} b_j b_l \int_{-\infty}^{\infty} e^{-i\omega t} \langle \varphi | e^{-i\mathbf{q} \cdot \mathbf{R}_j} | \varphi' \rangle e^{-iE_{\varphi'} t/\hbar} \langle \varphi' | e^{i\mathbf{q} \cdot \mathbf{R}_l} | \varphi \rangle e^{iE_\varphi t/\hbar} dt \\ &= \frac{1}{2\pi\hbar} \frac{k'}{k} \sum_{j,l=1}^{N_t} b_j b_l \int_{-\infty}^{\infty} e^{-i\omega t} \langle \varphi | e^{-i\mathbf{q} \cdot \mathbf{R}_j} | \varphi' \rangle \langle \varphi' | e^{-iE_{\varphi'} t/\hbar} e^{i\mathbf{q} \cdot \mathbf{R}_l} e^{iE_\varphi t/\hbar} | \varphi \rangle dt \quad (3.432)\end{aligned}$$

⁴⁰ Note that the scattering lengths are real and that the conjugate complex matrix element obeys $\langle \varphi' | \exp\{i\mathbf{q} \cdot \mathbf{R}_j\} | \varphi \rangle^* = \langle \varphi | \exp\{-i\mathbf{q} \cdot \mathbf{R}_j\} | \varphi' \rangle^*$, where $\exp\{-i\mathbf{q} \cdot \mathbf{R}_j\}$ is the unitary operator adjoint to $\exp\{i\mathbf{q} \cdot \mathbf{R}_j\}$. Definitions of the operator terminology can be found in textbooks on quantum mechanics and in compact form in the “toolbox” of Ref. [1].

⁴¹ Fourier transforms link conjugate variables the product of which is a phase angle. Examples are *angular frequency* and *time*, or *momentum* and *position vectors*. In the present case, the variables are energy, that is, $\hbar$ times angular frequency, and time divided by $\hbar$, so that the product is again a phase angle. Note that the energy-conserving delta function is of dimension [energy]⁻¹.

The matrix elements do not explicitly depend on time and can therefore be shifted as constant factors into the time integral. Likewise, the exponential factors $\exp\{-iE_{\varphi'}t/\hbar\}$ and $\exp\{iE_{\varphi}t/\hbar\}$ do not interfere with the space integral inherent to the matrix elements, and they commute moreover with the operator $\exp\{i\mathbf{q} \cdot \mathbf{R}_j\}$. They can therefore be arranged in “sandwich” form around $\exp\{i\mathbf{q} \cdot \mathbf{R}_j\}$ as shown in the last line of Eq. (3.432).

The third step transfers part of the explicit time dependences in the integrand to the position vectors of the target nuclei. This is achieved by the replacements⁴²

$$\langle \varphi' | e^{-E_{\varphi'}t/\hbar} = \langle \varphi' | e^{-i\mathcal{H}t/\hbar} \quad (3.433)$$

and

$$e^{iE_{\varphi}t/\hbar} |\varphi\rangle = e^{i\mathcal{H}t/\hbar} |\varphi\rangle \quad (3.434)$$

$\mathcal{H}$ is the Hamilton operator of the target nuclei with eigen-values $E_{\varphi}, E_{\varphi'}$ and eigen-kets $|\varphi\rangle, |\varphi'\rangle$. The validity of the relations in Eqs. (3.433) and (3.434) can readily be verified by multiplying Eq. (3.433) with the ket $|\varphi'\rangle$ from the right, and Eq. (3.434) with the bra $\langle \varphi |$ from the left, and taking into account the normalized eigen function properties of φ and φ' .

Inserting the identities given in Eqs. (3.433) and (3.434) in Eq. (3.432) gives

$$\begin{aligned} \frac{\partial^2 \sigma_{\varphi \rightarrow \varphi'}}{\partial \Omega \partial E_{k'}} &= \frac{1}{2\pi\hbar} \frac{k'}{k} \\ &\times \sum_{j,l=1}^{N_t} b_j b_l \int_{-\infty}^{\infty} e^{-i\omega t} \langle \varphi | e^{-i\mathbf{q} \cdot \mathbf{R}_j} | \varphi' \rangle \langle \varphi' | e^{-i\mathcal{H}t/\hbar} e^{i\mathbf{q} \cdot \mathbf{R}_l} e^{i\mathcal{H}t/\hbar} | \varphi \rangle dt \end{aligned} \quad (3.435)$$

The sandwich operator $e^{-i\mathcal{H}t/\hbar} e^{i\mathbf{q} \cdot \mathbf{R}_l} e^{i\mathcal{H}t/\hbar}$ implies the unitary transformation $e^{i\mathbf{q} \cdot \mathbf{R}_l(0)} \rightarrow e^{i\mathbf{q} \cdot \mathbf{R}_l(t)}$ according to

$$e^{i\mathbf{q} \cdot \mathbf{R}_l(t)} = e^{-i\mathcal{H}t/\hbar} e^{i\mathbf{q} \cdot \mathbf{R}_l(0)} e^{i\mathcal{H}t/\hbar} \quad (3.436)$$

In other terms, this operation mediates the conversion to the *Heisenberg representation*:

⁴² The effect of exponential operators, that is, exponential functions having an operator expression in the exponent, becomes obvious when the exponential is formally expanded in a power series and when the power terms are applied to the function the operator is supposed to act on. The power determines how often the application of the operator must be repeated.

$$\frac{\partial^2 \sigma_{\varphi \rightarrow \varphi'}}{\partial \Omega \partial E_{k'}} = \frac{1}{2\pi\hbar} \frac{k'}{k} \sum_{j,l=1}^{N_t} b_j b_l \int_{-\infty}^{\infty} e^{-i\omega t} \langle \varphi | e^{-i\mathbf{q} \cdot \mathbf{R}_j(0)} | \varphi' \rangle \langle \varphi' | e^{i\mathbf{q} \cdot \mathbf{R}_l(t)} | \varphi \rangle dt \quad (3.437)$$

It should be noted at this point that the time dependence of the positions of the target nuclei comes *explicitly* into play in Eq. (3.437). This is the link to molecular motion properties to be studied on this basis.

The double-differential scattering cross-section so far refers to a specific transition $\varphi \rightarrow \varphi'$ of the nuclear states. In the experiment, we cannot distinguish between different final states of the target nuclei. We therefore sum over all possible final states and use the so-called *closure relation*

$$\sum_{\varphi'} \langle \varphi | A | \varphi' \rangle \langle \varphi' | B | \varphi \rangle = \langle \varphi | AB | \varphi \rangle \quad (3.438)$$

The result is the double-differential scattering cross-section for all possible final states of the scattering centers:

$$\begin{aligned} \frac{\partial^2 \sigma_{\varphi}}{\partial \Omega \partial E_{k'}} &= \sum_{\varphi'} \frac{\partial^2 \sigma_{\varphi \rightarrow \varphi'}}{\partial \Omega \partial E_{k'}} \\ &= \frac{1}{2\pi\hbar} \frac{k'}{k} \sum_{j,l=1}^{N_t} b_j b_l \int_{-\infty}^{\infty} e^{-i\omega t} \langle \varphi | e^{-i\mathbf{q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{q} \cdot \mathbf{R}_l(t)} | \varphi \rangle dt \end{aligned} \quad (3.439)$$

Likewise, since we do not know the initial states of the target nuclei either, the expectation value $\langle \varphi | e^{-i\mathbf{q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{q} \cdot \mathbf{R}_l(t)} | \varphi \rangle$ in the integrand must be averaged over these states as well. That is, we form the mean expectation value in the ensemble of target nuclei in thermal equilibrium, $\overline{\langle \varphi | e^{-i\mathbf{q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{q} \cdot \mathbf{R}_l(t)} | \varphi \rangle} \equiv \langle e^{-i\mathbf{q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{q} \cdot \mathbf{R}_l(t)} \rangle$. In this notation, the experimentally relevant double-differential cross-section is represented by

$$\begin{aligned} \frac{\partial^2 \sigma_{\varphi}}{\partial \Omega \partial E_{k'}} &= \sum_{\varphi} p_{\varphi} \frac{\partial^2 \sigma_{\varphi}}{\partial \Omega \partial E_{k'}} \\ &= \frac{1}{2\pi\hbar} \frac{k'}{k} \sum_{j,l=1}^{N_t} b_j b_l \int_{-\infty}^{\infty} e^{-i\omega t} \langle e^{-i\mathbf{q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{q} \cdot \mathbf{R}_l(t)} \rangle dt \end{aligned} \quad (3.440)$$

where p_{φ} is the statistical weight of nuclear state φ . The correlation function $\langle e^{-i\mathbf{q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{q} \cdot \mathbf{R}_l(t)} \rangle$ implies the characteristics of molecular dynamics. It is therefore of central interest. In the following section, we will analyze it further and derive an explicit expression for a simple scenario of molecular motion.

3.6.4 Coherent and Incoherent Scattering

The scattering length b_j of the target nucleus j , which is normally a real quantity,⁴³ is a function of the nuclear spin and the mass number. Samples may contain different isotopes of the same element in natural abundance. Due to the different mass numbers and different spins, the scattering length can be distributed accordingly. Equation (3.440) must therefore be averaged over this distribution:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E_{k'}} = \frac{1}{2\pi\hbar} \frac{k'}{k} \sum_{j,l=1}^{N_t} \overline{b_j b_l} \int_{-\infty}^{\infty} e^{-i\omega t} \left\langle e^{-i\mathbf{q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{q} \cdot \mathbf{R}_l(t)} \right\rangle dt \quad (3.441)$$

where the ensemble average is indicated by the bar over the scattering lengths. The sum can be split in two parts with terms for different nuclei, $j \neq l$, and for the same nucleus, $j = l$. Employing the relations $\overline{b_j b_l} = \overline{b^2}$ for $j = l$ and $\overline{b_j b_l} = \overline{b}^2$ for $j \neq l$, that is, shortly

$$\overline{b_j b_l} = \overline{b^2} + \delta_{jl} (\overline{b^2} - \overline{b}^2) \quad (3.442)$$

leads to

$$\begin{aligned} \sum_{j,l} \overline{b_j b_l} \dots &= \sum_{j \neq l} \overline{b_j b_l} \dots + \sum_{j=l} \overline{b_j b_l} \dots \\ &= \overline{b}^2 \sum_{j \neq l} \dots + \overline{b^2} \sum_{j=l} \dots \\ &\equiv \overline{b}^2 \sum_{j,l} \dots + (\overline{b^2} - \overline{b}^2) \sum_{j=l} \dots \end{aligned} \quad (3.443)$$

where δ_{jl} is the Kronecker symbol (see footnote 16), and where the fact has been taken into account that the scattering lengths of different nuclei are uncorrelated. The dots in the above equation represent the integral in Eq. (3.441). Note that the running indices in the third line of Eq. (3.443) have been altered relative to the second line. This is compensated by the difference term in the third line.

On this basis, two contributions to the double-differential cross-section can be identified:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E_{k'}} \right) = \left(\frac{\partial^2 \sigma}{\partial \Omega \partial E_{k'}} \right)_{\text{coh}} + \left(\frac{\partial^2 \sigma}{\partial \Omega \partial E_{k'}} \right)_{\text{inc}} \quad (3.444)$$

⁴³ Taken as a complex quantity, the imaginary part of the scattering length corresponds to absorption of the incident neutron by the nucleus with which the neutron forms a compound nucleus while interacting. A compound formation, however, can only occur if the neutron energy matches an excitation energy level of the nucleus. For light nuclei as they are of interest in soft-matter science, and for cold neutrons, this condition is entirely unrealistic.

3.6.4.1 Coherent Dynamic Structure Factor

The first term on the right-hand side is the double-differential cross-section for *coherent-scattering*,

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E_{k'}} \right)_{\text{coh}} = \frac{1}{2\pi\hbar} \frac{k'}{k} \bar{b}^2 N_t \int_{-\infty}^{\infty} e^{-i\omega t} G_{\text{coh}}(\mathbf{q}, t) dt \quad (3.445)$$

where N_t is the number of scattering centers in the target area hit by the incident neutron beam. Essentially, this expression is the temporal Fourier transform of the correlation function

$$G_{\text{coh}}(\mathbf{q}, t) = \frac{1}{N_t} \sum_{j,l=1}^{N_t} \left\langle e^{-i\mathbf{q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{q} \cdot \mathbf{R}_l(t)} \right\rangle \quad (3.446)$$

called the *coherent dynamic structure factor* or synonymously *coherent-scattering function*. We have referred to this definition already in Eq. (1.14).

The double-differential cross-section for coherent-scattering, $(\partial^2 \sigma / \partial \Omega \partial E_{k'})_{\text{coh}}$, is thus proportional to the Fourier transform of the coherent dynamic structure factor $G_{\text{coh}}(\mathbf{q}, t)$ and probes *relative* pair diffusion. Strictly speaking, the double sum in Eq. (3.446) implies the cases $j = l$ as well, that is self-diffusion. We will nevertheless use the term ‘pair diffusion’ because it addresses the essence of the definition in Eq. (3.446). The relative displacement is defined by $r_{j,l}(t) = |\mathbf{R}_j(0) - \mathbf{R}_l(t)|$. For $t = 0$, the *static structure factor*

$$S(\mathbf{q}) = G_{\text{coh}}(\mathbf{q}, 0) = \frac{1}{N_t} \sum_{j,l=1}^{N_t} \left\langle e^{-i\mathbf{q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{q} \cdot \mathbf{R}_l(t)} \right\rangle \quad (3.447)$$

emerges from Eq. (3.446). It characterizes the *static* distance distribution of particle pairs.

The double-differential cross-section for coherent scattering reflects the constructive superposition of de Broglie waves of neutrons scattered at different nuclei. This term will dominate in cases where all nuclei in the system are characterized by the same scattering length $b_j = \bar{b}$. The coherent dynamic structure factor refers to positions of the *same* nucleus (i.e. $j = l$) at times 0 and t , as well as to the time-dependent positions of *different* (i.e., $j \neq l$) nuclei. The latter case suggests that constructive interference of de Broglie waves scattered at different nuclei matters. This contribution therefore implies structural information of the sample.

3.6.4.2 Incoherent Dynamic Structure Factor

The second contribution to Eq. (3.444), the *double-differential cross-section for incoherent scattering*, is spelt out as

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E_{k'}} \right)_{\text{inc}} = \frac{1}{2\pi\hbar} \frac{k'}{k} \left(\overline{b^2} - \bar{b}^2 \right) N_t \int_{-\infty}^{\infty} e^{-i\omega t} \mathcal{G}_{\text{inc}}(\mathbf{q}, t) dt \quad (3.448)$$

The temporal correlation function $\mathcal{G}_{\text{inc}}(t)$ is called the *incoherent dynamic structure factor* characterizing translational self-diffusion. A synonymous term is *incoherent-scattering function*. It is defined by

$$\begin{aligned} \mathcal{G}_{\text{inc}}(\mathbf{q}, t) &= \frac{1}{N_t} \sum_{j=1}^{N_t} \left\langle e^{-i\mathbf{q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{q} \cdot \mathbf{R}_j(t)} \right\rangle \\ &= \frac{1}{N_t} \sum_{j=1}^{N_t} \left\langle \exp \{ -i\mathbf{q} \cdot [\mathbf{R}_j(0) - \mathbf{R}_j(t)] \} \right\rangle \\ &= \frac{1}{N_t} \sum_{j=1}^{N_t} \left\langle \exp \{ i\mathbf{q} \cdot \mathbf{r}_{j,\text{self}} \} \right\rangle \end{aligned} \quad (3.449)$$

where the “self”-displacement is $\mathbf{r}_{j,\text{self}}(t) = \mathbf{R}_j(t) - \mathbf{R}_j(0)$. The essence of Eq. (3.448) is that the double-differential cross-section for incoherent scattering, $(\partial^2 \sigma / \partial \Omega \partial E_{k'})_{\text{inc}}$, is proportional to the Fourier transform of the incoherent dynamic structure factor, $\mathcal{G}_{\text{inc}}(t)$. In the case of homo-nuclear scattering centers in homogeneous samples, Eqs. (3.448) and (3.449) can be reduced to

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E_{k'}} \right)_{\text{inc}} = \frac{1}{2\pi\hbar} \frac{k'}{k} \left(\overline{b^2} - \bar{b}^2 \right) N_t \int_{-\infty}^{\infty} e^{-i\omega t} \mathcal{G}_{\text{inc}}(\mathbf{q}, t) dt \quad (3.450)$$

with

$$\mathcal{G}_{\text{inc}}(\mathbf{q}, t) = \left\langle e^{-i\mathbf{q} \cdot \mathbf{R}(0)} e^{i\mathbf{q} \cdot \mathbf{R}(t)} \right\rangle = \left\langle \exp \{ i\mathbf{q} \cdot \mathbf{r}_{\text{self}} \} \right\rangle \quad (3.451)$$

The latter version of $\mathcal{G}_{\text{inc}}(\mathbf{q}, t)$ is identical to Eq. (1.10).

The second contribution to Eq. (3.444) refers to *incoherent scattering* at independent scattering centers not giving rise to constructive interference of the scattered de Broglie waves. The double-differential cross-section for this contribution is weighted with the mean square fluctuation of the scattering lengths $\overline{b^2} - \bar{b}^2$. Any deviation from the mean scattering length $\bar{b}$ contributes to the incoherent-scattering process. In this case, the correlation function in the integral in Eq. (3.441),

the incoherent-scattering function, merely refers to the positions of the *same* nucleus at times 0 and t . Consequently, no structural interference patterns can be expected in this case.

The mean square fluctuation of the scattering lengths, $\overline{b^2} - \bar{b}^2$, strongly depends on the isotopical composition of the target. Let the isotope species in the system be characterized by the natural abundance c_v and the nuclear spin quantum number I_v . The scattering lengths of the isotope numbered by v are denoted by b_v^+ and b_v^- for interaction with neutrons with spin-“up” and spin-“down,” respectively. The mean values of the scattering length are then straightforwardly calculated as [97]

$$\begin{aligned}\bar{b} &= \sum_v \frac{c_v}{2I_v + 1} \{ (I_v + 1)b_v^+ + I_v b_v^- \} \\ \overline{b^2} &= \sum_v \frac{c_v}{2I_v + 1} \{ (I_v + 1)(b_v^+)^2 + I_v (b_v^-)^2 \}\end{aligned}\quad (3.452)$$

If only a single isotope exists in the system and if the nuclear spin is zero, a single value for the scattering length results, that is, $\bar{b} = b$ and $\overline{b^2} = b^2$. In this case, scattering will be entirely coherent, and the incoherent contribution vanishes. Values for coherent- and incoherent- scattering cross-sections of a number of typical isotopes are listed in Table 3.1. In hydrocarbon compounds, the incoherent scattering at the (light) hydrogen nuclei dominates. Since soft matter usually refers to organic materials with lots of hydrogen atoms, and since incoherent scattering specifically reveals dynamic information, we will focus on this contribution in the following.

3.6.5 Probing Translational Diffusion of Molecules by Incoherent Scattering

The dynamic structure factor for translational self-diffusion specified in Eq. (3.449) adopts the simple form Eq. (3.451) if all scattering nuclei in the sample are equivalent with respect to translational diffusion. The ensemble average $\langle e^{-i\mathbf{q}\cdot\mathbf{R}(0)} e^{i\mathbf{q}\cdot\mathbf{R}(t)} \rangle$ can then be evaluated with the aid of the probability density $P(\mathbf{r}_{\text{self}}, t)$ that a scattering center is displaced from a position $\mathbf{R}(0)$ to a position $\mathbf{R}(t)$ in the time interval t . The displacement vector is $\mathbf{r}_{\text{self}}(t) = \mathbf{R}(t) - \mathbf{R}(0)$.

In the case of ordinary diffusion in “infinite,” isotropic, and unrestricted media, displacements are expected to obey a Gaussian distribution (see Sect. 2.5) so that the probability density $P(\mathbf{r}_{\text{self}}, t)$ is given by

$$P(\mathbf{r}_{\text{self}}, t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left\{-\frac{r_{\text{self}}^2}{4Dt}\right\} \quad (3.453)$$

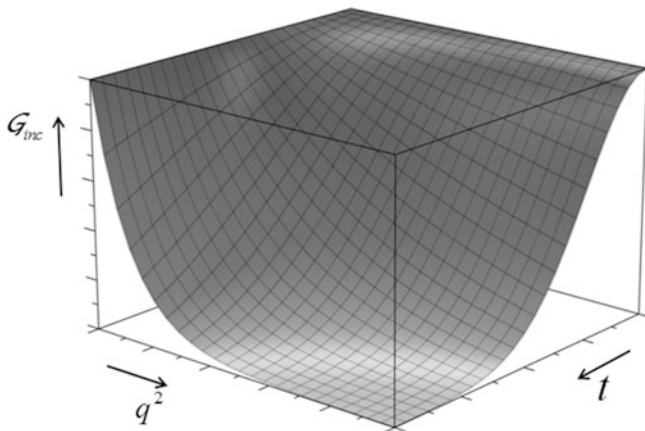


Fig. 3.42 Incoherent dynamic structure factor as a function of t and q^2 according to Eq. (3.454)

for positive times t . D is the diffusion coefficient of the molecule or the molecular group bearing the nucleus under consideration. We thus arrive at the dynamic structure factor for translational self-diffusion

$$\begin{aligned}
 G_{\text{inc}}(t) &= \left\langle e^{-i\mathbf{q} \cdot \mathbf{R}(0)} e^{i\mathbf{q} \cdot \mathbf{R}(t)} \right\rangle \\
 &= \int_{\text{space}} e^{-i\mathbf{q} \cdot \mathbf{R}(0)} e^{i\mathbf{q} \cdot \mathbf{R}(t)} P(\mathbf{r}_{\text{self}}, t) d^3 r_{\text{self}} \\
 &= \frac{1}{(4\pi Dt)^{3/2}} \int_{\text{space}} \exp\{i\mathbf{q} \cdot \mathbf{r}_{\text{self}}\} \exp\left\{-\frac{r_{\text{self}}^2}{4Dt}\right\} d^3 r_{\text{self}} \\
 &= \exp\{-q^2 Dt\} \\
 &= \exp\left\{-\frac{1}{6} q^2 \langle r_{\text{self}}^2 \rangle\right\}
 \end{aligned} \tag{3.454}$$

where we have made use of the Einstein relation for normal diffusion Eq. (2.169),

$$\langle r_{\text{self}}^2 \rangle = 6Dt \tag{3.455}$$

A graphical representation of Eq. (3.454) is rendered in Fig. 3.42.

Formally, Eq. (3.454) coincides with the spin-echo-attenuation functions we have derived for field-gradient NMR diffusometry in Sect. 3.2. The scattering vector $\mathbf{q}$ of neutron scattering and the so-called wave number of field-gradient NMR diffusometry are however of a different nature. The latter has nothing much to do with momentum transfer and is defined by the strength and duration of the encoding field gradient. Although the two techniques represent different experiments, a vague analogy may nevertheless be seen in neutron spin-echo scattering experiments where precession phase shifts accumulated in two different

time intervals are compared. After all, an identical expression is evaluated in both experiments.

The expressions in Eq. (3.454) are valid *cum grano salis* since we have tacitly and implicitly equated $\exp\{-i\mathbf{q} \cdot \mathbf{R}(0)\} \exp\{i\mathbf{q} \cdot \mathbf{R}(t)\} = \exp\{-i\mathbf{q} \cdot [\mathbf{R}(0) - \mathbf{R}(t)]\} = \exp\{i\mathbf{q} \cdot \mathbf{r}_{\text{self}}(t)\}$. Strictly speaking, this equality anticipates that $\mathbf{R}(t)$ and $\mathbf{R}(0)$ and hence $\exp\{-i\mathbf{q} \cdot \mathbf{R}(0)\}$ and $\exp\{i\mathbf{q} \cdot \mathbf{R}(t)\}$ commute which is not the case for finite t . The reason is that these expressions are operators as becomes obvious from the unitary transformation $\mathbf{R}(t) = \exp\{-i\mathcal{H}t/\hbar\}\mathbf{R}(0)\exp\{i\mathcal{H}t/\hbar\}$ or $\exp\{i\mathbf{q} \cdot \mathbf{R}(t)\} = \exp\{-i\mathcal{H}t/\hbar\} \exp\{i\mathbf{q} \cdot \mathbf{R}(0)\} \exp\{i\mathcal{H}t/\hbar\}$ used in Eq. (3.435). Exponential operators are interpreted by their expansions in power series. The molecular Hamiltonian $\mathcal{H}$ is a function of momentum. The problem is then that position and momentum components do not commute as manifested by Heisenberg's uncertainty relation. However, with the applications of interest here, we are dealing with relatively large particles (molecules or molecular groups). According to the correspondence principle, the uncertainty relation is therefore of minor importance, and a classical view can reliably be adopted. See also the discussion in Sect. 1.3.

The double-differential cross-section for incoherent scattering, Eq. (3.450), is proportional to the temporal Fourier transform of the incoherent-scattering function. Carrying out this operation on the basis of Eq. (3.454) leads to

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E_{k'}} \right)_{\text{inc}} = \frac{k'}{k} N_t (\overline{b^2} - \bar{b}^2) \frac{1}{\pi \hbar} \frac{Dq^2}{\omega^2 + (Dq^2)^2} \quad (3.456)$$

Using $\partial E_{k'} = \hbar \partial \omega$, this can be converted to the modified form

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} \right)_{\text{inc}} = \frac{k'}{k} N_t (\overline{b^2} - \bar{b}^2) \frac{1}{\pi} \frac{Dq^2}{\omega^2 + (Dq^2)^2} \quad (3.457)$$

Equations (3.456) and (3.457) predict a *Lorentzian* shape of the quasi-elastically broadened distribution of energies of the scattered neutrons. The maximum at $\omega = 0$ indicates the position of perfectly elastic scattering. The full width at half height is $\Delta\omega_{1/2} = 2Dq^2$ so that the molecular diffusion coefficient can be evaluated on this basis by plotting $\Delta\omega_{1/2}$ versus q^2 . A graphical representation of Eq. (3.457) can be found in Fig. 3.43.

3.7 Dynamic Light and X-Ray Scattering

As a further scattering phenomenon suitable for the detection of dynamic properties, let us now turn to the deflection of electromagnetic radiation by interaction with matter. Light is scattered by density fluctuations $\rho = \rho(\mathbf{R}, t)$ modifying the optical properties of the sample at the position $\mathbf{R}$. The fluctuations can be spatial and

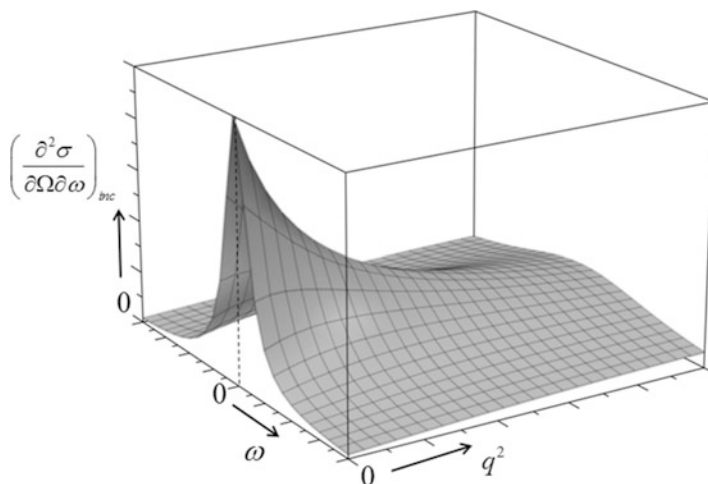


Fig. 3.43 Double-differential cross-section for incoherent scattering as a function of ω and q^2 according to Eq. (3.457)

temporal. The latter are due to Brownian motions. If the experiment is carried out in such a way that only spatial fluctuations matter, one speaks of *static light scattering* (which is of interest for the determination of molecular mass of macromolecules, for instance). By contrast, if the information content of the temporal fluctuations is exploited in the sense of molecular dynamics, one is dealing with *dynamic light scattering* (DLS). Other terms in use are *photon correlation spectroscopy* and *quasi-elastic light scattering*. This is to be distinguished from inelastic light scattering involving absorption phenomena such as in Raman, fluorescence and phosphorescence spectroscopy which we will not consider further here.

The treatment of dynamic light scattering is closely related to the formalism in the preceding section [99]. The main difference is that the scattering centers are now electrons in atoms and molecules instead of nuclei in the case of neutron scattering. On the other hand, DLS refers coherently to *collectives* of molecular scattering centers: Electromagnetic radiation is scattered by density fluctuations, that is, by fluctuations of the local refractive index [99, 108]. An incoherent counterpart referring to an ensemble of uncorrelated scattering centers as in the case of neutron scattering does not exist. However, density fluctuations are the consequence of self-diffusion of molecules so that DLS is expected to provide results formally resembling those of incoherent neutron scattering.

A feature of major interest is that the fluctuation time range probed by DLS is much larger and ranges from 100 ns to seconds. Application fields of DLS can be as different as macromolecules dissolved in a solvent of different refractive index, critical fluctuations near phase transitions, or the familiar Rayleigh scattering of sun light in the atmosphere.

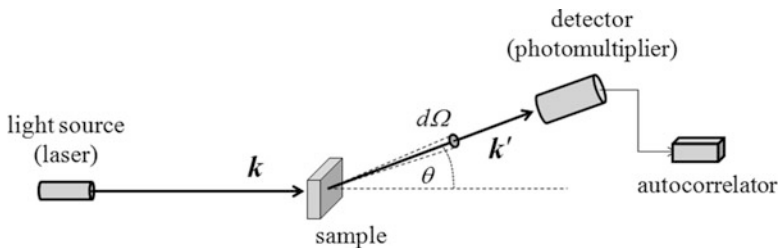


Fig. 3.44 Schematic setup of dynamic light scattering experiments

3.7.1 The Experiment

Figure 3.44 schematically shows the typical setup of light scattering experiments. The incident light can optionally be polarized with a polarizer, while the scattered light is analyzed with an analyzer. Light is usually detected with the aid of photomultipliers, the output of which is proportional to the energy of the absorbed light quanta. The primary quantity of interest is the autocorrelation function of the detected intensity as a function of varying time delays. This function can be evaluated in a digital autocorrelator directly implemented in the experimental setup.

The wavelength range of the electromagnetic radiation is in principle unlimited. This type of scattering can refer to visible light, X-rays, or synchrotron radiation. The theory is the same, but the most popular applications refer to light.

Anticipating linearity, that is, small electric-field strengths E relative to interactions in atoms and molecules, the coupling of electromagnetic waves with matter is characterized by the local polarization $P(\mathbf{R}, t)$ defined by

$$P(\mathbf{R}, t) = \varepsilon_0 \chi_e(\mathbf{R}, t) E(\mathbf{R}) \quad (3.458)$$

ε_0 is the electric-field constant, and $E(\mathbf{R})$ is the electric field at position $\mathbf{R}$. The local electric susceptibility $\chi_e(\mathbf{R}, t)$ can be split in a constant and a spatially as well as temporally fluctuating part:

$$\chi_e(\mathbf{R}, t) = \langle \chi_e \rangle + \delta \chi_e(\mathbf{R}, t) \quad (3.459)$$

Instead of the susceptibility, this expression can also be expressed in terms of the relative dielectric constant

$$\varepsilon_r = 1 + \chi_e \quad (3.460)$$

The fluctuating part is in both cases the same. Note that the constants χ_e and ε_r must be replaced by tensors if the scattering medium is anisotropic. That is,

$$\underline{\epsilon}_r = \underline{u} + \underline{\chi}_e \quad (3.461)$$

where $\underline{u}$ is the unit tensor. A situation of this sort will be encountered in Sect. 6.7 where we will consider dynamic light scattering in liquid crystals.

The fluctuating part can originate from any permanent or transient inhomogeneities and heterogeneities of the system. A potential anisotropy of the material which could give rise to a tensorial character of the susceptibility will however be disregarded here since this is of minor importance for the present discussion of the scattering principle. In the following, we will restrict ourselves to fluctuations of an exclusively thermal origin in an otherwise homogeneous system.

The spatial fluctuations at a certain time t are primarily responsible for the scattering process, whereas the fluctuating time dependence at a position $\mathbf{R}$ is evaluated in the photon correlation experiment. The local refractive index of the scattering medium is related to the local susceptibility by

$$n(\mathbf{R}, t) = \sqrt{1 + \chi_e(\mathbf{R}, t)} \quad (3.462)$$

The incident light will be deflected by the spatial fluctuations of the susceptibility (or equivalently of the refractive index). Since this is a *coherent* phenomenon resulting from many molecular scattering centers, one may also speak of *diffraction* at the instantaneous structure formed by the fluctuations: Electronic oscillators in the molecular scattering centers are excited by the incident wave. As a consequence, the oscillators radiate secondary electromagnetic waves. The effective scattered wave is then the superposition of the secondary waves emitted by the electronic oscillators. The scattered waves can be considered as first-order Bragg reflections at the distribution of “gratings” by which the spatial fluctuations can be analyzed with the aid of a spatial Fourier transformation.

3.7.2 Theory for Dilute Particle Dispersions

The treatment in the following refers to light wave lengths much larger than the correlation length of the density fluctuations not to speak of the size of the scattering centers (molecules, colloids, etc.). To illustrate the principle of light scattering, let us now consider the simplest case, namely, particles dispersed in an inert solvent. The susceptibility fluctuations $\delta\chi(\mathbf{R}, t)$ can then be attributed to fluctuations $\delta c(\mathbf{R}, t)$ of the local concentration of the particles,

$$c(\mathbf{R}, t) = \langle c \rangle + \delta c(\mathbf{R}, t) \quad (3.463)$$

where $\langle c \rangle$ is the mean concentration. Equations (3.459) and (3.463) suggest the proportionalities

$$E'(\mathbf{R}, t) \propto \delta\chi_e(\mathbf{R}, t) \propto \delta c(\mathbf{R}, t) \quad (3.464)$$

between the local amplitude of the electric-field strength of the scattered light, $E'(\mathbf{R}, t)$, and, on the one hand, the local fluctuation of the susceptibility and the local concentration on the other. The temporal evolution of a given initial concentration distribution $\delta c(\mathbf{R}, 0)$ can be calculated on the basis of Fick's diffusion equation for an unbounded isotropic medium,

$$\frac{\partial \delta c(\mathbf{R}, t)}{\partial t} = D \nabla^2 \delta c(\mathbf{R}, t) \quad (3.465)$$

where D is the translational-diffusion coefficient of the particles giving rise to scattering.

3.7.2.1 Fourier Analysis of Spatial Concentration Fluctuations

The concentration fluctuations $\delta c(\mathbf{R}, t)$ are related to their spatial Fourier transforms $\delta \tilde{c}(\mathbf{q}_r, t)$ according to

$$\delta c(\mathbf{R}, t) = \left(\frac{1}{2\pi} \right)^3 \int e^{i\mathbf{q}_r \cdot \mathbf{R}} \delta \tilde{c}(\mathbf{q}_r, t) d^3 q_r \quad (3.466)$$

where the wave vector $\mathbf{q}_r$ spans the reciprocal space and where the tilde indicates the Fourier transform. The transformation $c(\mathbf{R}, t) \rightarrow \tilde{c}(\mathbf{q}_r, t)$ analyzes the spatial concentration distribution by a superposition of concentration gratings $\cos(\mathbf{q}_r \cdot \mathbf{R}) + i \sin(\mathbf{q}_r \cdot \mathbf{R})$ of amplitudes $\delta \tilde{c}(\mathbf{q}_r, t)$ and grating constants q_r^{-1} .

3.7.2.2 Diffraction of Light at Spatial Concentration Fluctuations

The incident light with the wave vector $\mathbf{k}$ will (partially) be converted by diffraction to a new beam with wave vector $\mathbf{k}' = \mathbf{k} - \mathbf{q}$, where $\mathbf{q}$ is the scattering vector illustrated already in Fig. 3.41. The magnitude of $\mathbf{q}$ is

$$q = \frac{4\pi \langle n \rangle}{\lambda} \sin \frac{\theta}{2} \quad (3.467)$$

in analogy to Eq. (3.421). The quantity λ is the (vacuum) wavelength of the incident light, and $\langle n \rangle$ is the mean refractive index of the sample. Light whose scattering vector $\mathbf{q} = \mathbf{k} - \mathbf{k}'$ matches the inverse grating constant mentioned above,

$$\mathbf{q} = \mathbf{q}_r \quad (3.468)$$

will be diffracted constructively in the form of scattered light.

The proportionalities in Eq. (3.464) can be transformed as well, so that the spatial Fourier transform of the amplitude of the scattered light obeys

$$\tilde{E}'(\mathbf{q}, t) \propto \delta\tilde{\chi}(\mathbf{q}, t) \propto \delta\tilde{c}(\mathbf{q}, t) \quad (3.469)$$

where we have already taken into account the equality given by Eq. (3.468). Substituting Eq. (3.466) into Eq. (3.465) under the same matching condition gives

$$\frac{\partial}{\partial t} \int e^{i\mathbf{q}\cdot\mathbf{R}} \delta\tilde{c}(\mathbf{q}, t) d^3q = D \nabla^2 \int e^{i\mathbf{q}\cdot\mathbf{R}} \delta\tilde{c}(\mathbf{q}, t) d^3q \quad (3.470)$$

The time variable and the position coordinates are independent of the wave-vector $\mathbf{q}$. The partial derivatives on the left- and right-hand sides can therefore be shifted into the integrals:

$$\int e^{i\mathbf{q}\cdot\mathbf{R}} \frac{\partial}{\partial t} \delta\tilde{c}(\mathbf{q}, t) d^3q = D \int \nabla^2 e^{i\mathbf{q}\cdot\mathbf{R}} \delta\tilde{c}(\mathbf{q}, t) d^3q \quad (3.471)$$

The application of the Laplace operator ∇^2 in the integrand on the right-hand side gives

$$\int e^{i\mathbf{q}\cdot\mathbf{R}} \frac{\partial}{\partial t} \delta\tilde{c}(\mathbf{q}, t) d^3q = D \int (-q^2) e^{i\mathbf{q}\cdot\mathbf{R}} \delta\tilde{c}(\mathbf{q}, t) d^3q \quad (3.472)$$

The equality of the integrals entails the differential equation

$$\frac{\partial}{\partial t} \delta\tilde{c}(\mathbf{q}, t) = -q^2 D \delta\tilde{c}(\mathbf{q}, t) \quad (3.473)$$

3.7.2.3 Correlation of Light Scattered at Different Times

Let us now distinguish the fixed but arbitrary time t at which light is irradiated on the sample, and the variable τ characterizing the fluctuating interactions of the particle with the incident beam. That is, we substitute t by $t + \tau$ in Eq. (3.473):

$$\frac{\partial}{\partial \tau} \delta\tilde{c}(\mathbf{q}, t + \tau) = -q^2 D \delta\tilde{c}(\mathbf{q}, t + \tau) \quad (3.474)$$

The derivative refers now to the variable τ . With the initial condition for $\tau = 0$, that is, $\tilde{c}(\mathbf{q}, t + \tau) = \delta\tilde{c}(\mathbf{q}, t)$, the solution of Eq. (3.474) is

$$\delta\tilde{c}(\mathbf{q}, t + \tau) = \delta\tilde{c}(\mathbf{q}, t)e^{-q^2 D\tau} \quad (3.475)$$

The initial particle concentration $\delta\tilde{c}(\mathbf{q}, t)$ can be any value within the fluctuation range. Multiplying both sides with $\delta\tilde{c}(\mathbf{q}, t)$ and forming the average over the ensemble of scattering centers in the sample convert this expression to

$$\langle \delta\tilde{c}(\mathbf{q}, t + \tau) \delta\tilde{c}(\mathbf{q}, t) \rangle = \langle \delta\tilde{c}(\mathbf{q}, t)^2 \rangle e^{-q^2 D\tau} \quad (3.476)$$

The *first-order autocorrelation function* of the amplitude of the scattered light field is defined by

$$\mathcal{G}_1(\tau) \equiv \frac{\langle \tilde{E}'(\mathbf{q}, t + \tau) \tilde{E}'^*(\mathbf{q}, t) \rangle}{\langle |\tilde{E}'(\mathbf{q}, t)|^2 \rangle} \quad (3.477)$$

Based on the proportionality given in Eq. (3.469), we thus obtain

$$\mathcal{G}_1(\tau) = \frac{\langle \delta\tilde{c}(\mathbf{q}, t + \tau) \delta\tilde{c}(\mathbf{q}, t) \rangle}{\langle \delta\tilde{c}(\mathbf{q}, t)^2 \rangle} = e^{-q^2 D\tau} \quad (3.478)$$

Since normal diffusion has been anticipated, this result can be converted to the alternative expression

$$\mathcal{G}_1(\tau) = \exp\left\{-\frac{1}{6}q^2 \langle r^2 \rangle\right\} \quad (3.479)$$

where $\langle r^2 \rangle$ is the mean square displacement of the scattering centers in the interval τ .

Formally, this result is analogous to Eq. (3.454) for incoherent neutron scattering and to Eqs. (3.231) and (3.233) for field-gradient NMR diffusometry. That is, the first-order autocorrelation function is nothing else as the *incoherent dynamic structure factor* $\mathcal{G}_1(\tau) = \mathcal{G}_{\text{inc}}(\tau)$.

Dynamic light scattering experiments are usually evaluated under real-time conditions. A Fourier transform from the time interval τ to the Fourier conjugate variable angular-frequency ω is therefore not required, and the result given in Eq. (3.478) directly demonstrates how mean square particle displacements by translational diffusion, $\langle r^2 \rangle = 6D\tau$, affect dynamic light scattering.

The remaining problem is of a practical nature. Photo detectors, that is, photomultipliers, probe intensities of the scattered light, $I'(\mathbf{q}, t) \propto |\tilde{E}'(\mathbf{q}, t)|^2$, rather than electric-field amplitudes. One therefore evaluates the *second-order autocorrelation function* from the output signals [109]

$$G_2(\tau) \equiv \frac{\langle I'(\mathbf{q}, t + \tau) I'(\mathbf{q}, t) \rangle}{\langle |I'(\mathbf{q}, t)|^2 \rangle} \quad (3.480)$$

which correlates the scattered light intensities acquired before and after a time interval τ . Equation (3.480) is related to Eq. (3.478) by the *Siebert relation*

$$G_2(\tau) = 1 + [G_1(\tau)]^2 \quad (3.481)$$

which will be derived below. Substituting Eq. (3.478) thus gives

$$G_2(\tau) = 1 + e^{-2q^2 D \tau} \quad (3.482)$$

for the second-order autocorrelation function.

3.7.3 Derivation of the Siebert Relation

Consider N scattering centers of a diluted particle suspension. Each scattering center is the origin of a secondary wave with amplitude $\tilde{E}'_k(\mathbf{q})$ of the electric-field strength and phase-shift φ_k relative to the incident wave. The phase angle φ_k fluctuates with the displacements of the particle and is therefore a function of time. The total light scattered into the solid-angle element $d\Omega$ probed by the detector is the superposition of N scattered waves so that the total electric field strength is composed in complex form as⁴⁴

$$\tilde{E}'(t) = \sum_{k=1}^N \tilde{E}'_k e^{i\varphi_k(t)} \quad (3.483)$$

On this basis, the first-order autocorrelation function can be rewritten as

$$G_1(\tau) \equiv \frac{\langle \tilde{E}'(t + \tau) \tilde{E}'^*(t) \rangle}{\langle |\tilde{E}'(t)|^2 \rangle} = \frac{\sum_{k,l=1}^N \langle \tilde{E}'_k \tilde{E}'_l e^{i\varphi_l(t+\tau) - i\varphi_k(t)} \rangle}{\sum_{k,l=1}^N \langle \tilde{E}'_k \tilde{E}'_l e^{i\varphi_l(t) - i\varphi_k(t)} \rangle} = \frac{\sum_{k=1}^N \langle \tilde{E}'_k{}^2 e^{i\varphi_k(t+\tau) - i\varphi_k(t)} \rangle}{\sum_{k=1}^N \langle \tilde{E}'_k{}^2 \rangle} \quad (3.484)$$

where we have exploited the fact that the phases of different particles $k \neq l$ are uncorrelated. That is, their motional fluctuations are stochastically independent.

⁴⁴ In reality, each scattering wave contains a propagation phase factor of the type $\exp(i\omega t + i\mathbf{k} \cdot \mathbf{r})$ in addition. This is however irrelevant here since we are merely interested in amplitudes and relative phases.

The second-order autocorrelation function for the intensity of the scattered light, $I' \propto \langle \tilde{E}' \tilde{E}'^* \rangle$, reads analogously

$$\begin{aligned}
 G_2(\tau) &\equiv \frac{\langle I'(\mathbf{q}, t + \tau) I'(\mathbf{q}, t) \rangle}{\langle I'(\mathbf{q}, t) \rangle^2} \\
 &= \frac{\langle \sum_k \tilde{E}'_k e^{i\varphi_k(t+\tau)} \sum_l \tilde{E}'_l e^{-i\varphi_l(t+\tau)} \sum_m \tilde{E}'_m e^{i\varphi_m(t)} \sum_n \tilde{E}'_n e^{-i\varphi_n(t)} \rangle}{\langle \sum_k \tilde{E}'_k e^{i\varphi_k(t)} \sum_l \tilde{E}'_l e^{-i\varphi_l(t)} \rangle \langle \sum_m \tilde{E}'_m e^{i\varphi_m(t)} \sum_n \tilde{E}'_n e^{-i\varphi_n(t)} \rangle} \\
 &= \frac{\sum_{k,l,m,n} \langle \tilde{E}'_k \tilde{E}'_l \tilde{E}'_m \tilde{E}'_n e^{i(\varphi_l(t)-\varphi_k(t)+\varphi_n(t+\tau)-\varphi_m(t+\tau))} \rangle}{\left(\sum_k \langle \tilde{E}'_k{}^2 \rangle \right)^2} \quad (3.485)
 \end{aligned}$$

Each addend in the fourfold sum in the numerator refers to the four indices k, l, m, n . If these subscripts indicate four different particles or if only two subscripts are identical, the sum vanishes owing to the stochastic independence of the displacements of different particles. The remaining sum can be subdivided into the partial sums $A = \langle \sum_{k=1; m=n; k \neq m} \dots \rangle$, $B = \langle \sum_{k=n; l=m; k \neq l \text{ or } k=m; l=n; k \neq l} \dots \rangle$, and $C = \langle \sum_{k=l=m=n} \dots \rangle$.

According to the stochastic independence of the particle motions, the terms A and B can be evaluated as

$$\begin{aligned}
 A &= \sum_{k \neq m} \langle \tilde{E}'_k{}^2 \tilde{E}'_m{}^2 \rangle \\
 &= N(N-1) \langle \tilde{E}'_k{}^2 \tilde{E}'_m{}^2 \rangle = N(N-1) \langle \tilde{E}'_k{}^2 \rangle \langle \tilde{E}'_m{}^2 \rangle = \left(1 - \frac{1}{N}\right) \left(\sum_k \langle \tilde{E}'_k{}^2 \rangle \right)^2 \\
 &\xrightarrow{N \rightarrow \infty} \left(\sum_k \langle \tilde{E}'_k{}^2 \rangle \right)^2 \quad (3.486)
 \end{aligned}$$

and

$$\begin{aligned}
 B &= \sum_{k=n; l=m; k \neq l \text{ or } k=m; l=n; k \neq l} \langle \tilde{E}'_k{}^2 \tilde{E}'_l{}^2 e^{i(\varphi_l(t)-\varphi_k(t)+\varphi_l(t+\tau)-\varphi_k(t+\tau))} \rangle \\
 &= N(N-1) \langle \tilde{E}'_k{}^2 \tilde{E}'_l{}^2 e^{i(\varphi_l(t)-\varphi_k(t)+\varphi_l(t+\tau)-\varphi_k(t+\tau))} \rangle \\
 &= \left(1 - \frac{1}{N}\right) N^2 \langle \tilde{E}'_k{}^2 e^{i(\varphi_k(t+\tau)-\varphi_k(t))} \rangle \langle \tilde{E}'_l{}^2 e^{i(\varphi_l(t)-\varphi_l(t+\tau))} \rangle \\
 &= \left(1 - \frac{1}{N}\right) \left| \sum_k \langle \tilde{E}'_k{}^2 e^{i(\varphi_k(t+\tau)-\varphi_k(t))} \rangle \right|^2 \\
 &= \xrightarrow{N \rightarrow \infty} \left| \sum_k \langle \tilde{E}'_k{}^2 e^{i(\varphi_k(t+\tau)-\varphi_k(t))} \rangle \right|^2 \\
 &= \left[G_1(\tau) \sum_k \langle \tilde{E}'_k{}^2 \rangle \right]^2 \quad (3.487)
 \end{aligned}$$

respectively. Assuming a Gaussian distribution of the amplitudes $\tilde{E}'_k$, one can finally show that the sum C vanishes:

$$C = N \langle \tilde{E}'^4_k \rangle = 3N \langle \tilde{E}'^2_k \rangle^2 = \frac{3}{N} \left[G_1(0) \sum_k \langle \tilde{E}'^2_k \rangle \right]^2 \xrightarrow{N \rightarrow \infty} 0 \quad (3.488)$$

Here we have exploited a property specific for Gaussian distributions, namely, that the fourth moment is equal to three times the square of the second moment.

Combining Eqs. (3.485), (3.486), and (3.487) results in the Siegert relation mentioned above:

$$G_2(\tau) = 1 + [G_1(\tau)]^2 \quad (3.489)$$

$G_2(\tau)$ decays from the initial value $G_2(0) = 2$ to the value $G_2(\infty) = 1$ in the long-time limit. This is in contrast to $G_1(\tau)$ which starts with the initial value 1 and approaches 0 at long times.

3.8 Mechanical Relaxation

In mechanical-relaxation experiments, thermal equilibrium of the sample is distorted by abrupt or periodic exertion of deformations or stress. The macroscopically detected response reflects microscopic molecular rearrangements in the material due to thermal motions. This relaxation phenomenon thus permits studies of molecular dynamics in an indirect way.

3.8.1 Viscoelasticity and Classification of Experiments Probing It

The quantities to be focused on in this context have been introduced in Sect. 2.3. In tensorial form, these are in particular stress σ , strain ε , shear angle γ , Young's modulus E , shear modulus G , and shear compliance J . Since isotropic media are of predominant interest here, we can restrict ourselves to the particular tensor *elements*, that is, scalar quantities, specific for the diverse variants of mechanical-relaxation experiments. The scalar relations to be regarded in the following are

$$\begin{aligned} \sigma_{\text{strain}} &= E\varepsilon \\ \sigma_{\text{shear}} &= G\gamma \\ \gamma &= J\sigma_{\text{shear}} \\ J &= G^{-1} \end{aligned} \quad (3.490)$$

A further quantity of interest is the viscosity η introduced in Sect. 2.3.4 in the context of shear flow. For the sake of simplicity, all mechanical deformations will be assumed to comply with the Hookean limit. The moduli E and G and the compliance J are then independent of strain and of the shear angle. Under such conditions, the analytical form of the relations in Eq. (3.490) is linear. The field of mechanical-relaxation phenomena restricted in this way is often circumscribed as *linear viscoelasticity*.

The mechanical perturbations giving rise to relaxation phenomena can be time-dependent deformations, stress, or strain rates. The primary effect is that molecular configurations and interactions in the sample temporally deviate from thermal equilibrium. That is, the Helmholtz free energy is elevated. As a consequence, the system tends to return to the minimum of Helmholtz free energy by molecular processes reducing molecular interaction energies and increasing configurational entropy. The elastic moduli of interest, that is, Young's modulus E and the shear modulus G , thus become dynamic quantities depending on the rate of molecular fluctuations in the sample.

Soft matter is normally neither purely elastic like crystalline solids for small strains nor purely viscous like very low-molecular fluids. The response to time-dependent mechanical perturbations rather depends on the time scale of the distortions. Perturbations rapidly varying relative to molecular rearrangements in the material lead to elastic behavior in the Hookean limit of small deformations. This is in contrast to long-lasting perturbations giving rise to viscous flow in the same material. The response of such *viscoelastic* bodies to (time-dependent) mechanical perturbations will be determined by *mechanical relaxation* due to molecular dynamics [110–115].

Mechanical relaxation can be studied on the basis of different experimental protocols to be outlined in the following sections. Two principal variants can be distinguished via the quantity subject to the observed relaxation process: (1) With mechanical-relaxation experiments in the narrower sense, a predetermined time-dependent deformation (strain or shear) is applied to the sample, while the stress response is recorded. The time dependence of the deformation can be a step function or is of a periodic nature. Accordingly, this sort of experiment is referred to as *step stress relaxation* and *dynamic stress relaxation*, respectively. (2) In the second variant, the situation is reversed: A predetermined time-dependent stress load is applied to the sample, and the deformation response is recorded. This experiment is called *shear* or *strain creep experiment*. The time dependence of the load can again be a step or an alternating function. The experimental protocols are correspondingly referred to as *step* and *dynamic shear* or *strain creep*, respectively. The bulk modulus of soft condensed matter is much larger than the other elastic moduli. Soft matter can therefore be regarded as essentially incompressible. Under this condition, the elastic moduli E and G for stretching and shearing, respectively, are proportional to each other (see Eq. (2.126)):

$$E = 3G \quad (3.491)$$

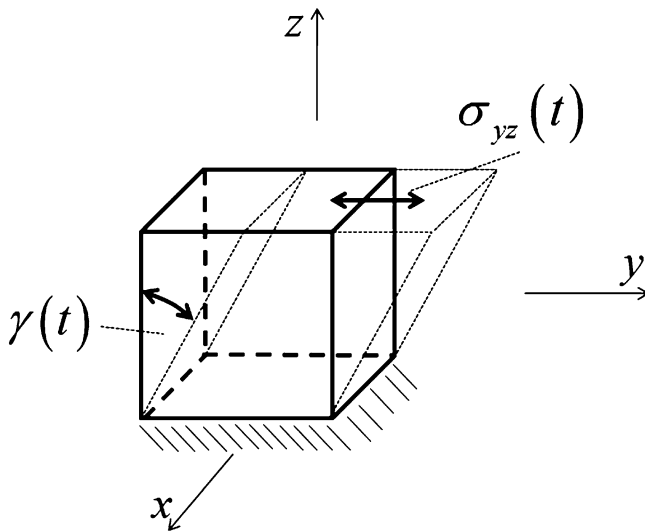


Fig. 3.45 Illustration of the time-dependent functions characterizing mechanical shearing of a volume element

As a consequence, model treatments can refer to either form of deformation.

3.8.2 Fundamental Response Equations for Linear Viscoelasticity

3.8.2.1 Shear-Stress Relaxation

Most commonly, the sample under investigation is subjected to time-dependent shear deformations causing time-dependent shear stress as illustrated in Fig. 3.45. The shear-stress component σ_{yz} specified in the figure will be referred to in the following by the symbol σ_{shear} for simplicity.

Since we are dealing with *linear* problems in the limit of small deformations or loads, Boltzmann's superposition principle can be applied. The shear-stress building up after shear deformations at different times can simply be added. A shearing deformation by an infinitesimal angle element $d\gamma$ which happened at time t' contributes to the shear stress at a later time t by an amount

$$d\sigma_{\text{shear}}(t) = G(t - t')d\gamma(t') = G(t - t')\dot{\gamma}(t')dt' \quad (3.492)$$

where $G(t - t')$ is the *shear-relaxation modulus* effective a period $t - t'$ ago. The time dependence of the shear-relaxation modulus reflects the relaxation process. In the long-time limit, the shear-relaxation modulus $G(t - t')$ therefore decays toward zero for fluids and toward a constant value G_s in solid or cross-linked

materials. Integrating Eq. (3.492) from $t' = -\infty$ to $t' = t$ gives the *constitutive equation for shear-stress relaxation* in the limit of linear viscoelasticity:

$$\sigma_{\text{shear}}(t) = \int_{-\infty}^t G(t-t') \dot{\gamma}(t') dt' \quad (3.493)$$

We note that this relation has the formal structure of the linear-response relation given in Eq. (1.20).

Equation (3.493) links shear stress at time t with the evolution of the shear rate in the past. The memory kernel character of the integral represents the relaxation properties of the system under investigation. The *shear-relaxation modulus* $G(t-t')$ thus acts as the *linear-response function* of the system deformed by a (time-dependent) shear rate $\dot{\gamma}(t)$. It is often approached by an exponential decay function or by a discrete or continuous distribution of exponential functions. Based on Eq. (3.493), the stress response to any time dependence of the shear angle can be evaluated. A number of typical time dependences relevant for practical experiments will now be discussed in the following sections.

3.8.2.2 Shear Creep

Shear-creep experiments consist of the variation of shear stress while the shear-angle response is observed. Analogous to Eq. (3.492), the infinitesimal shear stress $d\sigma_{\text{shear}}$ applied at time t' contributes to the shear angle at a later time t by an amount

$$d\gamma(t) = J(t-t') d\sigma_{\text{shear}}(t') = J(t-t') \dot{\sigma}_{\text{shear}}(t') dt' \quad (3.494)$$

where $J(t-t')$ is the shear compliance effective a period $t-t'$ ago. Integrating Eq. (3.494) from $t' = -\infty$ to $t' = t$ gives the *constitutive equation for shear creep* in the frame of linear viscoelasticity:

$$\gamma(t) = \int_{-\infty}^t J(t-t') \dot{\sigma}_{\text{shear}}(t') dt' \quad (3.495)$$

It relates the shear angle at time t with the history of the shear stress. This equation again reveals the memory kernel character typical for linear-response problems.

3.8.3 Step Relaxation Experiments

3.8.3.1 Shear-Angle Step

Shear-step relaxation experiments probe the stress response to a step of the shear angle at time 0 (see Fig. 3.46):

$$\gamma(t) = \begin{cases} 0 & \text{for } t < 0 \\ \gamma_0 & \text{for } t \geq 0 \end{cases} \quad (3.496)$$

According to the linear-response relation Eq. (3.493), the resulting stress evolves according to

$$\sigma_{\text{shear}}(t) = \int_{-\infty}^t G(t-t') \dot{\gamma}(t') dt' = \gamma_0 \int_{-\infty}^t G(t-t') \delta(t') dt' = \gamma_0 G(t) \quad (3.497)$$

where $\delta(t')$ is Dirac's delta function.

The time-dependent shear-relaxation modulus can thus be determined on the basis of

$$G(t) = \frac{\sigma_{\text{shear}}(t)}{\gamma_0} \quad (3.498)$$

3.8.3.2 Shear-Rate Step

Another way of probing mechanical material properties is to apply a predetermined time-dependent strain *rate* to the sample and to observe the stress response. The time dependence of the strain rate is usually a step function leading to flow of the material. In the case of a steady shear rate beginning at time 0,

$$\dot{\gamma}(t') = \begin{cases} 0 & \text{for } t' < 0 \\ \dot{\gamma}_t = \text{const} & \text{for } t' \geq 0 \end{cases} \quad (3.499)$$

Equation (3.493) takes the form

$$\sigma_{\text{shear}}(t) = \dot{\gamma}_t \int_0^t G(t-t') dt' \quad (3.500)$$

Since the proportionality factor linking shear rate and shear stress is of dimension [viscosity], the time-dependent viscosity function

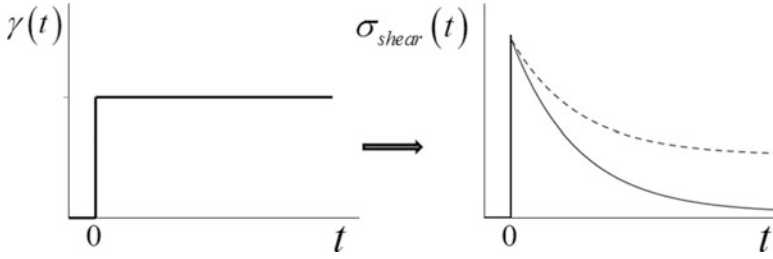


Fig. 3.46 Shear-step relaxation experiment: The sample is sheared by a step function at time 0 (*left*). The response is measured in the form of the relaxation decay of the shear stress. With liquids (*solid line*), it decays to zero in the long-time limit whereas a finite constant stress remains in the case of solids or cross-linked materials (*dashed curve*)

$$\eta(t) \equiv \frac{\sigma_{\text{shear}}(t)}{\dot{\gamma}_t} = \int_0^t G(t-t') dt' = \int_0^t G(\bar{t}) d\bar{t} \quad (3.501)$$

can be introduced, and the variable substitution $\bar{t} = t - t'$ can be applied. In the long-time limit, $\eta(t)$ approaches the steady state characterized by the *steady-state viscosity*

$$\eta_{\text{steady}} = \lim_{t \rightarrow \infty} \eta(t) = \int_0^\infty G(\bar{t}) d\bar{t} \quad (3.502)$$

3.8.3.3 Shear-Creep Step

In a shear-creep step experiment, shear stress is increased abruptly from zero to a constant value σ_0 according to

$$\sigma_{\text{shear}}(t') = \begin{cases} 0 & \text{for } t' < 0 \\ \sigma_0 & \text{for } t' \geq 0 \end{cases} \quad (3.503)$$

The time derivative of the shear stress can consequently be expressed by Dirac's delta function so that the shear-angle response according to Eq. (3.495) is

$$\begin{aligned} \gamma(t) &= \int_{-\infty}^t J(t-t') \dot{\sigma}_{\text{shear}}(t') dt' \\ &= \sigma_0 \int_{-\infty}^t J(t-t') \delta(t') dt' \\ &= \sigma_0 J(t) \end{aligned} \quad (3.504)$$

Different contributions to this shear-angle response can be identified: (1) For small shear loads as anticipated throughout, there will be an *instantaneous* deformation on a time scale much shorter than relaxation times,

$$\gamma_0 = J_0 \sigma_0 \quad (3.505)$$

which is sometimes called *unrelaxed response*. The corresponding compliance obeys $J_0 = G^{-1}$, where G is the shear modulus in the absence of relaxation processes. (2) On the *relaxation (or better “retardation”) time scale*, an additional, time-dependent contribution becomes effective. It is often referred to as *relaxed response*. The respective compliance, $J_{\text{relax}} = J_{\text{relax}}(t)$, increases to a certain limiting value at long times. (3) Finally, in the case of viscoelastic liquids, flow sets on according to the *steady-state* asymptote

$$J_{\text{flow}}(t) = t/\eta \quad (3.506)$$

in the long-time limit (relative to relaxation times). With this additional contribution, the total compliance is thus composed according to

$$J(t) = J_0 + J_{\text{relax}}(t) + J_{\text{flow}}(t) = G^{-1} + J_{\text{relax}}(t) + t/\eta \quad (3.507)$$

3.8.4 Periodic Relaxation Experiments

3.8.4.1 The Shear-Modulus Functions $G(t)$, $G'(\omega)$, $G''(\omega)$

If the shear angle is subjected to the forced oscillatory time dependence

$$\gamma(t) = \gamma_0 \sin \omega t \quad (3.508)$$

the experiment is called *dynamic mechanical relaxation*. ω is the angular frequency of the shear deformation, and γ_0 is the amplitude. Inserting Eq. (3.508) in Eq. (3.493) gives the time-dependent stress response

$$\sigma_{\text{shear}}(t) = \int_{-\infty}^t G(t-t') \gamma_0 \omega \cos \omega t' dt' \quad (3.509)$$

where $G(t)$ is the shear-relaxation modulus. The right-hand side of Eq. (3.509) can be modified by the variable substitution

$$t - t' = \bar{t}; \quad t' = t - \bar{t}; \quad dt' = -d\bar{t}; \quad t' = -\infty \rightarrow \bar{t} = \infty; \quad t' = t \rightarrow \bar{t} = 0 \quad (3.510)$$

Equation (3.509) thus adopts the form

$$\begin{aligned}
 \sigma_{\text{shear}}(t) &= -\gamma_0 \omega \int_{-\infty}^0 G(\bar{t}) \cos \omega(t - \bar{t}) \, d\bar{t} \\
 &= \gamma_0 \omega \int_0^{\infty} G(\bar{t}) \cos \omega(t - \bar{t}) \, d\bar{t} \\
 &= \gamma_0 \omega \Re \left\{ \int_0^{\infty} G(\bar{t}) e^{i\omega(t - \bar{t})} d\bar{t} \right\} \\
 &= \gamma_0 \omega \Re \left\{ e^{i\omega t} \int_0^{\infty} G(\bar{t}) e^{-i\omega \bar{t}} d\bar{t} \right\}
 \end{aligned} \tag{3.511}$$

where $\Re\{\dots\}$ represents the real part of the complex expression in the curly brackets. The integral is the Laplace transform of the function $G(\bar{t})$ for the variable $s = i\omega$ which is conjugate to $\bar{t}$. Assuming an exponential decay of the shear-relaxation modulus,⁴⁵

$$G(\bar{t}) = G_0 \exp\{-\bar{t}/\tau_R\} \tag{3.512}$$

with the relaxation time τ_R gives

$$\int_0^{\infty} G(\bar{t}) e^{-i\omega \bar{t}} d\bar{t} = G_0 \frac{\tau_R}{1 - i\omega \tau_R} = G_0 \left[\frac{\tau_R}{1 + \omega^2 \tau_R^2} - i \frac{\omega \tau_R^2}{1 + \omega^2 \tau_R^2} \right] \tag{3.513}$$

Combining Eqs. (3.511) and (3.513) leads to

$$\begin{aligned}
 \sigma_{\text{shear}}(t) &= \gamma_0 G_0 \frac{\omega^2 \tau_R^2}{1 + \omega^2 \tau_R^2} \sin \omega t + \gamma_0 G_0 \frac{\omega \tau_R}{1 + \omega^2 \tau_R^2} \cos \omega t \\
 &= \gamma_0 G'(\omega) \sin \omega t + \gamma_0 G''(\omega) \cos \omega t
 \end{aligned} \tag{3.514}$$

⁴⁵ For an interpretation of exponential functions in terms of random processes, see Sect. 1.1.3. A derivation of exponential relaxation functions or the establishment of distributions (superpositions) of such functions requires however well-defined models of molecular dynamics. Instead, mechanical analogues, that is, parallel and series circuits of ideal springs and dissipative dashpots, are often used to justify certain relaxation function decays phenomenologically. Simple examples are the *Maxwell model* (spring and dashpot in series) and the *Voigt model* (spring and dashpot in parallel). Unfortunately, the linkage to molecular pictures often remains formal and qualitative. An exception may be the entropic elasticity of polymer chains treated in Chap. 5. This property can be considered to act as an elastic element in the sense of spring/dashpot models.

where the coefficients of the in-phase ($\sin \omega t$) and quadrature-phase ($\cos \omega t$) terms have been expressed by

$$\begin{aligned} G'(\omega) &= \omega \int_0^{\infty} G(\bar{t}) \sin(\omega \bar{t}) d\bar{t} = G_0 \frac{\omega^2 \tau_R^2}{1 + \omega^2 \tau_R^2} \text{ (“storage modulus”)} \\ G''(\omega) &= \omega \int_0^{\infty} G(\bar{t}) \cos(\omega \bar{t}) d\bar{t} = G_0 \frac{\omega \tau_R}{1 + \omega^2 \tau_R^2} \text{ (“loss modulus”)} \end{aligned} \quad (3.515)$$

A graphical representation can be found in Fig. 3.47.

According to Eqs. (2.120), (3.508), and (3.514), the energy dissipated in the sample per cycle and volume unit is

$$\begin{aligned} W &= \int_0^{2\pi} \sigma d\gamma' \\ &= \int_0^{2\pi/\omega} \sigma \dot{\gamma}' dt = \omega \gamma_0^2 \int_0^{2\pi/\omega} (G' \sin \omega t + G'' \cos \omega t) \cos \omega t dt = \gamma_0^2 \pi G'' \end{aligned} \quad (3.516)$$

This is the energy the system “looses” to the thermal degrees of freedom. As indicated by the vanishing term, the *storage modulus* G' is not connected with any energy dissipation. The reason is that the in-phase part of the stress *stores* energy via elastic deformations (which explains the name of that modulus). This is in contrast to the component oscillating in quadrature to the shear deformation. The result in Eq. (3.516) specifies the total energy dissipated per cycle and volume unit as $W = \pi \gamma_0^2 G''$. This is the origin of the term *loss modulus* for G'' .

The oscillatory shear leads to a periodic shear stress as revealed by Eq. (3.514). The phase angle of the shear stress is shifted by a lag angle δ according to

$$\sigma_{\text{shear}}(t) = \sigma_0 \sin(\omega t + \delta) \quad (3.517)$$

δ is called the *loss angle*. Using a known trigonometric relation, Eq. (3.517) can be converted into

$$\sigma_{\text{shear}}(t) = \sigma_0 \sin \omega t \cos \delta + \sigma_0 \cos \omega t \sin \delta \quad (3.518)$$

The shear stress consequently consists of a contribution $\sigma_0 \sin \omega t \cos \delta$ *in phase* with shear and a component $\sigma_0 \cos \omega t \sin \delta$ which is 90° *out of phase*. The amplitudes are $\sigma_0 \cos \delta = \gamma_0 G'$ and $\sigma_0 \sin \delta = \gamma_0 G''$, respectively, as can be seen

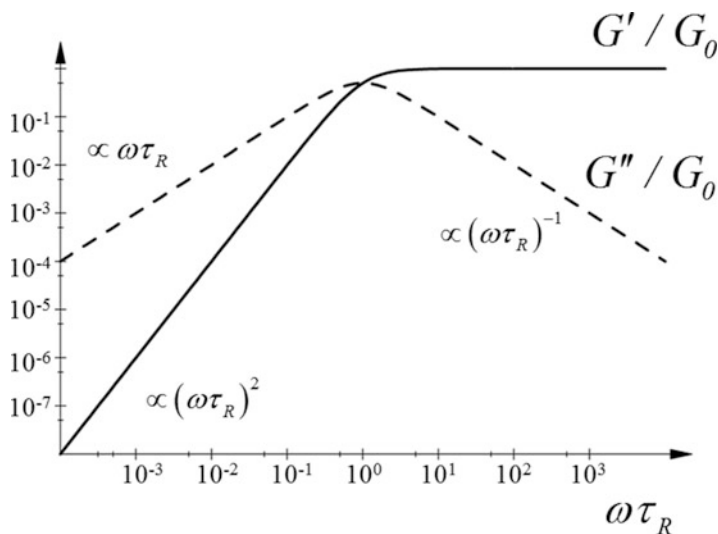


Fig. 3.47 Dynamic shear moduli as functions of angular frequency times the relaxation time according to Eq. (3.515). The low- and high-frequency limits are specified

by comparison with Eq. (3.514). The loss angle is related to the moduli defined in Eq. (3.515) by

$$\tan \delta = \frac{\sigma_0 \sin \delta}{\sigma_0 \cos \delta} = \frac{G''}{G'} = \frac{1}{\omega \tau_R} \quad (3.519)$$

The moduli in Eq. (3.515) are related to each other via the famous *Kronig/Kramers dispersion relations* (for details see Ref. [76], for instance). That is, the information content of either expression is equivalent: Knowing the frequency dependence of one quantity in the full range permits one to calculate the conjugate counterpart on this basis. The Kronig/Kramers relations are a manifestation of linearity as anticipated in the derivation of the Hookean elasticity relations in Sect. 2.3.3.

The formalism of periodic shear experiments is often represented more conveniently in complex form. With the definitions⁴⁶

$$\bar{\gamma} = \gamma_0 e^{i\omega t} (\text{complex shear angle}) \quad (3.520)$$

$$\bar{\sigma} = \sigma_0 e^{i(\omega t + \delta)} (\text{complex shear stress}) \quad (3.521)$$

⁴⁶ In the literature, complex mechanical quantities are often marked by star superscripts. Since star superscripts usually indicate conjugate complex quantities, we prefer overlines instead.

$$\bar{G} = G' + iG'' = (G'^2 + G''^2)^{1/2} e^{i\delta} \text{ (complex shear modulus)} \quad (3.522)$$

the stress/shear relations can be rendered by the complex equation

$$\bar{\sigma} = \bar{G}\bar{\gamma} \quad (3.523)$$

The magnitudes are related as

$$\sigma_0 = (G'^2 + G''^2)^{1/2} \gamma_0 \quad (3.524)$$

Assuming an exponential relaxation function as in Eq. (3.512), the complex shear modulus is predicted to obey

$$\bar{G} = G_0 \frac{\omega\tau_R}{1 - i\omega\tau_R} = G_0 \frac{\omega\tau_R - i\omega^2\tau_R^2}{1 + \omega^2\tau_R^2} \quad (3.525)$$

3.8.4.2 The Functions $\eta'(\omega)$, $\eta''(\omega)$, $J'(\omega)$, $J''(\omega)$

The *complex viscosity* of viscoelastic liquids subjected to a sinusoidally modulated shear-angle rate is defined by

$$\bar{\eta} = \eta' - i\eta'' = \frac{\bar{G}}{i\omega} = \frac{G''}{\omega} - i\frac{G'}{\omega} \quad (3.526)$$

The real and imaginary parts of the complex viscosity are closely related to those of the complex shear modulus. The difference is that the real and imaginary parts refer to “loss” and “storage” just in the reversed sense.

For exponential relaxation functions, the components of the complex viscosity can be expressed by

$$\begin{aligned} \eta' &= \frac{G''}{\omega} = G_0 \frac{\tau_R}{1 + \omega^2\tau_R^2} \\ \eta'' &= \frac{G'}{\omega} = G_0 \frac{\omega\tau^2}{1 + \omega^2\tau_R^2} \end{aligned} \quad (3.527)$$

In the limit of low frequencies relative to relaxation rates, the real and imaginary parts of Eq. (3.526) approach

$$\eta_0 \equiv \lim_{\omega\tau_R \ll 1} \eta' = \lim_{\omega\tau_R \ll 1} \frac{G''}{\omega}; \quad \lim_{\omega \rightarrow 0} \eta'' = \lim_{\omega\tau_R \ll 1} \frac{G'}{\omega} \quad (3.528)$$

where η_0 is the constant *zero-shear viscosity*. In terms of exponential relaxation functions, these expressions are specified as

$$\begin{aligned} \eta_0 &= \lim_{\omega\tau_R \ll 1} \left\{ G_0 \frac{\tau_R}{1 + \omega^2 \tau_R^2} \right\} = G_0 \tau_R \\ \lim_{\omega\tau_R \ll 1} \left\{ G_0 \frac{\omega \tau_R^2}{1 + \omega^2 \tau_R^2} \right\} &= G_0 \omega \tau_R^2 \end{aligned} \quad (3.529)$$

Reversely, the components of the complex shear modulus adopt the forms

$$\begin{aligned} G'(\omega\tau_R \ll 1) &= G_0 \omega^2 \tau_R^2 = \omega^2 \tau_R \eta_0 \\ G''(\omega\tau_R \ll 1) &= G_0 \omega \tau_R = \omega \eta_0 \end{aligned} \quad (3.530)$$

in this limit as illustrated in Fig. 3.47.

Likewise, one can define the *complex compliance*:

$$\bar{J} = J' - iJ'' = \frac{1}{G} \quad (3.531)$$

Combining this with Eq. (3.525) gives

$$\begin{aligned} J' &= \frac{1}{G_0 \omega \tau_R} \\ J'' &= \frac{1}{G_0} \end{aligned} \quad (3.532)$$

Note that the real part J' diverges in the limit $\omega\tau_R \rightarrow 0$ and that the imaginary part J'' is constant.

3.9 Dielectric Relaxation Spectroscopy

(Broadband) dielectric relaxation spectroscopy is the last example of noninvasive techniques to be described in the frame of this book. It is of interest for materials containing molecules with *permanent electric dipoles*. The measuring principle is to expose the sample to time-varying electric fields and to record the polarization response. Since this is a matter of molecular reorientations controlled by thermal motions, the method permits one to probe molecular dynamics in a rather direct

way. For the sake of simplicity and clarity of presentation, we will restrict ourselves to isotropic materials so that tensorial properties of interactions do not matter.

Strictly speaking, it would be more precise to speak of *para-electric* instead of *dielectric* relaxation. This however would be a terminology uncommon in the literature. In this context, it should also be noted that the *induction* of dipoles follows the time dependence of the applied electric field practically instantaneously relative to the time scale of molecular reorientations so that it is of minor interest in the present context. Depending on the sample material and the frequency, effects due to electrical conductivity can also be relevant but will not be considered further here. For more comprehensive representations of all facets that can arise with dielectric spectroscopy, the reader is referred to Ref. [116].

3.9.1 Some Basic Relations and Definitions for Stationary Electric Fields

The interaction energy W of a permanent molecular dipole of moment $\boldsymbol{\mu}$ exposed to an electric field of strength $\mathbf{E}$ is

$$W = -\boldsymbol{\mu} \cdot \mathbf{E} \quad (3.533)$$

This potential energy tends to be minimized by alignment of the dipole along the electric-field direction in competition to thermal motions. In a system of N_d permanent dipoles in a volume V , the external electric field thus generates the *electric polarization*

$$\mathbf{P} = \frac{1}{V} \sum_{j=1}^{N_d} \boldsymbol{\mu}_j \quad (3.534)$$

This is the sum over all electric dipole-moment vectors in the system divided by the volume. $\boldsymbol{\mu}_j$ is the instantaneous dipole-moment vector of dipole number j .

The buildup of a polarization is opposed by the orientational randomization tendency due to thermal motions of the molecules or molecular groups bearing the dipoles. The polarization resulting in equilibrium can be calculated in complete analogy to the Curie's magnetization given in Eq. (3.8). With the polar angle ϑ between the applied electric field and the dipole-moment vector, the magnitude of the polarization Eq. (3.534) in a homogeneous medium with just one dipole species μ reads

$$P = \frac{N_d}{V} \mu \langle \cos \vartheta \rangle \quad (3.535)$$

The angle brackets indicate an ensemble average to be evaluated with the aid of Boltzmann factors according to

$$\langle \cos \vartheta \rangle = \frac{\int_0^\pi d\vartheta \cos \vartheta \exp\{-(\mu E \cos \vartheta)/(k_B T)\} \sin \vartheta}{\int_0^\pi d\vartheta \exp\{-(\mu E \cos \vartheta)/(k_B T)\} \sin \vartheta} \quad (3.536)$$

In the high-temperature limit $k_B T \gg \mu E$, this ensemble average can readily be evaluated. The resulting equilibrium polarization $\mathbf{P}_0$ is aligned along the applied field $\mathbf{E}$ and obeys

$$\mathbf{P}_0 \approx \frac{N_d}{V} \frac{\mu^2}{3k_B T} \mathbf{E} = \frac{N_d}{V} \alpha \mathbf{E} \quad (3.537)$$

where

$$\alpha = \frac{\mu^2}{3k_B T} \quad (3.538)$$

is the *orientational polarizability*. As a matter of course, the approximate relation in Eq. (3.537) is only valid far away from orientational saturation.

In Eqs. (3.533) and (3.537), we have referred to the electric-field strength E “seen” by the dipoles. There is a little complication that must be taken into account: Inside dielectric materials, the externally applied field strength is modified just due to the presence of the dipoles as illustrated in Fig. 3.48. Variations on these grounds require the distinction of three different electric fields:

1. The *external* electric-field strength applied to a dielectric material, $\mathbf{E}_0$. This is the field that would exist in the absence of the dielectric material.
2. The *effective* or *mean* electric-field strength $\mathbf{E}_e$ in the dielectric material considered as a homogeneous continuum. In equilibrium, $\mathbf{E}_e$ is reduced relative to $\mathbf{E}_0$ by the so-called *depolarization field* $-\mathbf{P}_0/\varepsilon_0$ according to

$$\mathbf{E}_e = \mathbf{E}_0 - \frac{\mathbf{P}_0}{\varepsilon_0} \quad (3.539)$$

where ε_0 is the electric-field constant (also called vacuum permittivity). The reason is that any surface of a dielectric material containing permanent dipoles effectively adopts a (bound) surface charge when being polarized in an external electric field. This is just the direct consequence of the preferential orientation of the dipoles along the electric field. The electric field produced by these surface charges acts opposite to the external field, so that the resulting field has a *reduced* strength. An illustration for a dielectric placed between two capacitor plates is shown in Fig. 3.48. The field reduction effect of the dielectric can be taken into

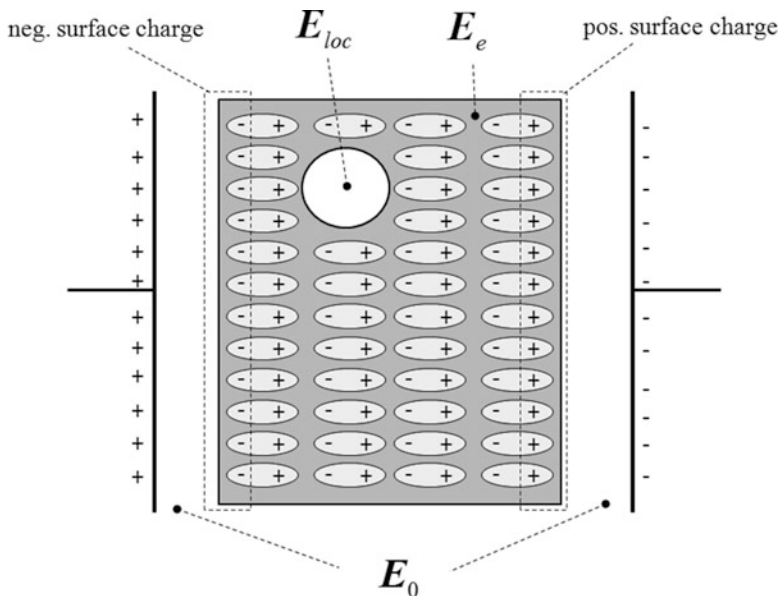


Fig. 3.48 Schematic representation of a dielectric between two charged capacitor plates. Edge effects are disregarded. In the absence of the dielectric, the electric-field strength between the plates would be E_0 . Polarization of the dipoles in the dielectric leads to charges of opposite sign at the surfaces facing the capacitor plates. The electric-field produced by the surface charges reduces the electric-field strength in the dielectric so that the effective field strength is given by $E_e = E_0/\epsilon_r$. The local field in a small spherical cavity is $E_{loc} = (\epsilon_r + 2)(3\epsilon_r)^{-1}E_0$

account by the material parameters ϵ_r , the *relative permittivity*, and χ_e , the *electric susceptibility*. With these parameters, the equilibrium relations read

$$E_e = \frac{E_0}{\epsilon_r} = \frac{E_0}{1 + \chi_e} = \frac{P_0}{\epsilon_0 \chi_e} \quad (3.540)$$

or

$$P_0 = \epsilon_0 \chi_e E_e = \frac{\epsilon_0 (\epsilon_r - 1)}{\epsilon_r} E_0 \quad (3.541)$$

Equations (3.540) and (3.541) imply

$$\epsilon_r = 1 + \chi_e \quad (3.542)$$

ϵ_r and χ_e are in principle second-rank tensors, but can be identified with scalars in isotropic systems such as ordinary liquids.

- Finally, the *local* or *internal* electric-field strength E_{loc} existing in a cavity inside the dielectric material (see Fig. 3.48). Analogous to the outer surfaces of the

dielectric, a bound surface charge arises at the inner surfaces formed by the cavity. This leads to an *increase* of the electric-field strength depending on the geometry of the cavity. The local field in small spherical cavities, for example, the so-called *Lorentz* or *Mosotti field*, is given by

$$\mathbf{E}_{\text{loc}} = \frac{\epsilon_r + 2}{3\epsilon_r} \mathbf{E}_0 \quad (3.543)$$

The orientation polarization can be expressed in terms of the local field by $P = N_d \alpha E_{\text{loc}}/V$. The magnitudes of the three field strengths $\mathbf{E}_0, \mathbf{E}_{\text{loc}}, \mathbf{E}_e$ relevant in the present context are related as $E_0 > E_{\text{loc}} > E_e$.

3.9.2 Time-Varying Electric Fields

Equation (3.541) indicates a *linear* relationship between the equilibrium polarization $\mathbf{P}_0$ and the mean electric-field strength $\mathbf{E}_e$ in the dielectric, where it is anticipated that the material parameters ϵ_r and χ_e do not depend on the field strength. Far away from any polarization saturation phenomena, this property can be taken for granted. Turning now to time-dependent fields, we can therefore make use of the *linear-response theory* (see Sect. 1.2). Linearity means that the superposition principle applies. That is, the polarization at a time t can be expressed as an integral over the responses to all previous values of the field strength. In electric fields varying with time in general and in oscillating fields in particular, the linear polarization response thus is

$$\mathbf{P}(t) = \int_{-\infty}^t \psi(t - t') \mathbf{E}_e(t') dt' \quad (3.544)$$

The *response function* $\psi(t - t')$ quantifies the response to the electric field a period $t - t'$ ago. The integral covers the whole prehistory the sample was subjected to before time t .

For an impulse perturbation occurring at $t' = t_1 < t$ in the form of a Dirac's delta function, $\mathbf{E}_e(t') = \hat{\mathbf{E}}_e \delta(t' - t_1)$, the response will be

$$\mathbf{P}(t) = \int_{-\infty}^t \psi(t - t') \hat{\mathbf{E}}_e \delta(t' - t_1) dt' = \hat{\mathbf{E}}_e \psi(t - t_1) \quad (3.545)$$

That is, the response function can be interpreted as the response to a delta function perturbation. The time dependence of this response function reflects the relaxation processes by thermal orientation fluctuations of the dipoles.

Equation (3.544) can be expressed in equivalent form by the substitution $t'' = t - t'$:

$$\mathbf{P}(t) = \int_0^{\infty} \psi(t'') \mathbf{E}_e(t - t'') dt'' = \int_{-\infty}^{\infty} \psi(t'') \mathbf{E}_e(t - t'') dt'' \quad (3.546)$$

where we have taken into account that the response function is subject to *causality*, that is, $\psi(t'') = 0$, for $t'' < 0$: The response does not depend on future developments.

In the so-called dynamic experiments, the electric-field strength is alternating with an angular-frequency ω . It is then more convenient to express Eq. (3.546) in the form of Fourier transforms of both sides. Using the *convolution theorem*, we find

$$\tilde{\mathbf{P}}(\omega) = \tilde{\psi}(\omega) \tilde{\mathbf{E}}_e(\omega) \quad (3.547)$$

where the (complex) Fourier conjugates to the respective quantities in the time domain read

$$\begin{aligned} \tilde{\mathbf{P}}(\omega) &= \int_{-\infty}^{\infty} \mathbf{P}(t) e^{-i\omega t} dt \\ \tilde{\psi}(\omega) &= \int_{-\infty}^{\infty} \psi(t) e^{-i\omega t} dt \\ \tilde{\mathbf{E}}_e(\omega) &= \int_{-\infty}^{\infty} \mathbf{E}_e(t) e^{-i\omega t} dt \end{aligned} \quad (3.548)$$

In the frame of the *fluctuation-dissipation theorem* (see Sect. 1.2 and Ref. [117], for instance) the response function after an external perturbation of thermal equilibrium is generally related to the equilibrium fluctuations of the system. In the present case, the perturbation is due to the electric field applied to the sample. The result is based on first-order perturbation theory in the high-temperature approximation. The latter means that the mean thermal energy per degree of freedom is much larger than any energy change by the perturbation. Under this condition, the dielectric response function obeys

$$\psi(t) = -\frac{V}{3k_B T} \frac{d}{dt} \langle \mathbf{P}(0) \cdot \mathbf{P}(t) \rangle = -\frac{V}{k_B T} \frac{d}{dt} \langle P_z(0) P_z(t) \rangle \quad (3.549)$$

in accordance with Eq. (1.24). V is the sample volume. That is, the response is characterized by the correlation function of the polarization fluctuating owing to

molecular dynamics. The factor 1/3 in the vectorial version of Eq. (3.549) indicates that only the polarization component along the electric field is relevant, that is, along the z direction by definition.

The complex susceptibility for orientation polarization is related to the response function according to

$$\chi_e(\omega) - \chi_e(\infty) = \frac{\tilde{\psi}(\omega)}{\varepsilon_0} = \frac{1}{\varepsilon_0} \int_0^{\infty} \psi(t) e^{-i\omega t} dt \quad (3.550)$$

where $\chi_e(\infty)$ symbolizes the *displacement polarization*. It is subtracted since it is not of interest in the present context. The lower integration limit has been equated to zero because of the causality property $\psi(t < 0) = 0$. Inserting Eq. (3.549) in Eq. (3.550) gives

$$\begin{aligned} \chi_e(\omega) - \chi_e(\infty) &= \varepsilon_r(\omega) - \varepsilon_r(\infty) \\ &= -\frac{1}{\varepsilon_0} \frac{V}{k_B T} \int_0^{\infty} \frac{d}{dt} \langle P_z(0) P_z(t) \rangle e^{-i\omega t} dt \end{aligned} \quad (3.551)$$

Here we have made use of the relation between the complex susceptibility and the complex (relative) permittivity,⁴⁷ $\chi_e(\omega) = \varepsilon_r(\omega) - 1$. Integration by parts leads to

$$\varepsilon_r(\omega) - \varepsilon_r(\infty) = \frac{1}{\varepsilon_0} \frac{V}{k_B T} \left[\langle P_z^2(0) \rangle - i\omega \int_0^{\infty} \langle P_z(0) P_z(t) \rangle e^{-i\omega t} dt \right] \quad (3.552)$$

With the normalized orientation correlation function,

$$\mathcal{G}(t) = \frac{\langle P_z(0) P_z(t) \rangle}{\langle P_z^2(0) \rangle} \quad (3.553)$$

Equation (3.552) can be rewritten in a form crucial for all further considerations of dielectric relaxation [118–120]:

⁴⁷ Note that the real and imaginary parts of $\chi_e(\omega)$ on the one hand and of $\varepsilon_r(\omega)$ on the other are related by *Kronig/Kramers relations* as suggested by the linear conditions.

$$\begin{aligned}
\frac{\varepsilon_r(\omega) - \varepsilon_r(\infty)}{\varepsilon_r(0) - \varepsilon_r(\infty)} &= 1 - i\omega \int_0^{\infty} G(t) e^{-i\omega t} dt \\
&= 1 - i\omega \lim_{\kappa \rightarrow 0} \int_0^{\infty} G(t) e^{-(\kappa + i\omega)t} dt \\
&= 1 - i\omega \mathcal{L}\{G(t)\}
\end{aligned} \tag{3.554}$$

The operator $\mathcal{L}\{\dots\}$ stands for the Laplace transform.

The autocorrelation function of the electric polarization in Eq. (3.549) refers to a volume V containing N_d permanent electric dipoles of moment μ so that

$$\langle P_z(0)P_z(t) \rangle = \frac{\mu^2}{V^2} \sum_{j,k=1}^{N_d} \langle \cos \vartheta_j(t) \cos \vartheta_k(0) \rangle \tag{3.555}$$

Inserting this in Eq. (3.553) gives

$$G(t) = \frac{\sum_{j,k=1}^{N_d} \langle \cos \vartheta_j(t) \cos \vartheta_k(0) \rangle}{\sum_{j,k=1}^{N_d} \langle \cos \vartheta_j(0) \cos \vartheta_k(0) \rangle} \tag{3.556}$$

The polar angles ϑ_j and ϑ_k are defined between the electric-field vector and the orientation of the j -th and k -th dipole, respectively. The angle brackets indicate the ensemble average over the spatial orientations of the dipoles in the system in terms of the polar and azimuthal angles defining the orientation of the dipoles (see Fig. 3.49).

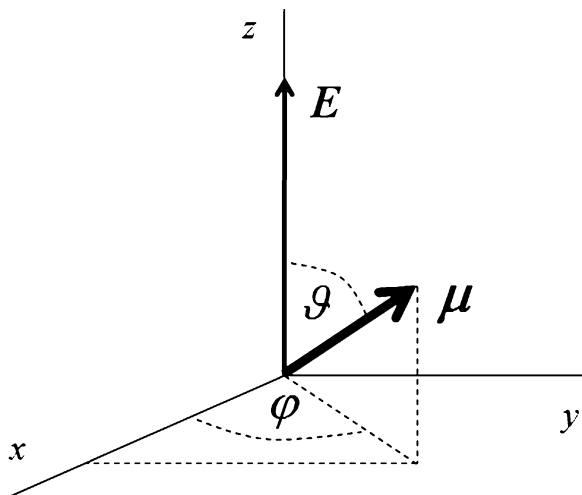
The correlation function Eq. (3.555) implies the sum over all dipole moments in the sample. The situation becomes much simpler if the dipole concentration is homogeneously distributed and dilute. In this case, cross-terms $j \neq k$ can be neglected because the dipoles fluctuate in an uncorrelated manner. Equation (3.556) can then be approximated as a *single-particle correlation function*. In terms of spherical harmonics, it reads

$$G(t) \approx \frac{\langle \cos \vartheta(t) \cos \vartheta(0) \rangle}{\langle \cos^2 \vartheta \rangle} = 4\pi \langle Y_{1,0}(\vartheta_t) Y_{1,0}(\vartheta_0) \rangle \tag{3.557}$$

The polar angles at times t and 0 are defined by $\vartheta_t \equiv \vartheta(t)$ and $\vartheta_0 \equiv \vartheta(0)$, respectively. The spherical harmonics relevant here is

$$Y_{1,0}(\vartheta) = \sqrt{\frac{3}{4\pi}} \cos \vartheta \tag{3.558}$$

Fig. 3.49 Polar coordinates of an electrical dipole moment μ relative to an electric field strength E



Note that this function depends solely on the polar angle ϑ . The azimuthal angle φ enters merely as a weighting parameter in the evaluation of ensemble averages. Both the macroscopic correlation function Eq. (3.556) and the single-particle correlation function Eq. (3.557) reflect dynamic reorientation properties so that dielectric relaxation spectroscopy can suitably be employed for studies of rotational fluctuations.

3.9.3 Isotropic Rotational Diffusion of Uncorrelated Fluctuating Dipoles

Isotropic rotational diffusion of the dipole-bearing molecules is the paradigm of molecular-dynamics scenarios for dielectric relaxation spectroscopy. In the following, we will evaluate the orientation correlation function Eq. (3.557) for uncorrelated fluctuating dipoles for this sort of molecular motions in complete analogy to the treatment in Sect. 3.1.7.1 for NMR relaxation.

The angles defining the orientation of a dipole are defined in Fig. 3.49. The initial and final orientations are characterized by the respective polar angles $\vartheta(0) \equiv \vartheta_0$ and $\vartheta(t) \equiv \vartheta_t$. The initial and final azimuthal angles, $\varphi(0) \equiv \varphi_0$ and $\varphi(t) \equiv \varphi_t$, can be assumed arbitrarily since the correlation function Eq. (3.557) does not depend on them. The initial and final angle sets φ_0, ϑ_0 and φ_t, ϑ_t , respectively, can be expressed by the initial and final unit vectors $\mathbf{u}_0$ and $\mathbf{u}_t$. With these definitions, Eq. (3.557) can be rewritten as

$$\mathcal{G}(t) = 4\pi \langle Y_{1,0}\{\varphi_t, \vartheta_t\} Y_{1,0}\{\varphi_0, \vartheta_0\} \rangle \equiv 4\pi \langle Y_{1,0}\{\mathbf{u}_t\} Y_{1,0}\{\mathbf{u}_0\} \rangle \quad (3.559)$$

where the angle brackets indicate the averages over all possible initial and final polar and azimuthal angles.

This ensemble average can be expressed in terms of the probability density

$$W(\mathbf{u}_t, t; \mathbf{u}_0, 0) = \frac{1}{4\pi} w_c(\mathbf{u}_0, \mathbf{u}_t, t) \quad (3.560)$$

that the reference dipole points in the direction $\mathbf{u}_0$ at time 0, *and* is aligned along $\mathbf{u}_t$ at time t . In the isotropic case, this probability density can be split in the *a priori* probability density $(4\pi)^{-1}$ for a certain initial space direction $\mathbf{u}_0$ and the conditional probability density $w_c(\mathbf{u}_0, \mathbf{u}_t, t)$ that the final orientation is $\mathbf{u}_t$ if the initial orientation was $\mathbf{u}_0$. On this basis, the ensemble average in Eq. (3.559) can be spelt out by integrals over all initial and all final dipole orientations:

$$\mathcal{G}(t) = \int_0^{2\pi} d\varphi_t \int_0^\pi d\vartheta_t \int_0^{2\pi} d\varphi_0 \int_0^\pi d\vartheta_0 w_c(\mathbf{u}_0, \mathbf{u}_t, t) Y_{1,0}(\mathbf{u}_t) Y_{1,0}(\mathbf{u}_0) \sin \vartheta_t \sin \vartheta_0 \quad (3.561)$$

The conditional probability density $w_c(\mathbf{u}_0, \mathbf{u}_t, t)$ can be found as the solution of the rotational diffusion equation

$$\frac{\partial w_c(\mathbf{u}_0, \mathbf{u}_t, t)}{\partial t} = D_r \nabla^2 w_c(\mathbf{u}_0, \mathbf{u}_t, t) \quad (3.562)$$

where D_r is the rotational diffusion coefficient and ∇^2 is the Laplace differential operator for polar coordinates r, φ, ϑ (see Eq. (2.63)). With the Dirac's delta function, the initial condition is

$$w_c(\mathbf{u}_0, \mathbf{u}_t, 0) = \delta(\mathbf{u}_t - \mathbf{u}_0) \quad (3.563)$$

Proceeding in complete analogy to the formalism in Sect. 3.1.7, the solution of Eq. (3.562) can be expressed by

$$w_c(\mathbf{u}_0, \mathbf{u}_t, t) = 4\pi \sum_{\ell, m} Y_{\ell, -m}(\mathbf{u}_0) Y_{\ell, m}(\mathbf{u}_t) \exp\{-\ell(\ell+1)D_r t\} \quad (3.564)$$

Inserting this result in Eq. (3.561) and exploiting the known property of spherical harmonics

$$\int_0^{2\pi} d\varphi \int_0^\pi d\vartheta \sin \vartheta Y_{\ell, m}^*(\vartheta, \varphi) Y_{\ell', m'}(\vartheta, \varphi) = \delta_{\ell\ell'} \delta_{mm'} \quad (3.565)$$

lead to the dielectric orientation correlation function

$$G(t) = \exp\{-\ell(\ell+1)D_r t\} = \exp\{-2D_r t\} = \exp\{-t/\tau_d\} \quad (3.566)$$

where the degree of the relevant spherical harmonics is $\ell = 1$. $\delta_{\ell\ell'}$ and $\delta_{mm'}$ are Kronecker symbols as defined in footnote 16. The *dielectric rotational correlation time* (often termed *dielectric relaxation time*) is defined by

$$\tau_d = \frac{1}{2D_r} \quad (3.567)$$

Combining this with the Stokes/Einstein/Debye relation Eq. (2.204) leads to the more detailed expression

$$\tau_d = \frac{4\pi\eta a_h^3}{k_B T} \quad (3.568)$$

where η is the dynamic viscosity of the medium and a_h is the hydrodynamic radius of the dipole-bearing particle.

By comparison, the rotational correlation time for spin relaxation given in Eq. (3.205) is three times *shorter*, that is, $\tau_d = 3\tau_{\text{NMR}}$, where we have renamed τ_c by τ_{NMR} . This is a consequence of the different degrees ℓ of the relevant spherical harmonics. The orientational fluctuations referred to are nevertheless identical in both cases, of course.

Inserting Eq. (3.566) in Eq. (3.554) gives the real (*dispersion*) and imaginary (*absorption*) parts of the complex permittivity

$$\begin{aligned} \varepsilon'_r(\omega) &= \varepsilon_r(\infty) + \frac{\varepsilon_r(0) - \varepsilon_r(\infty)}{1 + \omega^2 \tau_d^2} \quad \text{and} \\ \varepsilon''_r(\omega) &= (\varepsilon_r(0) - \varepsilon_r(\infty)) \frac{\omega \tau_d}{1 + \omega^2 \tau_d^2} \end{aligned} \quad (3.569)$$

These are the so-called *Debye equations*. They can mathematically be converted into each other with the aid of the *Kronig/Kramers dispersion relations* (see, e.g., Ref. [76]) which are valid under the conditions of the linear-response theory outlined in Sect. 1.2.

The real and imaginary parts of the complex permittivity can be combined in the form of the so-called *loss tangent*

$$\tan \delta(\omega) = \frac{\varepsilon''_r(\omega)}{\varepsilon'_r(\omega)} = \frac{(\varepsilon_r(0) - \varepsilon_r(\infty))\omega \tau_d}{\varepsilon_r(0) + \varepsilon_r(\infty)\omega^2 \tau_d^2} \quad (3.570)$$

The functions $\varepsilon'_r(\omega)$, $\varepsilon''_r(\omega)$, and $\tan \delta(\omega)$ are the measurands on which dielectric relaxation spectroscopy is usually based. A graphical representation of Eqs. (3.569) and (3.570) for the case of isotropic rotational diffusion can be found in Fig. 3.50.

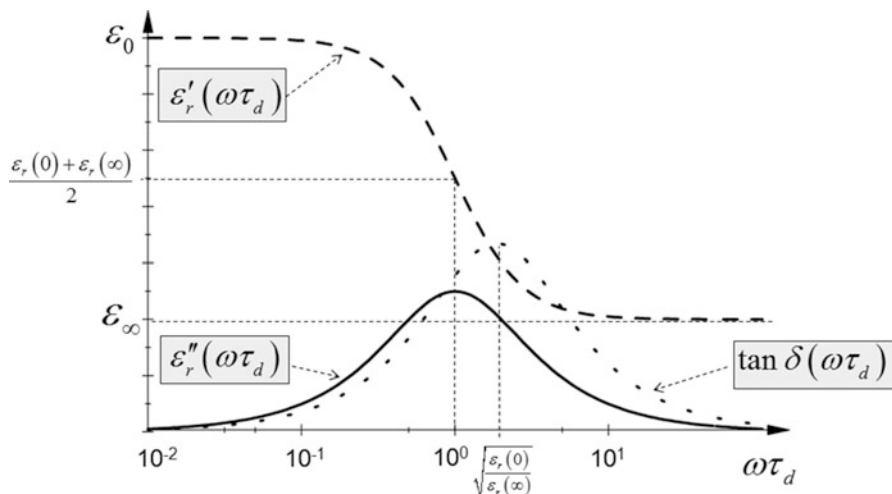


Fig. 3.50 The quantities ϵ'_r , ϵ''_r and $\tan \delta$ as functions of $\omega\tau_d$ for isotropic rotational diffusion (see Eqs. 3.569 and 3.570)

The exponential correlation function Eq. (3.566) was derived for isotropic rotational diffusion. If the shape of the molecules bearing the dipoles is nonspherical, the reorientation rates are no longer isotropic. In this case, a superposition of several exponential functions with different time constants will be more adequate.

3.9.4 Defect Diffusion

Orientation correlation functions in complex systems tend to deviate considerably from mono-exponential decays. A criterion predicting such strongly non-exponential correlation losses in homogeneous systems is *non-Markovian statistics* of molecular fluctuations. In the following, a *defect diffusion* model will be outlined as an instructive example for this category.

Notabene, we are not speaking of distributions of relaxation or correlation times here as they are often assumed in the literature for purely formal reasons. Such a distribution would be adequate only in *heterogeneous* samples in the sense that different correlation times apply to different volume elements due to structural variations. As a matter of fact, heterogeneity is the only justification for this sort of analysis in contrast to the *homogeneous* conditions assumed here. Distributions of correlation times may describe but cannot explain molecular dynamics in homogeneous samples, and will therefore not be considered any further here.

The idea behind defect diffusion models is that a dipole can only be reoriented if a structural defect happens to arrive at the site of the dipole. This gives rise to temporal changes of the local structure and, hence, to fluctuations of the dipole

orientation. The conditional probability in Eq. (3.560) is then a function of the initial distances of the defects from the dipole under consideration. Whether a given dipole will be reoriented in a certain time interval depends on the prehistory of the relative constellation of defects. The primary diffusion process is that of the defects. Various versions of such defect diffusion models have been reported in Refs. [121–124]. The formalisms in these chapters have partly been elaborated for dielectric as well as for NMR relaxation.

The exemplary model to be described here is *one-dimensional defect diffusion restricted by two reflecting barriers* [121, 122]. The scenario is schematically depicted in Fig. 3.51. A structural defect of width b diffuses between two reflecting barriers separated by a distance d . The center position of the defect fluctuates according to the trajectory $x_d = x_d(t)$. A dipole located at the position $x = r$ will be reoriented if the defect arrives and resides in the range $r - b/2 \leq x_d \leq r + b/2$. When the defect leaves this range again, the undisturbed orientation will be restored. The reorientational fluctuations of the dipole thus depend on the statistics with which the defect encounters the dipole under consideration.

The terms *defect* and *barrier* have so far been introduced heuristically. Tangible specifications need to be detailed depending on the applications. In Ref. [124], for instance, localized rotational isomers of polymer chains are considered as “defects,” whereas chemical or physical cross-links between the chains are thought to act as “barriers.” The restriction to one dimension is stipulated by the chain character of the polymers. Likewise, this sort of defect is also expected to be relevant in the alkane chain phase of lipid bilayers. In this case, the barriers are the polar headgroups terminating the alkane phase as illustrated in Fig. 2.10. Actually, experimental NMR relaxometry data have been interpreted on this basis as reported in Ref. [125] (see Sect. 6.8.3).

The result of the formalism derived in Refs. [121, 122] is based on the two time constants $\tau_b = b^2/2D$ and $\tau_d = d^2/2D$, that is, the mean diffusion times across a distance equal to the defect width b on the one hand and over the distance d between the reflecting barriers on the other. The quantity D is the (one-dimensional) diffusion coefficient of the – notabene – defect. Assuming $d \gg b$ or equivalently $\tau_d \gg \tau_b$, the following limits for the complex permittivity can be deduced from Eq. (3.554):

$$\begin{aligned} \frac{\varepsilon_r(\omega) - \varepsilon_r(\infty)}{\varepsilon_r(0) - \varepsilon_r(\infty)} &\approx \\ &\approx \begin{cases} 1 + i\frac{\omega}{3} \left(\sqrt{\tau_b \tau_d} - \frac{\tau_b \tau_d}{(\sqrt{\tau_d} - \sqrt{\tau_b})^2} \right) & \text{for } \omega \tau_d \ll 1 \\ \frac{1}{2} \frac{\sqrt{\tau_d}}{(\sqrt{\tau_d} - \sqrt{\tau_b})^2} [2\sqrt{\tau_d} - 3\sqrt{\tau_b} - \sqrt{\omega}(\sqrt{\tau_b \tau_d} - 2\tau_b) + i\sqrt{\omega}(\sqrt{\tau_b \tau_d} - 2\tau_b)] & \text{for } \omega \tau_b \ll 1 \ll \omega \tau_d \\ (1 + i)^{\frac{1}{2}} \frac{\sqrt{\tau_d}}{\sqrt{\tau_b \tau_d} - \tau_b} \omega^{-1/2} & \text{for } \omega \tau_b \gg 1 \end{cases} \end{aligned} \quad (3.571)$$

Equation (3.571) strongly deviates from the results for isotropic rotational diffusion, Eq. (3.569) and Fig. 3.50. The characteristic features of the one-

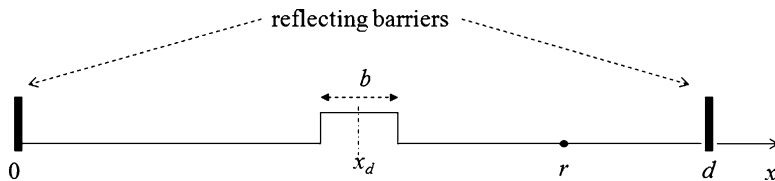


Fig. 3.51 One-dimensional defect diffusion restricted by two reflecting barriers in a distance d . The width of the diffusing defect is b . A dipole at a position r will be temporally reoriented when the defect passes the position $x_d = r$. The base line along the x -axis means “undistorted” dipole orientation, while the section drawn as an *elevated line* indicates orientational distortions. The model has been suggested as an explanation for the local dynamics of amorphous polymers and of the alkane phase in lipid bilayers [122–125]. The reflecting barriers are thought to be formed by other structural defects in the case of amorphous polymers and by polar headgroups in the context of lipid bilayers (see Fig. 2.10)

dimensional defect diffusion model are indicated in Fig. 3.52. In these plots, data for the spin–lattice relaxation time T_1 calculated on the same basis are shown as well for comparison.

The strong tendency toward non-exponential correlation functions intrinsic to such defect diffusion models can partly be counterbalanced in three-dimensional versions. The increased chance for repeated reorientational fluctuations by a defect diffusing near a dipole is compensated by the increased escape rate of the defect from the proximity of that dipole. Under such circumstances, one can show that an exponential correlation function will be approached again [123].

3.10 Comparison and Discussion of Dynamic Ranges

The methods to which this chapter is devoted are typical and in widespread use for studies of soft-matter dynamics. The time, frequency, and wave-number scales that can be probed on this basis are extremely broad in principle. In the following, the respective technical limits will be juxtaposed. As we have seen, all methods are based on time correlation functions of various quantities. This brings another aspect into play, namely, the classification of molecular motions that can be detected with the diverse techniques. The question is in particular whether the dynamics to which the methods are sensitive is more of a translational or more of a rotational character.

In the introduction, Chap. 1, two methodological categories of time correlation functions have been identified. The first category is based on spherical harmonics of degree l and order m :

$$G_{l,m}(t) = 4\pi(-1)^m \langle Y_{l,m}(t) Y_{l,-m}(0) \rangle \quad (3.572)$$

The primarily fluctuating parameters are the polar and azimuthal angles $\vartheta(t)$ and $\varphi(t)$, respectively. In experiments, an external electric or magnetic field is applied.

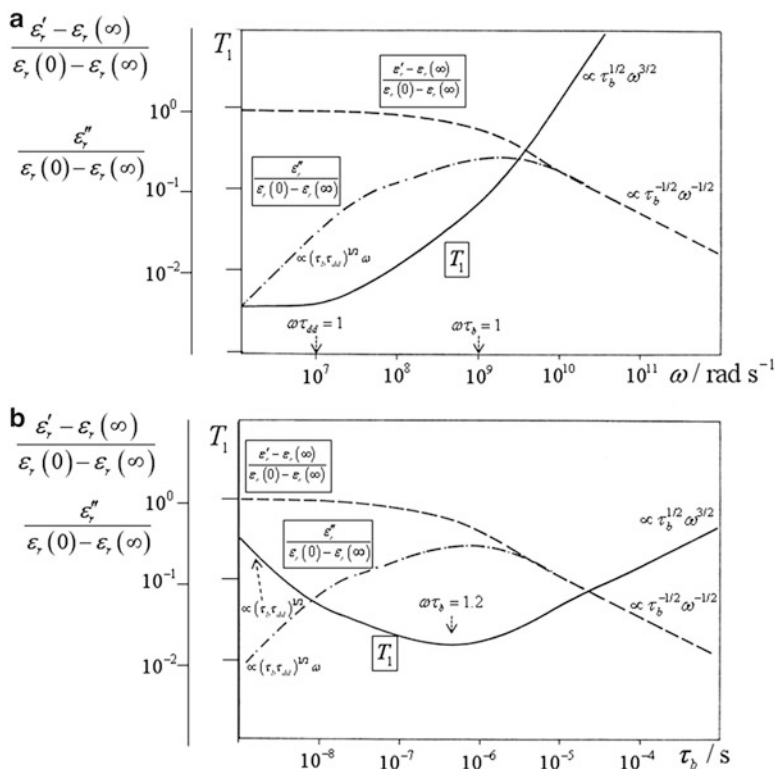


Fig. 3.52 Dielectric relaxation quantities calculated for one-dimensional defect diffusion restricted by two reflecting barriers. **(a)** Frequency dependence. **(b)** Dependence on the characteristic (and representatively temperature-dependent) time constant τ_b . The data have been calculated for the complete theory. The limiting dependences given in Eq. (3.571) are indicated as well. The behavior of the spin-lattice relaxation time T_1 calculated on the same basis is plotted for comparison (see Sect. 6.8.3 and Eqs. (6.110) and (6.111))

The angles define the orientation of a molecular axis relative to that field. Since Eq. (3.572) reflects features of *rotational fluctuations*, it is referred to as *orientation correlation function*.

As we have seen in the previous sections, there are several techniques probing such orientation correlation functions. If we restrict ourselves for the moment to the most important case of intramolecular spin interactions, that is, to fixed internuclear distances, *spin relaxation* is a typical example probing orientation correlation functions. The spherical harmonics in Eq. (3.572) are then of the degree $l = 2$ and order $m = 0, 1, 2$.

Provided that molecular dynamics is slow (and anisotropic) enough to ensure residual dipolar couplings among nuclear spins, *multiple-quantum buildup spectroscopy* can be employed as a further method probing orientational fluctuations [126]. “Slow” means that the couplings are not averaged out by molecular motions

on the NMR time scale. The existence of residual dipolar couplings suggests that this technique is particularly sensitive to *anisotropic* molecular reorientations. The degree and order of the spherical harmonics are in this case $l = 2$ and $m = 0$, respectively, that is,

$$G_{2,0}(t) = 4\pi \langle Y_{2,0}(t) Y_{2,0}(0) \rangle = 5 \langle P_2(t) P_2(0) \rangle \quad (3.573)$$

where the second-order Legendre polynomial is defined by $P_2(t) = \frac{1}{2} [3 \cos^2 \vartheta(t) - 1]$. The time and frequency ranges probed by a number of typical NMR techniques are schematically compared in Fig. 3.53.

Likewise, it was shown that *dielectric relaxation* both in frequency- [116] and time-domain [127] experiments is determined by an orientation correlation function of the type Eq. (3.572). In this case, the degree and order of the spherical harmonics are $l = 1$ and $m = 0$, respectively. The frequency range that can be covered by this method is in principle relatively broad and is extended from below kHz to above GHz. At low frequencies, dielectric losses will however be dominated by ionic conductivity effects. If ionic charges are separated and blocked at interfaces of heterogeneous samples or just at the contacts between the sample and the electrodes, the so-called Maxwell/Wagner effect can arise which can be orders of magnitude larger than that due to molecular fluctuations. To avoid this problem, *dielectric noise spectroscopy* has been applied in recent studies [128, 129]. Instead of applying external electric fields as a perturbation, thermal equilibrium noise of the dielectric polarization is measured and evaluated in the sense of the fluctuation-dissipation theorem.

Finally, we have dealt with *mechanical relaxation* with particular emphasis of shear deformations. The sheared volume elements of the material under investigation can in principle have molecular dimensions so that molecular fluctuations are probed. As before, molecular rotations are best described by spherical harmonics, and orientation correlation functions of the type defined in Eq. (3.572) should be relevant again in principle. Unfortunately, no such theory has been elaborated in the literature so far. This is likely a consequence of the preference of the community to employ continuum mechanical pictures and formal dashpot/spring replacement schemes instead of molecular models (see footnote 45). On the other hand, in Refs. [130, 131], the dynamic viscosity probed in periodic shear experiments has been traced back to the time correlation function of the momentum flux in terms of a Fourier transform relation. On this basis, molecular-dynamics-related theories have been developed. An example is the zero-shear viscosity η_0 in polymer melts which can be expressed as the time integral over the time correlation function of the polymer end-to-end vector [132].

The second category of correlation functions is of the *dynamic structure factor* type based on translational displacements of particles. The correlation functions

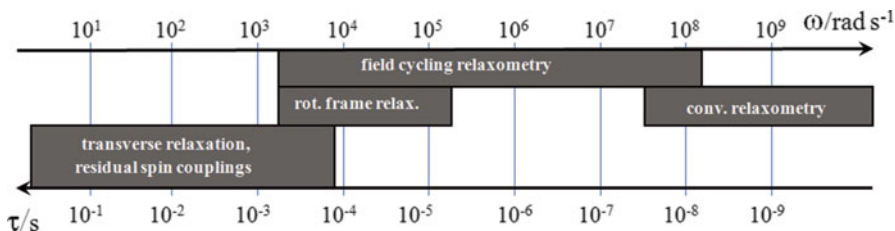


Fig. 3.53 Comparison of some popular NMR methods sensitive to rotational fluctuations. The shaded boxes indicate the time (τ) and angular-frequency (ω) scales to which typical NMR relaxation techniques are sensitive at proton resonance. Field-cycling NMR relaxometry permits measurements of spin-lattice relaxation times on a frequency scale down to the kHz regime. Above 10 MHz, the experimental frequency scale can be supplemented by conventional fixed-field NMR spectrometers operating at frequencies up to several hundred MHz. To some limited degree, information on low-frequency dynamics can also be obtained with the aid of rotating-frame spin-lattice relaxation. Transverse relaxation and methods probing residual dipolar couplings extend the scales in the slow-motion regime

$$\begin{aligned} G_{\text{inc}}(t) &= \left\langle e^{-i\mathbf{q} \cdot \mathbf{R}(0)} e^{i\mathbf{q} \cdot \mathbf{R}(t)} \right\rangle = \left\langle \exp\{-i\mathbf{q} \cdot [\mathbf{R}(0) - \mathbf{R}(t)]\} \right\rangle \\ &= \left\langle \exp\{i\mathbf{q} \cdot \mathbf{r}_{\text{self}}\} \right\rangle \end{aligned} \quad (3.574)$$

and

$$\begin{aligned} G_{\text{coh}}(t) &= \frac{1}{N_t} \sum_{j,l=1}^{N_t} \left\langle e^{-i\mathbf{q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{q} \cdot \mathbf{R}_l(t)} \right\rangle \\ &= \frac{1}{N_t} \sum_{j,l=1}^{N_t} \left\langle e^{-i\mathbf{q} \cdot (\mathbf{R}_j(0) - \mathbf{R}_l(t))} \right\rangle = \frac{1}{N_t} \sum_{j,l=1}^{N_t} \left\langle e^{i\mathbf{q} \cdot \mathbf{r}_{j,l}(t)} \right\rangle \end{aligned} \quad (3.575)$$

are referred to as *incoherent* and *coherent* dynamic structure factors, respectively.

The *incoherent* variant Eq. (3.574) reflects *self-diffusion* of particles, that is, displacements $\mathbf{r}_{\text{self}}$ from the initial position $\mathbf{R}(0)$ to the final position $\mathbf{R}(t)$. Three different techniques have been identified as probes for this type of correlation function, namely, *field-gradient NMR diffusometry*, *incoherent (quasi-elastic) neutron scattering*, and *dynamic light scattering*. Depending on the technique, the quantity $\mathbf{q}$ is referred to as *wave* or *scattering vector*. The magnitudes are given by

$$\begin{aligned} q_{\text{NMR}} &= \gamma g \delta & (\rightarrow \text{wave vector}) \\ q_{\text{neutron}} &= 4\pi\lambda^{-1} \sin \theta/2 & (\rightarrow \text{scattering vector}) \\ q_{\text{light}} &= 4\pi\langle n \rangle \lambda^{-1} \sin \theta/2 & (\rightarrow \text{scattering vector}) \end{aligned} \quad (3.576)$$

where the notation is defined in the respective sections.

The *coherent* dynamic structure factor Eq. (3.575) correlates displacements of particle *pairs* j, l relative to each other in an ensemble of N_l particles. The particles can be located on the same or on different molecules depending on the system under investigation. The examination of the coherent dynamic structure factor of *intra*-molecular particle pairs is a standard application of coherent (quasi-elastic) neutron scattering.

Under suitable circumstances, the *intermolecular* variant can be examined with the aid of spin–lattice relaxation arising from intermolecular dipolar interactions as mentioned in Sect. 3.1.9. This sort of experiment is particularly promising for studies of polymers and was demonstrated in Ref. [38]. The only condition for the applicability is a *subdiffusive* power law, $\langle r^2 \rangle \propto t^\kappa$ (Eq. 2.175) with an exponent $\kappa < 2/3$, for the time dependence of the mean square displacement as it is typical for the chain-mode regime in polymer liquids (see the diverse model scenarios discussed in Chap. 5). Using field-cycling NMR relaxometry, an effective diffusion time range from nano- to almost milliseconds can be probed on this basis. Using the formalism elaborated in Ref. [38], the intermolecular spin–lattice relaxation rate $(T_1^{\text{inter}})^{-1}$ can be determined with the aid of isotopic dilution, that is, by mixing undeuterated and deuterated polymers of the same species and of the same molecular mass. From this, the mean square displacement can be evaluated according to

$$\langle r^2 \rangle = 2 \left\{ \left(\frac{4\pi}{\mu_0} \right)^2 \frac{2\pi\sqrt{3}(1 + 2\sqrt{2})\gamma^4 \hbar^2 \rho_{\text{spin}} T_1^{\text{inter}}}{5\omega} \right\}^{2/3} \quad (3.577)$$

where ρ_{spin} is the number density of (proton) spins. The diffusion time is given by the inverse angular Larmor frequency $t = \omega^{-1}$. The time range over which the mean square segment displacements can be evaluated from such data has been shown to cover five decades from about 10^{-9} s to about 10^{-4} s. This is of particular interest since the time-scale gap between incoherent neutron scattering and field-gradient NMR diffusometry can be bridged in this way (see Fig. 3.54).

Another NMR method probing translational diffusion is *spin-density diffusometry*. As already outlined in Sect. 3.3.1, this technique is of interest for *extremely long* diffusion times and correspondingly long root mean square displacements. The diffusometry techniques described so far are schematically compared in Fig. 3.54. Combinations of various methods of this catalog open the access to an enormous range of diffusion times and a correspondingly wide spread of mean square displacements reaching from atomistic to macroscopic dimensions.

The need to distinguish the two principal classes of correlation functions, namely, those probing *translational* fluctuations from those probing *rotational* fluctuations, can formally be illustrated by the molecular motions permitted in an infinitely extended nematic domain of a liquid crystal: Within the domain, translational fluctuations of molecules are *unrestricted*, whereas rotational fluctuations are subject to substantial *constraints*. There are two totally different appearances of the dynamics of one and the same particle species.

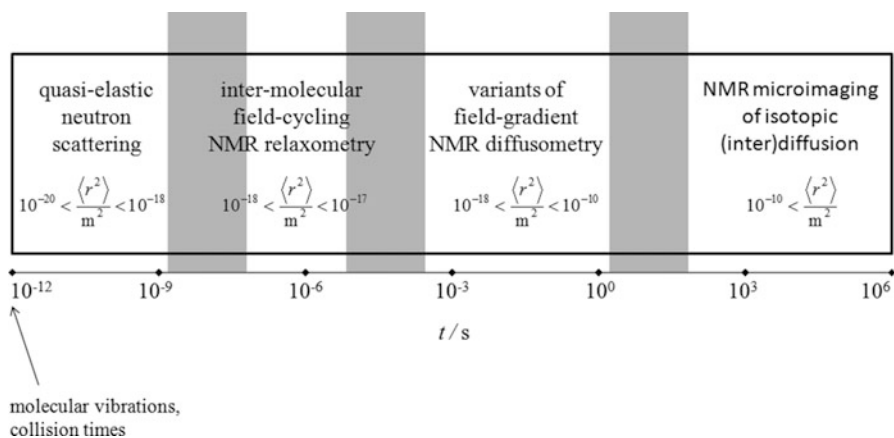


Fig. 3.54 Comparison of typical methods probing translational displacements of molecules. The experimentally accessible time scales and the corresponding ranges of mean square displacements $\langle r^2 \rangle$ are specified

Another well-known case revealing the need of this distinction is molecular dynamics of fluids near surfaces: Relative to bulk fluids, there is a strong effect on rotational diffusion as probed by field-cycling NMR relaxometry, for instance [133]. On the other hand, the influence on translational diffusion is only minor. The latter finding was observed both by field-gradient NMR diffusometry [134] and neutron scattering [135, 136].

Of course, translational and rotational fluctuations are not entirely independent of each other in isotropic systems (as it would be the case in the nematic liquid crystal domain discussed above). Some correlation must be expected. The question how strongly translational and rotational fluctuations are correlated will be reconsidered in Chaps. 5 (polymer dynamics) and 7 (surface-related effects).

A further diffusometry approach, which is especially of interest for biological systems, is *single-particle tracking* [137, 138]. Using video-enhanced contrast microscopy, the diffusive trajectories of individual particles such as proteins or small clusters of molecules can be tracked in quasi-two-dimensional systems. Biological membranes are typical examples of this sort. In this way, the influence of heterogeneities on the particle displacements can be examined.

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Chapter 4

Fluid Dynamics

Abstract Treatments of molecular dynamics in general and especially if they are based on Langevin equations of motions are hardly possible without referring to hydrodynamics. Basic hydrodynamic concepts such as Stokes' friction law of particles in a viscous medium are ubiquitously employed in molecular dynamics. The present treatise is unique in the sense that it juxtaposes the principles of the analytical formalism in the form of computer simulations with real experiments. If the topology of objects is known or predetermined by suitable sample preparations, hydrodynamics can be simulated and measured under identical conditions. This option opens a promising application field of utmost importance for chemical engineering. The term fluid dynamics is moreover understood in a generalized sense. Apart from pressure-driven flow, a wealth of related transport phenomena will be addressed in this chapter. The scope covers examples as different as the spatially resolved probing of thermal convection, heat conduction, electroosmosis, and ionic currents.

This is the first of the four chapters in this book dealing with applications of the methodology described in Chap. 3. Since fluid dynamics has always to do with spatial distributions of dynamic parameters, we will mainly refer to the mapping experiments outlined in Sect. 3.3.

Dynamics in fluids can be subdivided into *coherent* and *incoherent* motions of the moving entities. Typical processes subsumed by the attribute “incoherent” are *diffusion*, *Brownian particle motion*, and *hydrodynamic dispersion*. By contrast, the property “coherent” refers to any sort of more or less *uniform transport* of molecules.¹ This is the primary subject of the present chapter.

¹ Note that the transport uniformity refers in principle to *uncoupled* particles here. This is in contrast to the less stringent version of coherence, namely, *collective* relaxation modes, that will be discussed in Chap. 5 (polymer dynamics) and in Chap. 6 (dynamics in liquid crystals). The coherence is then a consequence of *chain connectivity* and *interactions* among molecular entities.

In the following, we will not restrict ourselves to pressure-driven hydrodynamic flow, that is, the classical area addressed by fluid dynamics. As further transport mechanisms, we will rather imply more general variants such as electroosmotic flow, heat transport, and ionic currents. Comparisons of such different phenomena will be shown to be most instructive for the understanding of the laws governing transport.

Fluid dynamics is the umbrella term for hydro- and aerodynamics referring to liquid as well as gaseous media [1–3]. Although we will mainly be concerned with liquid systems, it is nevertheless common practice to speak of fluids in this context. Computer simulations, for example, a tool most important for the elucidation of flow properties of liquids, are correspondingly termed *computational fluid dynamics* (see Sect. 4.8).

The primary objective of any theory of fluid dynamics is to predict the spatial and temporal distribution of the flow velocity, $\mathbf{v} = \mathbf{v}(\mathbf{r}, t)$, if pressure gradients or other external forces are applied. Solid surfaces confining the fluid are taken into account by boundary conditions which are usually and for plausible reasons assumed to be of the non-slipping type, that is, $\mathbf{v} = 0$.²

On length scales much larger than molecular dimensions, fluids can be treated as continua. If atomistic and molecular phenomena matter, that is, if dynamics on mesoscopic scales are of interest, discrete-particle-based formalisms may be more appropriate. In extreme cases, this can mean that the equations of motion of all participating and interacting particles need to be treated numerically with the aid of *molecular-dynamics simulations*.

The dynamic behavior of fluids can be subdivided into two classes: *laminar* and *turbulent*. “Laminar” means that fluid elements move along streamlines without lateral mixing with adjacent fluid layers. If the pressure gradients and all other external driving forces are stationary, the streamlines will be stationary as well. Otherwise, they follow the time dependence externally impressed on the system. In experiments, laminar flow can readily be demonstrated by marking the fluid by locally injecting a dye which moves then along *streamlines*: Streamlines visualize the trajectories of fluid elements.

Turbulent motions are by contrast characterized by time-dependent chaotic trajectories of fluid elements irrespective of any externally impressed time dependence of the driving forces. There is a stochastic element in the appearance of eddies which are characteristic for turbulence. The evolution of the flow patterns then exhibits an extremely strong dependence on the initial and boundary conditions. The criteria under which turbulent flow can be expected will be discussed in Sect. 4.5.

The formalisms for the treatment of coherent transport are based on a number of simplifying assumptions. Let us first classify the framework of those analyses and

² A more detailed and modified picture of the conditions at fluid–surface interfaces will be outlined in Sect. 7.5.7 in the context of the NMR flow-relaxation effect.

then proceed to the equations of motions permitting predictions of flow patterns for given boundary conditions.

4.1 Compressible and Incompressible Fluids

Consider a volume element $dV = dx dy dz$ in a fluid of mass density $\rho = \rho(x, y, z, t)$. The density may vary from position to position and may be a function of time. The fluid is assumed to be subject to a flow field as schematically illustrated in Fig. 4.1. While passing the volume element dV , the velocity of a flowing particle changes by $d\mathbf{v} = \mathbf{v}_{\text{out}} - \mathbf{v}_{\text{in}}$, where $\mathbf{v}_{\text{in}}$ and $\mathbf{v}_{\text{out}}$ refer to inflow and outflow, respectively. The densities of the in- and outflowing fluid are analogously termed ρ_{in} and ρ_{out} , respectively.

In an infinitesimal period dt , the fluid mass entering the volume element is

$$dm_{\text{in}} = \rho_{\text{in}}(v_{\text{in},x} dt dy dz + v_{\text{in},y} dt dx dz + v_{\text{in},z} dt dx dy) \quad (4.1)$$

Analogously, the outflowing mass amounts

$$dm_{\text{out}} = \rho_{\text{out}}(v_{\text{out},x} dt dy dz + v_{\text{out},y} dt dx dz + v_{\text{out},z} dt dx dy) \quad (4.2)$$

The mass residing in $dV = dx dy dz$ consequently changes during dt by

$$\begin{aligned} dm &= dm_{\text{in}} - dm_{\text{out}} \\ &= -[d(\rho v_x) dy dz + d(\rho v_y) dx dz + d(\rho v_z) dx dy] dt \\ &= -\left[d(\rho v_x) \frac{dV}{dx} + d(\rho v_y) \frac{dV}{dy} + d(\rho v_z) \frac{dV}{dz}\right] dt \end{aligned} \quad (4.3)$$

where $d(\rho v_x) = \rho_{\text{out}} v_{\text{out},x} - \rho_{\text{in}} v_{\text{in},x}$ etc. During the infinitesimal period dt , the density in dV thus varies by

$$d\rho = \frac{dm}{dV} = -\left[\frac{\partial(\rho v_x)}{\partial x} + \frac{\partial(\rho v_y)}{\partial y} + \frac{\partial(\rho v_z)}{\partial z}\right] dt \quad (4.4)$$

This is the *continuity equation* which is usually represented in the more compact form:

$$\frac{d\rho}{dt} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (4.5)$$

where the nabla differential vector operator in Cartesian coordinates is defined by $\nabla \equiv \mathbf{u}_x(\partial/\partial x) + \mathbf{u}_y(\partial/\partial y) + \mathbf{u}_z(\partial/\partial z)$ with the unit vectors $\mathbf{u}_x$, $\mathbf{u}_y$, and $\mathbf{u}_z$ along the

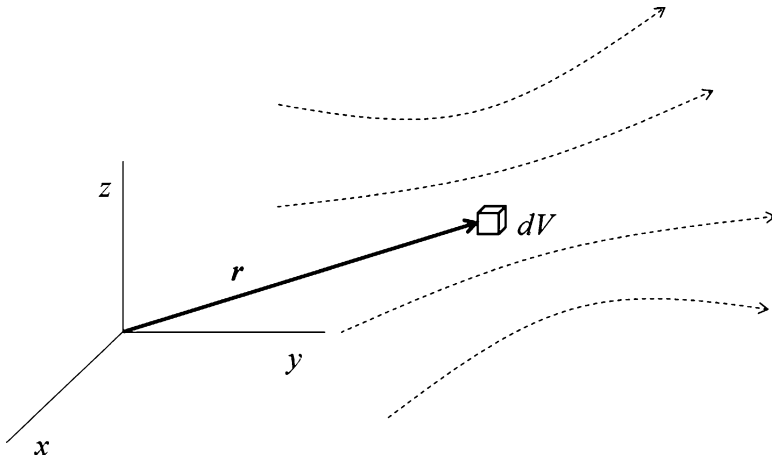


Fig. 4.1 Volume element $dV = dx dy dz$ at a position $\mathbf{r}$ in a flow field. The *dashed lines* are to represent streamlines

three space directions. The particular effect of the nabla operator in Eq. (4.5) is spelt out in the square brackets of Eq. (4.4). Under the nonrelativistic circumstances of interest here, the continuity equation states that matter is conserved. Nothing is lost that was there before, and nothing is gained that was not there before.

The compressibility of liquids is extremely low relative to the gaseous state. The density ρ can therefore be taken to be constant with respect to time and space. In this limit of *incompressible fluids*, the continuity equation reduces to

$$\nabla \cdot \mathbf{v} = 0 \quad (4.6)$$

Equation (4.6) tells us that there are neither sources nor sinks of matter. Integrating this relation over a certain volume V of the fluid and applying *Gauss' theorem* provide the integral form of the continuity equation for incompressible fluids:

$$\int_V (\nabla \cdot \mathbf{v}) dV' = \int_A \mathbf{v} \cdot d\mathbf{A}' = \text{const} \quad (4.7)$$

where A is the surface area encasing the volume V . The differential surface elements are denoted by normal vectors $d\mathbf{A}'$.

4.2 Lagrangian and Eulerian Description of Coherent Flow

Principally, there are two different pictures suitable for the description of coherent flow. In the *Lagrangian specification of flow*, motions of fluid elements are considered explicitly. The trajectory of the i -th element is described by its time-dependent position vector $\mathbf{r}_i = \mathbf{r}_i(t)$. The particle velocity is correspondingly

$$\mathbf{v}_i(t) = \frac{\partial \mathbf{r}_i(t)}{\partial t} \quad (4.8)$$

This is in contrast to the *Eulerian picture*, where one considers volume elements at (static) positions $\mathbf{r}_{\text{Eu}}$ instead of moving fluid elements. The fluid velocity $\mathbf{v}_{\text{Eu}}(\mathbf{r}_{\text{Eu}}, t)$ is then attributed to static volume elements. In other terms, $\mathbf{v}_{\text{Eu}}(\mathbf{r}_{\text{Eu}}, t)$ is the instantaneous velocity of the fluid particles that happen to be in the volume element at the static position $\mathbf{r}_{\text{Eu}}$ at time t . Note that the time dependence implies potentially nonsteady flow conditions.

The fluid velocity at a certain position is identical irrespective of whether considered in the Eulerian or in the Lagrangian picture, of course. That is, if the position $\mathbf{r}_i(t)$ of a moving fluid element coincides at a certain time t with the static position $\mathbf{r}_{\text{Eu}}$ of the considered volume element, that is, $\mathbf{r}_i(t) = \mathbf{r}_{\text{Eu}}$, the Eulerian and the Lagrangian velocities will be momentarily identical:

$$\mathbf{v}_{\text{Eu}}(\mathbf{r}_i(t), t) \equiv \mathbf{v}_i(t) \quad (4.9)$$

We will therefore use the unspecified symbol $\mathbf{v} = \mathbf{v}(\mathbf{r}, t)$ throughout for the fluid velocity at a position $\mathbf{r}$ at time t .

However, the instantaneous identity in Eq. (4.9) does not mean that the time derivatives of the velocities are the same! Here, the two representations must clearly be distinguished. In particular, the acceleration of a fluid element, $\mathbf{a}_i = \mathbf{a}_i(\mathbf{r}_i, t)$, obeys

$$\mathbf{a}_i \equiv \frac{d\mathbf{v}_i}{dt} = \frac{\partial \mathbf{v}_{\text{Eu}}}{\partial t} + (\mathbf{v}_{\text{Eu}} \cdot \nabla) \mathbf{v}_{\text{Eu}} \quad (4.10)$$

The Eulerian specification of flow is the standard representation in the literature on fluid dynamics. It is suitable for the presentation of flow velocity fields $\mathbf{v} = \mathbf{v}(\mathbf{r}, t)$, that is, the spatial distribution of the velocity at a given time t (in the case of nonsteady flow). We will therefore use this notation throughout for the description of flow patterns.

4.3 Total, Local, and Convective Acceleration

Employing Eq. (4.9) and using the unspecified velocity symbol $\mathbf{v}$, Eq. (4.10) can be rewritten as³

³The (total) differential operator d/dt refers to derivations by *implicit* as well as by *explicit* time dependences, whereas the partial derivative $\partial/\partial t$ is restricted to *explicit* time dependences only.

$$\frac{d\mathbf{v}}{dt} = \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \quad (4.11)$$

or, in the form of Cartesian components, as

$$\begin{pmatrix} \frac{dv_x}{dt} \\ \frac{dv_y}{dt} \\ \frac{dv_z}{dt} \end{pmatrix} = \begin{pmatrix} \frac{\partial v_x}{\partial t} \\ \frac{\partial v_y}{\partial t} \\ \frac{\partial v_z}{\partial t} \end{pmatrix} + \begin{pmatrix} v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} + v_z \frac{\partial v_x}{\partial z} \\ v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} + v_z \frac{\partial v_y}{\partial z} \\ v_x \frac{\partial v_z}{\partial x} + v_y \frac{\partial v_z}{\partial y} + v_z \frac{\partial v_z}{\partial z} \end{pmatrix} \quad (4.12)$$

Three different acceleration terms are related in this way: The *total* (or *substantial*) acceleration of the fluid element, $\mathbf{a}^{\text{tot}} = d\mathbf{v}/dt$, on the left side is equal to the sum of the *local* acceleration, $\mathbf{a}^{\text{loc}} = \partial \mathbf{v}/\partial t$, and the *convective* acceleration, $\mathbf{a}^{\text{conv}} = (\mathbf{v} \cdot \nabla) \mathbf{v}$. Remarkably, a nabla differential operator ∇ incurs in this relation, that is, *spatial* derivatives.

The local acceleration $\mathbf{a}^{\text{loc}} = \partial \mathbf{v}/\partial t$ is due to any *nonsteady* flow conditions characterized by an *explicit* time dependence of the velocity. This is in contrast to the convective acceleration $\mathbf{a}^{\text{conv}} = (\mathbf{v} \cdot \nabla) \mathbf{v}$ which appears if the velocity of the fluid element depends on the position, that is, if it changes along its trajectory even in case the flow field is *stationary*. In other words, the flow field is *inhomogeneous*. The time dependence of the velocity will then be of an *implicit* nature.

The formal representation and the meaning of the convective acceleration in the form $\mathbf{a}^{\text{conv}} = (\mathbf{v} \cdot \nabla) \mathbf{v}$ can best be conceived when spelling out the scalar product and the derivatives:

$$\mathbf{a}^{\text{conv}} = (\mathbf{v} \cdot \nabla) \mathbf{v} = \begin{pmatrix} v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} + v_z \frac{\partial v_x}{\partial z} \\ v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} + v_z \frac{\partial v_y}{\partial z} \\ v_x \frac{\partial v_z}{\partial x} + v_y \frac{\partial v_z}{\partial y} + v_z \frac{\partial v_z}{\partial z} \end{pmatrix} \quad (4.13)$$

For example, the x component of the convective acceleration thus reads

$$\begin{aligned} a_x^{\text{conv}} &= v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} + v_z \frac{\partial v_x}{\partial z} \\ &= \frac{\partial v_x}{\partial x} \frac{dx}{dt} + \frac{\partial v_x}{\partial y} \frac{dy}{dt} + \frac{\partial v_x}{\partial z} \frac{dz}{dt} \end{aligned} \quad (4.14)$$

In more detail, take the first term on the right-hand side of the second line, $\frac{\partial v_x}{\partial x} \frac{dx}{dt}$. The first factor, $\partial v_x / \partial x$, tells us how strongly the velocity varies if the fluid particle is displaced by ∂x . The second factor, dx/dt , that is, the x component of the flow velocity, specifies how fast this displacement is traversed. The product thus represents the acceleration of the fluid element upon being displaced a stretch ∂x irrespective of any additional nonsteady acceleration. All other terms and components can be interpreted analogously.

As an example, the streamlines through a duct are illustrated in Fig. 4.2. Owing to the continuity equation, displacements along any such trajectory from left to right obviously stipulate an increase of the flow velocity and therefore a nonvanishing convective acceleration $\mathbf{a}^{\text{conv}} = (\mathbf{v} \cdot \nabla)\mathbf{v}$.

4.4 Equations of Motion

4.4.1 Navier/Stokes Equation

The distinction of the substantial, local, and convective accelerations in Eqs. (4.11) and (4.12) is decisive for the equation of motion a mass element $dm = \rho dV$ is subjected to. In the Lagrangian picture, Newton's equation of motion states that the sum of forces acting on dm is equal to the mass times the (substantial) acceleration:

$$\sum_i d\mathbf{F}_i = \frac{d\mathbf{v}}{dt} dm \quad (4.15)$$

Note that we have expressed the acceleration on the right-hand side by the time derivative of the velocity, $d\mathbf{v}/dt$, and not by the second derivative of the position, $d^2\mathbf{r}/dt^2$. The reason is that the equation of motion to be derived in the present context is supposed to represent the *velocity* or *flow field* of the fluid rather than trajectories of individual particles. Note furthermore that Eq. (4.15) and the subsequent formalism are valid for incompressible-fluid conditions, that is, constant density.

The sum on the left side of Eq. (4.15) comprises three differential forces:

$$d\mathbf{F}_p + d\mathbf{F}_g + d\mathbf{F}_\eta = \rho \frac{d\mathbf{v}}{dt} dV \quad (4.16)$$

The first force on the left side, $d\mathbf{F}_p$, is the *pressure force*, the components of which are given as force differences between opposite faces of the considered fluid volume element (see Fig. 4.1). The x component, for example, can be written as

$$dF_{p,x} = -[p(x + dx) - p(x)]dydz = -\frac{\partial p}{\partial x} dx dy dz = -\frac{\partial p}{\partial x} dV \quad (4.17)$$

where the differential operator $\partial/\partial x$ indicates the partial derivation with respect to any *explicit* dependence on the variable x . In vector form, the pressure force thus reads

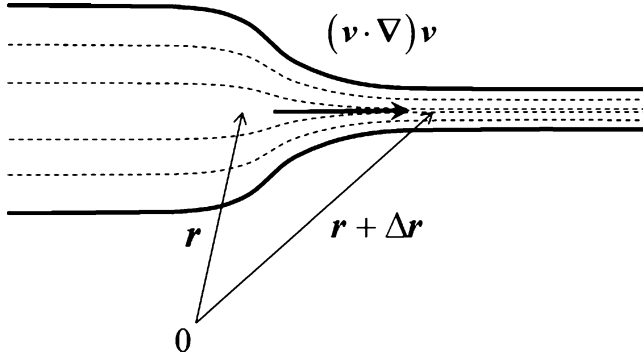


Fig. 4.2 Streamline sketch illustrating inhomogeneous flow through a duct as an example. A fluid particle being displaced from position $\mathbf{r}$ to position $\mathbf{r} + \Delta\mathbf{r}$ will be accelerated even under steady flow conditions. This exemplifies the convective acceleration $\mathbf{a}^{\text{conv}} = (\mathbf{v} \cdot \nabla)\mathbf{v}$. According to the integral form of the continuity equation for incompressible fluids, Eq. (4.7), the flow velocity increases with decreasing cross-sectional area A_{cross} of the duct: $\int_A \mathbf{v} \cdot d\mathbf{A}_{\text{cross}} = \text{const}$

$$d\mathbf{F}_p = - \begin{pmatrix} \partial p / \partial x \\ \partial p / \partial y \\ \partial p / \partial z \end{pmatrix} dV \equiv -(\nabla p) dV \quad (4.18)$$

It acts in a direction opposite to that of the pressure gradient (therefore the minus sign).

The second force term on the left side of Eq. (4.16) is the *gravitation force* given by

$$d\mathbf{F}_g = \mathbf{g} \rho dV \quad (4.19)$$

where $\mathbf{g}$ is the gravity acceleration vector. This is a so-called *body force* acting directly on the fluid element. Other body forces such as electrostatic interactions in electrolyte solutions, for instance, may be relevant depending on the system under consideration. They can analogously be taken into account in an additive way, but will be disregarded for the moment.

The third force contribution refers to *internal friction*. Its analytical form can be derived in the following way: Assume for the moment that the fluid is flowing along the z direction and that a velocity gradient

$$\nabla v_z \equiv \begin{pmatrix} \partial v_z / \partial x \\ 0 \\ 0 \end{pmatrix} \quad (4.20)$$

exists. That is, the components $\partial v_z / \partial y$ and $\partial v_z / \partial z$ are assumed to vanish so that the flow velocity varies only along the x -axis. The difference of the internal friction

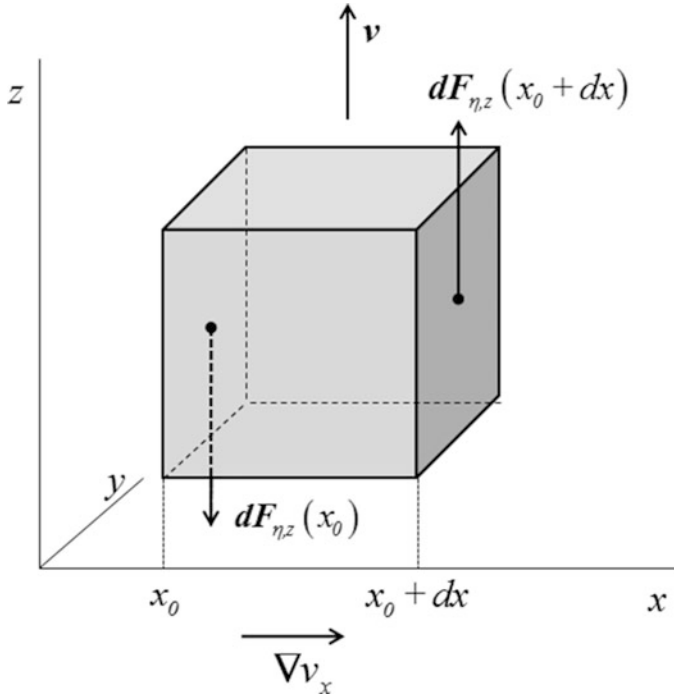


Fig. 4.3 Internal friction force pair at a volume element $dV = dx dy dz$

force pair acting on the faces of the volume element at $x = x_0$ and $x = x_0 + dx$ (see Fig. 4.3) is then

$$\delta F_{\eta,z} = dF_{\eta,z}(x_0 + dx) - dF_{\eta,z}(x_0) \quad (4.21)$$

where we denote the difference of two differentials by the symbol δ . Combining *Newton's friction law*⁴ for flow of a fluid of (dynamic) viscosity η along a surface of area A

$$F_{\eta,z} = \eta A \frac{\partial v_z}{\partial x} \quad (4.22)$$

with Eq. (4.21) leads to

⁴ As already mentioned in Sect. 2.3.4, fluids with a viscosity η independent of the shear rate are called *Newtonian liquids*. This is what we anticipate here and in the following. In contrast to this ordinary viscous behavior, one distinguishes *shear thinning* and *shear thickening* in cases where the viscosity decreases or increases with the shear rate, respectively. Respective examples are blood and granular suspensions. In some relatively exotic systems, the viscosity may also increase or decrease with the duration of the applied stress. One then speaks of *rheoplectic* and *thixotropic* fluids, respectively. Usually, these are extremely viscous materials.

$$\begin{aligned}
\delta F_{\eta,z} &= \eta dx dz \left[\left(\frac{\partial v_z}{\partial x} \right)_{x_0+dx} - \left(\frac{\partial v_z}{\partial x} \right)_{x_0} \right] \\
&= \eta dV \frac{\left(\frac{\partial v_z}{\partial x} \right)_{x_0+dx} - \left(\frac{\partial v_z}{\partial x} \right)_{x_0}}{dx} \\
&= \eta \left(\frac{\partial^2 v_z}{\partial x^2} \right) dV
\end{aligned} \tag{4.23}$$

Extending this result to all three space directions gives

$$dF_{\eta,z} = \eta \nabla^2 v_z dV \tag{4.24}$$

where the Laplacian ∇^2 is defined in Cartesian coordinates by $\nabla^2 \equiv \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$. Moreover, generalizing this to arbitrary flow directions results in

$$d\mathbf{F}_\eta = \eta \left(\begin{array}{ccc} \frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_x}{\partial z^2} \\ \frac{\partial^2 v_y}{\partial x^2} + \frac{\partial^2 v_y}{\partial y^2} + \frac{\partial^2 v_y}{\partial z^2} \\ \frac{\partial^2 v_z}{\partial x^2} + \frac{\partial^2 v_z}{\partial y^2} + \frac{\partial^2 v_z}{\partial z^2} \end{array} \right) dV \equiv \eta \nabla^2 \mathbf{v} dV \tag{4.25}$$

Combining Eqs. (4.11), (4.16), (4.18), (4.19), and (4.25) gives the most fundamental *Navier/Stokes equation* for the force densities acting in a flowing medium:

$$\rho \left[\frac{\partial}{\partial t} + (\mathbf{v} \cdot \nabla) \right] \mathbf{v} = -\nabla p + \rho \mathbf{g} + \eta \nabla^2 \mathbf{v} \tag{4.26}$$

This is the equation of motion for *incompressible* fluids subjected to pressure, gravitation, and internal friction force densities. The solutions primarily refer to the flow velocity field $\mathbf{v} = \mathbf{v}(\mathbf{r}, t)$ at position $\mathbf{r}$ and at time t based on a (possibly time-dependent) pressure gradient.

The boundary conditions at the surfaces confining the fluid, $\mathbf{r} = \mathbf{r}_{\text{surface}}$, are typically assumed to be of the *Dirichlet* type

$$\mathbf{v}(\mathbf{r}_{\text{surface}}) = 0 \tag{4.27}$$

or of the *Neumann* category for the derivatives of the velocity

$$\nabla \mathbf{v}(\mathbf{r}_{\text{surface}}) = 0 \tag{4.28}$$

The former version is also referred to as *non-slipping* boundary condition, whereas the latter represents *impermeable* container walls.

Note that the Navier/Stokes equation refers both to *laminar* and *turbulent* flow depending on whether inertial effects are irrelevant or relevant. The latter means that the time derivative in Eq. (4.26) plays a dominant role.

The convective acceleration can be analyzed on the basis of the *Weber vector relation*

$$(\mathbf{v} \cdot \nabla) \mathbf{v} = (\nabla \times \mathbf{v}) \times \mathbf{v} + \frac{1}{2} \nabla v^2 \quad (4.29)$$

It can readily be verified by evaluating the expressions on the left- and right-hand sides component by component in order to demonstrate the identity of the respective vectors. The second term on the right-hand side of Eq. (4.29) represents changes of the velocity magnitude upon displacement. By contrast, the first term on the right-hand side gives the directional dependence of the velocity and is therefore indicative for flow vortices. If this term vanishes, that is, $\boldsymbol{\zeta}_{\text{rot}} \equiv \nabla \times \mathbf{v} = 0$, one speaks of *irrotational flow*. $\boldsymbol{\zeta}_{\text{rot}}$ is called the *vorticity* of the flow field.

The Navier/Stokes equation is a *nonlinear partial differential* equation. There are square, that is, nonlinear terms of the velocity as demonstrated in Eq. (4.29) for the convective acceleration. This is the reason why the Navier/Stokes equation is mathematically so difficult to solve with the exception of very simple problems. Examples are one-dimensional flow or creeping motion (see Sect. 4.6).

4.4.2 Euler Equation

The Navier/Stokes equation can be simplified for a number of special cases. The most important one is that of *frictionless* fluids, that is, $\eta = 0$. Equation (4.26) reduces then to the *Euler equation* for inviscid flow:

$$\rho \left[\frac{\partial}{\partial t} + (\mathbf{v} \cdot \nabla) \right] \mathbf{v} = -\nabla p + \rho \mathbf{g} \quad (4.30)$$

It refers to incompressible fluids as assumed before. According to the discussion above and as the name suggests, this relation corresponds again to the Eulerian description of flow. In the context of numerical simulations, one also speaks of the *conservation form*. That is, the force densities refer to a control volume fixed in space.

4.4.3 Bernoulli Equation

Beyond the conditions for incompressible fluids and inviscid flow, that is, $\rho = 0$ and $\eta = 0$, the next step of simplification is the assumption that flow is *stationary* and

irrotational. Analytically this is expressed on the one hand by $\partial \mathbf{v} / \partial t = 0$ and by a vanishing vorticity $\nabla \times \mathbf{v} = 0$ on the other (see Eq. 4.29). The result is the well-known *Bernoulli equation*:

$$\frac{1}{2} \rho \nabla v^2 = -\nabla p - \nabla w \quad (4.31)$$

The gravitational force density has been replaced by $\rho \mathbf{g} = -\nabla w$, where w is the density of the potential energy. Equation (4.31) can be reformulated as

$$\frac{1}{2} \rho \nabla v^2 + \nabla p + \nabla w = \nabla \left(\frac{1}{2} \rho v^2 + p + w \right) = 0 \quad (4.32)$$

or

$$\frac{1}{2} \rho v^2 + p + w = \text{const} \quad (4.33)$$

This is the form one often encounters in textbooks.

4.4.4 Laplace Equation

Especially for numerical evaluations, it may be useful to relate flow problems formally with the potential theory as it is known from electromagnetism and gravitation. The condition for *irrotational* flow

$$\nabla \times \mathbf{v} = 0 \quad (4.34)$$

can be used in this sense to formally introduce a *velocity potential* Φ valid for this particular case. Mathematically, the condition Eq. (4.34) is fulfilled if

$$\mathbf{v} = \nabla \Phi \quad (4.35)$$

Inserting this into the continuity equation for *incompressible* fluids, $\nabla \cdot \mathbf{v} = 0$, leads to⁵

$$\nabla \cdot \mathbf{v} = \nabla \cdot \nabla \Phi = \nabla^2 \Phi = 0 \quad (4.36)$$

⁵ In principle, a velocity potential can also be introduced for the description of irrotational flow of compressible fluids. The formalism is however much more complicated [3].

The obvious analogy to the *Laplace equation* for electrostatic or gravitational potentials is however entirely formal: The velocity potential has nothing much to do with energy. Nevertheless, solutions of Laplace's equation known for certain electrostatic or gravitational geometries can conveniently be adopted for problems of irrotational flow of incompressible fluids. Approaches based on Eq. (4.36) are subsumed as *potential flow*.

4.5 Reynolds Number

Reynolds number is a dimensionless flow parameter which has been introduced for two purposes. The first reason has to do with the two principal flow categories, namely, laminar and turbulent flow. Laminar flow is characterized by smooth streamlines. Referring to steady flow conditions as concerns external forces, each fluid element starting at the same position at different times will follow the same trajectory. There is no temporal fluctuation of the flow patterns. This is in contrast to turbulent flow where the flow velocity fluctuates rapidly both in space and time even if the external forces and parameters the fluid is subjected to are stationary.

The most striking phenomenon of turbulent flow is vortices as they manifest themselves in whitewater creeks, for example, in contrast to very slowly and therefore smoothly flowing rivers. The crossover from laminar to turbulent flow arises at certain critical conditions to be specified below. The corresponding parameters are summarized in the Reynolds number (see Eq. 4.41). Flow is laminar at relatively low Reynolds numbers ($<10^3$) for sure. If the Reynolds number exceeds 10^5 , flow becomes turbulent. Between these two limits, geometrical perturbations not taken into account by the Reynolds number determine whether flow is formed in a laminar or turbulent way.

The second motivation for the definition of the Reynolds number is to have a dimensionless criterion for flow similarities. The Navier/Stokes equation, Eq. (4.26), tells us that flow will be influenced by the density ρ , the (dynamic) viscosity η , the average flow speed v_{av} (as a measure of the pressure gradient), and the length scale l of the flow field determined by the boundary conditions. All these quantities are dimensional. The question is then, under what circumstances do we get geometrically *similar* flow patterns for different values of the above parameters. The answer is as follows: Similar streamline patterns and equivalent hydraulic resistances of different flow scenarios can be expected if (1) the geometries of the flow boundaries are scale-preserving (geometrical similarity) and (2) if the Reynolds numbers are the same. This situation is called *hydrodynamic similarity*.

If gravitation does not matter, that is, for horizontal flow, the Navier/Stokes equation reads

$$\rho \left[\frac{\partial}{\partial t} + (\mathbf{v} \cdot \nabla) \right] \mathbf{v} = -\nabla p + \eta \nabla^2 \mathbf{v} \quad (4.37)$$

The boundary conditions of the system confining the flowing fluid can be characterized by a length dimension ℓ . The time unit of transport be τ . On this basis, the dimensionless quantities $t', \mathbf{v}', p'$ and the nondimensional nabla operator ∇'

$$t = t'\tau, \quad \mathbf{v} = \mathbf{v}'\frac{\ell}{\tau}, \quad p = p'\left(\frac{\ell}{\tau}\right)^2 \rho, \quad \nabla = \nabla'\frac{1}{\ell} \quad (4.38)$$

can be introduced. Inserting these definitions into Eq. (4.37) gives

$$\frac{\partial \mathbf{v}'}{\partial t} + (\mathbf{v}' \cdot \nabla') \mathbf{v}' = -\nabla' p' + \frac{1}{R_e} \nabla'^2 \mathbf{v}' \quad (4.39)$$

where the dimensionless quantity

$$R_e = \frac{\rho \ell^2}{\eta \tau} = \frac{\rho \ell u}{\eta} \quad (4.40)$$

is the aforesaid *Reynolds number*. The reference flow velocity is defined by $u = \ell/\tau$.

The Reynolds number can also be understood as the ratio of twice the kinetic energy W_{kin} and the friction work W_η . The kinetic energy refers to a control volume ℓ^3 traveling with a velocity u . The friction work is dissipated during the displacement of that volume element over a distance ℓ . In this interpretation, the Reynolds number reads

$$R_e = \frac{\rho \ell u}{\eta} = \frac{\rho \ell^3 u^2}{\eta \ell^2 u} \approx \frac{2W_{\text{kin}}}{W_\eta} \quad (4.41)$$

where we have made use of Newton's friction law Eq. (4.22). In the following, we will restrict ourselves to laminar transport, that is, $R_e \ll 10^5$. A number of typical flow problems will be discussed on this basis.

4.6 Equation of Creeping Motion

Laminar flow anticipates low Reynolds numbers. Let us now assume extremely low values of the Reynolds number, that is, $R_e \ll 1$. Under such circumstances, the inertial term in Eq. (4.39), that is, the left side, can be neglected. This is a situation analogous to what we were already facing in the context of the overdamped Langevin equation given in Eq. (2.157). The steady version of Eq. (4.39) thus takes the *linearized* form

$$\nabla' p' = \frac{1}{R_e} \nabla'^2 \mathbf{v}' \quad (4.42)$$

or

$$\nabla p = \eta \nabla^2 \mathbf{v} \quad (4.43)$$

after combination with Eqs. (4.38) and (4.41). This formula is known as the *equation of creeping motion*. As an application, steady laminar flow past a sphere will be treated in the next section.

4.7 Stokes' Law

Stokes' law refers to the viscous drag of a fluid laminarly flowing past a sphere at rest or, equivalently, the motion of a sphere in a viscous medium at rest. The quantity to be derived in the following is the friction force acting on the sphere. The equivalence of whether the fluid or the sphere is moving is evident in view of the Galilei relativity of motions. It is merely a matter of the choice of the reference frame. However, since we are interested in stationary flow conditions, we prefer the version where the sphere is at rest, so that the steady version of the Navier/Stokes equation can be employed. Otherwise, the flow velocity field would be not only a function of position but also of time.

The Stokes flow problem illustrated in Fig. 4.4 can be treated on the basis of the equation of creeping motion, Eq. (4.43), and the continuity equation for incompressible fluids, Eq. (4.6). To account for the symmetry of the object, it is favorable to convert these expressions to spherical coordinates.⁶ The spherical coordinates r, ϕ, θ used for the present purpose are defined in Fig. 4.4. The z -axis of the Cartesian reference frame is assumed along the main flow direction. The velocity vector in spherical coordinates is given by

$$\mathbf{v} = v_r \mathbf{u}_r + v_\theta \mathbf{u}_\theta + v_\phi \mathbf{u}_\phi \quad (4.44)$$

where $\mathbf{u}_r, \mathbf{u}_\theta, \mathbf{u}_\phi$ are the respective unit vectors in radial and in the two orthogonal directions tangential to the sphere as defined by the three spherical coordinates. The spherical components of the velocity vector can be expressed by its Cartesian components in the form

⁶Details of the conversion to spherical coordinates can be found in mathematical-physics textbooks such as Ref. [4], for instance.

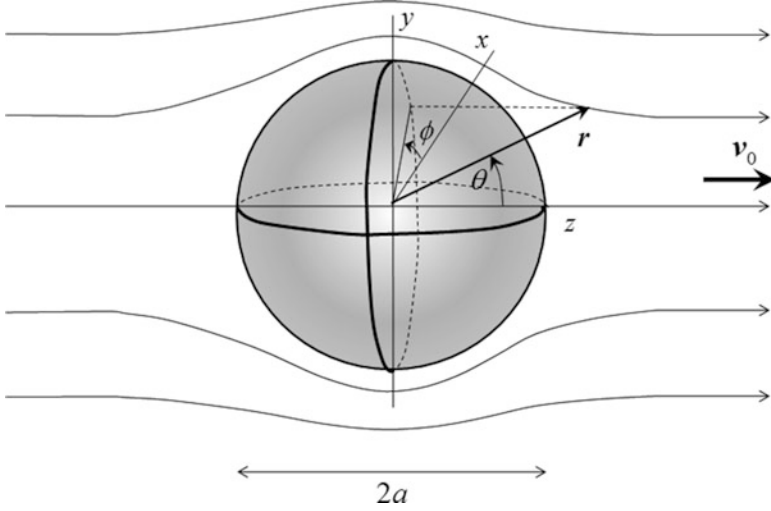


Fig. 4.4 Spherical coordinates r, ϕ, θ used for the description of flow past a sphere

$$\begin{aligned} v_r &= \cos \theta \cos \phi \, v_x + \cos \theta \sin \phi \, v_y + \sin \theta \, v_z \\ v_\theta &= \sin \theta \cos \phi \, v_x + \sin \theta \sin \phi \, v_y - \cos \theta \, v_z \\ v_\phi &= -\sin \phi \, v_x + \cos \phi \, v_y \end{aligned} \quad (4.45)$$

In terms of spherical coordinates (see, e.g., Ref. [4]), the vector operation ∇p reads

$$\nabla p = \frac{\partial p}{\partial r} \mathbf{u}_r + \frac{1}{r} \frac{\partial p}{\partial \theta} \mathbf{u}_\theta + \frac{1}{r \sin \theta} \frac{\partial p}{\partial \phi} \mathbf{u}_\phi \quad (4.46)$$

On the same basis, the three spherical components of the vector $\nabla^2 \mathbf{v}$ can be detailed as

$$\begin{aligned} \nabla^2 \mathbf{v}|_r &= \left(-\frac{2}{r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} + \frac{\cot \theta}{r^2} \frac{\partial}{\partial \theta} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) v_r \\ &\quad + \left(-\frac{2}{r^2} \frac{\partial}{\partial \theta} - \frac{2 \cot \theta}{r^2} \right) v_\theta + \left(-\frac{2}{r^2 \sin \theta} \frac{\partial}{\partial \phi} \right) v_\phi \\ \nabla^2 \mathbf{v}|_\theta &= \frac{2}{r^2} v_r + \left(-\frac{1}{r^2 \sin^2 \theta} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} + \frac{\cot \theta}{r^2} \frac{\partial}{\partial \theta} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) v_\theta \\ &\quad - \frac{2 \cos \theta}{r^2 \sin^2 \theta} \frac{\partial v_\phi}{\partial \phi} \\ \nabla^2 \mathbf{v}|_\phi &= \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \phi} v_r + \frac{2 \cos \theta}{r^2 \sin^2 \theta} \frac{\partial}{\partial \phi} v_\theta \\ &\quad + \left(-\frac{1}{r^2 \sin^2 \theta} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} + \frac{\cot \theta}{r^2} \frac{\partial}{\partial \theta} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) v_\phi \end{aligned} \quad (4.47)$$

In the present case, the azimuthal velocity component vanishes, $v_\phi = 0$, because of the symmetry of the problem (see Fig. 4.4). Likewise, all derivatives $\partial/\partial\phi$ vanish since there is no dependence on the azimuth angle ϕ . Using Eqs. (4.46) and (4.47), the equation of creeping motion, Eq. (4.43), can thus be split in two equations for the spherical velocity components v_r and v_θ :

$$\begin{aligned} \frac{\partial p}{\partial r} = \eta & \left[\left(-\frac{2}{r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} + \frac{\cot \theta}{r^2} \frac{\partial}{\partial \theta} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) v_r \right. \\ & \left. - \left(\frac{2}{r^2} \frac{\partial}{\partial \theta} + \frac{2 \cot \theta}{r^2} \right) v_\theta \right] \\ \frac{1}{r} \frac{\partial p}{\partial \theta} = \eta & \left[\frac{2}{r^2} v_r + \left(-\frac{1}{r^2 \sin^2 \theta} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} + \frac{\cot \theta}{r^2} \frac{\partial}{\partial \theta} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right) v_\theta \right] \end{aligned} \quad (4.48)$$

The third equation needed for the determination of the three unknowns v_r, v_θ, p to be determined as functions of the variables r, θ is the continuity condition for incompressible fluids, that is, $\nabla \cdot \mathbf{v} = 0$. Expressing the nabla operation in spherical coordinates and dropping the term depending on the azimuthal angle ϕ converts this into

$$\frac{1}{r^2} \frac{\partial(r^2 v_r)}{\partial r} + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (v_\theta \sin \theta) = 0 \quad (4.49)$$

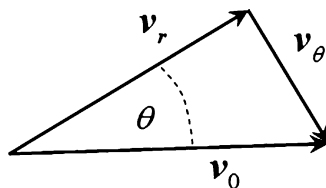
as a further equation of condition.

Moreover, non-slipping boundary conditions are assumed at the surface of the sphere, that is, $v_r(r = a) = 0$ and $v_\theta(r = a) = 0$. In the opposite limit (see Fig. 4.5), at infinite distances, we have $v_r(r \rightarrow \infty) = v_0 \cos \theta$, $v_\theta(r \rightarrow \infty) = -v_0 \sin \theta$, and $p(r \rightarrow \infty) = p_0$, where v_0 is the free-stream velocity and p_0 is the ambient pressure. On this basis, the solutions of the set of the three equations Eqs. (4.48) and (4.49) are⁷

$$\begin{aligned} v_r &= v_0 \left(1 - \frac{3a}{2r} + \frac{a^3}{2r^3} \right) \cos \theta \\ v_\theta &= -v_0 \left(1 - \frac{3a}{4r} - \frac{a^3}{4r^3} \right) \sin \theta \\ v_\phi &= 0 \\ p - p_0 &= -\frac{3}{2} \frac{\eta v_0 a}{r^2} \cos \theta \end{aligned} \quad (4.50)$$

⁷ These results can be cross-checked by inserting them in Eqs. (4.49) and (4.47). However, the expressions to be handled tend to be extremely lengthy. It may therefore be recommendable to employ a computer algebra software package for this endeavor.

Fig. 4.5 Velocity vectors in the limit $r \rightarrow \infty$



for $r \geq a$ and $0 \leq \theta \leq \pi$. a is the radius of the sphere.

The relations given in Eq. (4.50) describe the flow field. This is the basis of the further treatment. The question is now what forces act on the sphere as a consequence of flow. Two different forces need to be distinguished, friction and pressure-induced forces. According to Newton's friction law, Eq. (4.22), the magnitude of the viscous drag force per unit area of the surface is

$$\sigma_\eta = \eta \left(\frac{\partial v_\theta}{\partial r} \right)_{r=a} \quad (4.51)$$

The direction of this local friction force is tangential to the surface of the sphere. Since we have assumed that the sphere is at rest and that the fluid flows around it, the friction force is directed along the flow direction. In the reverse (totally equivalent) case, that is, if the sphere moves in a resting fluid, the force direction would be opposite to the motion of the sphere.

The component of the viscous drag force parallel to the main flow direction, that is, the z -axis in Fig. 4.4, is

$$\sigma_{\eta,z} = \eta \left(\frac{\partial v_\theta}{\partial r} \right)_{r=a} \sin \theta \quad (4.52)$$

Since the sign of the derivative is negative, this force component acts in the negative z direction opposite to the main flow direction. The complementary component perpendicular to the z -axis is not of interest here since it cancels owing to the axial symmetry around this direction.

The second force of interest is due to the pressure acting on the surface of the sphere. Related to unit area, the magnitude of this force is

$$\sigma_p = (p - p_0)_{r=a} \quad (4.53)$$

It acts orthogonally to the surface so that the component along the main flow direction v_0/v_0 is

$$\sigma_{p,z} = (p - p_0)_{r=a} \cos \theta \quad (4.54)$$

The sign of this component is again negative so that it opposes the main stream. The second component acting at right angles is irrelevant for symmetry reasons as before.

Inserting the solutions for the flow field, Eq. (4.50), leads to the total force per unit area of the surface

$$\sigma_z = \sigma_{\eta,z} + \sigma_{p,z} = \frac{3}{2} \frac{\eta v_0}{a} \quad (4.55)$$

This result does obviously not depend on the angle θ . The total force on the sphere by the fluid (or vice versa on the fluid by the sphere) consequently is just the expression in Eq. (4.55) times the surface area $A_{\text{sphere}} = 4\pi a^2$:

$$F_{\text{Stokes}} = \sigma_z A_{\text{sphere}} = 6\pi\eta a v_0 = \zeta v_0 \quad (4.56)$$

This is the famous *Stokes' friction law* for laminar flow past a sphere in the limit of low Reynolds numbers. Empirically, the validity of Eq. (4.56) was verified within the experimental accuracy up to Reynolds numbers $Re \approx 1$ [1, 2]. The quantity $\zeta = 6\pi\eta a$ is termed *friction coefficient*.

In treatments of molecular dynamics, reference to the Stokes relation is frequently made even in problems where it appears to be a bit far-fetched at first sight. An example is friction of small molecules in a bulk fluid of the same species or in solution. In models of polymer chain dynamics, one even employs this law for the description of friction of chain segments. In all these cases, deviations from the spherical shape turn out to be of minor importance. The justification is that the sphere radius a can be replaced by the hydrodynamic radius a_h which is an effective one for nonspherical geometries: It equals the radius of a sphere that would be subject to the same friction force.

4.8 Computational Fluid Dynamics

Analytical solutions of the Navier/Stokes equation for incompressible fluids, Eq. (4.26), are only possible for relatively simple topologies of the systems in which hydrodynamic flow takes place. The nonlinear and partial derivative character prevents exact mathematical solutions. The same applies to other partial differential equations of interest in the present context. Therefore, one is often forced to rely on numerical solutions, the software basis of which is subsumed as *computational fluid dynamics* (CFD) [5].

4.8.1 Governing Equations

For numerical purposes, the Navier/Stokes equation, Eq. (4.26), which is basically a consequence of Newton's second law for a fluid element, is usually expanded to a set including all other equations relevant for fluid dynamics. Apart from the Navier/Stokes equation in the original version, this set of equations includes the continuity equation, Eq. (4.5), and the energy conservation equation. In this context, one therefore speaks of the Navier/Stokes equations in plural form. For the sake of clarity and in order to avoid confusion, we will use the term “*extended set of Navier/Stokes equations*” in the following. This set is usually represented in conservative form referring to the conservation of mass, momentum, and energy [5]. In the following sections, these conservation laws will be considered separately one by one.

4.8.1.1 Conservation of Mass

Conservation of mass in a compressible fluid is reflected by the *continuity equation* for the flow velocity $\mathbf{v} = \mathbf{v}(\mathbf{r})$ already given in Eq. (4.5):

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = \frac{\partial \rho}{\partial t} + \mathbf{v} \cdot \nabla \rho + \rho \nabla \cdot \mathbf{v} = 0 \quad (4.57)$$

where the mass density ρ can be a function of position and time. In the case of incompressible liquids, Eq. (4.57) reduces to $\rho = \text{const}$, that is, $\nabla \cdot \mathbf{v} = 0$.

Equation (4.57) can be generalized to imply transport by molecular *diffusion* in addition to *convection* (as flow is sometimes referred to). This primarily refers to solutes dissolved in a solvent with a nonhomogeneous and nonstationary distribution of the concentration $c(\mathbf{R}, t)$. The equation of continuity for the solute adopts then the extended form

$$\frac{\partial c}{\partial t} + \nabla \cdot (c \mathbf{v}) - \nabla \cdot (D \nabla c) = 0 \quad (4.58)$$

where $D = D(c)$ is the (potentially concentration-dependent) diffusion coefficient of the solute. The convective transport term $\nabla \cdot (c \mathbf{v})$ (corresponding to $\nabla \cdot (\rho \mathbf{v})$ in Eq. 4.57) has been supplemented by the diffusive transport term $-\nabla \cdot (D \nabla c)$ we know already from Fick's second law in the version of Eq. (2.171).

Equation (4.58) is called the *convective-diffusion equation*. It is also applicable to the case of self-diffusion, that is, if there is no chemical-potential gradient for the solute. In this case, the “solute” is considered as a subensemble of the “solvent” molecules marked in a manner insensitive for the chemical potential. Examples for such experiments are the diverse NMR and scattering diffusometry techniques described in Chap. 3. Instead of the concentration $c(\mathbf{R}, t)$, the propagator $P(\mathbf{r}, t)$ is then taken as the relevant variable, and D is now understood as the self-diffusion coefficient (compare the discussion in Sect. 2.5.1.2). The propagator $P(\mathbf{r}, t)$ is the

probability density to find a tagged molecule at position $\mathbf{r}$ at time t while it was at position 0 at time 0. In this terminology, the convective-diffusion equation for self-diffusion reads

$$\frac{\partial P}{\partial t} + \nabla \cdot (P\mathbf{v}) - D\nabla^2 P = 0 \quad (4.59)$$

where the self-diffusion coefficient D is a constant independent of the position. If the fluid is stagnant, that is, $\mathbf{v} = 0$, this relation reduces to the ordinary diffusion equation:

$$\frac{\partial P}{\partial t} - D\nabla^2 P = 0 \quad (4.60)$$

(see Eq. 2.167).

4.8.1.2 Conservation of Momentum

The fundamental background of conservation of momentum is Newton's second law. Reformulated in a form suitable for fluid dynamics, that is, referring to fluid volume elements such as the one depicted in Fig. 4.3, it can be expressed by

$$\frac{\partial(\rho\mathbf{v})}{\partial t} + \nabla \cdot (\rho\mathbf{v}\mathbf{v}) = -\nabla p + \nabla \cdot \boldsymbol{\tau} + \rho\mathbf{f}. \quad (4.61)$$

Relative to a Cartesian frame of reference, this vector relation implies three scalar equations for the three Cartesian components of the vectors. The left side comprises the total momentum variation per unit time and unit volume, and the right-hand side sums all forces per unit volume acting on the fluid.

The first term on the left side, $\partial(\rho\mathbf{v})/\partial t$, is the *nonsteady* momentum variation per unit time and unit volume. The time dependence is *explicit* in this case. The second term, $\nabla \cdot (\rho\mathbf{v}\mathbf{v})$, reflects the momentum variation per unit time and unit volume due to *in- and outflow*, that is, by fluid transport. The expression $\nabla \cdot (\rho\mathbf{v}\mathbf{v})$ is an abbreviation defined by the vector identity:

$$\nabla \cdot (\rho\mathbf{v}\mathbf{v}) \equiv \begin{pmatrix} \nabla \cdot (\rho v_x \mathbf{v}) \\ \nabla \cdot (\rho v_y \mathbf{v}) \\ \nabla \cdot (\rho v_z \mathbf{v}) \end{pmatrix} \quad (4.62)$$

For example, the x component of this vector, that is, the scalar $\nabla \cdot (\rho v_x \mathbf{v})$, is the momentum transfer per unit time and unit volume accompanying the in- and outflow along the x -axis: The expression in parentheses, the vector $\rho v_x \mathbf{v}$, is the

momentum crossing a unit area of the y/z plane per unit time. The divergence of this vector, $\nabla \cdot (\rho v_x \mathbf{v})$, is then the net variation per unit time and unit volume of the x component of the momentum. The other two components of Eq. (4.62) can be interpreted analogously.

The first term on the right-hand side, the vector $-\nabla p$, is the pressure force per unit volume as in the Navier/Stokes equation. The second term, the vector $\nabla \cdot \underline{\underline{\tau}}$, is the deviatoric stress per unit volume. It is calculated as the divergence of the deviatoric stress tensor according to

$$\nabla \cdot \underline{\underline{\tau}} \equiv \begin{pmatrix} \frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{yx}}{\partial y} + \frac{\partial \tau_{zx}}{\partial z} \\ \frac{\partial \tau_{xy}}{\partial x} + \frac{\partial \tau_{yy}}{\partial y} + \frac{\partial \tau_{zy}}{\partial z} \\ \frac{\partial \tau_{xz}}{\partial x} + \frac{\partial \tau_{yz}}{\partial y} + \frac{\partial \tau_{zz}}{\partial z} \end{pmatrix} \quad (4.63)$$

The elements of the deviatoric stress tensor have been specified in Eq. (2.133) for incompressible fluids as⁸

$$\tau_{ik} = \eta \left(\frac{\partial v_i}{\partial k} + \frac{\partial v_k}{\partial i} \right) \quad (4.64)$$

where $i, k = x, y, z$. The off-diagonal elements $i \neq k$ represent *shear* stress, whereas the diagonal elements $i = k$ indicate deviatoric *normal* stress. The dynamic viscosity η is assumed to be constant. That is, the formalism refers to Newtonian fluids.

The last term on the right-hand side of Eq. (4.61), the vector $\rho \mathbf{f}$, is the total body force per *unit volume*, where $\mathbf{f}$ is defined as the resultant of all relevant body force vectors *per unit mass*. Examples of body forces are gravity (see Eq. 4.19) and electromagnetic interactions.

4.8.1.3 Conservation of Energy

The change rate of energy contained in a fluid element equals the power exerted by body and surface forces on the fluid element plus the net heat flux to or from the element. This principle results in

$$\begin{aligned} \frac{\partial}{\partial t} \left[\rho \left(\varepsilon_{\text{int}} + \frac{v^2}{2} \right) \right] + \nabla \cdot \left[\rho \left(\varepsilon_{\text{int}} + \frac{v^2}{2} \right) \mathbf{v} \right] \\ = \rho \dot{q} + \nabla \cdot (\kappa \nabla T) - \nabla \cdot (p \mathbf{v}) + \mathbf{v} \cdot (\nabla \underline{\underline{\tau}}) + \rho \mathbf{f} \cdot \mathbf{v} \end{aligned} \quad (4.65)$$

⁸ In gaseous media where the finite compressibility needs to be taken into account, it may be necessary to add a further diagonal term of the form $\lambda (\nabla \cdot \mathbf{v}) \delta_{ik}$ with λ the *second viscosity coefficient* analogous to the first Lamé constant [1].

On the left-hand side, we distinguish the internal energy per unit mass, ε_{int} , and the kinetic energy per unit mass, $v^2/2$. The internal energy refers on the one hand to chemical and electromagnetic interactions and to random molecular motions, that is, dissipated energy or heat, on the other. By contrast, the kinetic energy characterizes coherent motions of the whole fluid element with the velocity $\mathbf{v}$. Altogether, the left side of Eq. (4.65) represents the total variation of energy in the fluid element per unit time and unit volume.

The right-hand side comprises all contributions *exchanging* energy between the fluid element and its environment (in both directions). The first term refers to heat flux per unit mass to or from the fluid element via *radiation*. The quantity $\dot{q}$ is the heat variation on these grounds per unit time and unit mass. $\rho\dot{q}$ is consequently the radiant heat flux per unit volume. The internal energy of the fluid element will increase for positive $\dot{q}$ and will decrease in the opposite case.

The heat in the fluid element can furthermore vary by heat conduction if a gradient ∇T of the absolute temperature T exists at the fluid element. The material parameter relevant for this process is the thermal conductivity⁹ κ . Heat conduction is taken into account by the second term on the right-hand side which is based on *Fourier's law of heat conduction*. The heat transferred in this way to or from the fluid element per unit time and unit volume across the element surfaces is

$$\nabla \cdot (\kappa \nabla T) \equiv \frac{\partial}{\partial x} \left(\kappa \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(\kappa \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(\kappa \frac{\partial T}{\partial z} \right) \quad (4.66)$$

Analogous to radiant heat flux, the heat content of the fluid element will increase if $\nabla \cdot (\kappa \nabla T)$ is positive and decrease otherwise.

The third term on the right-hand side of Eq. (4.65)

$$-\nabla \cdot (p\mathbf{v}) \equiv -\frac{\partial(v_x p)}{\partial x} - \frac{\partial(v_y p)}{\partial y} - \frac{\partial(v_z p)}{\partial z} \quad (4.67)$$

is the work per unit time and unit volume supplied by the pressure p . That is, this term refers to normal surface forces acting on the fluid element. If the term $-\nabla \cdot (p\mathbf{v})$ is positive, work will be exerted on the fluid element by the adjacent fluid, and the energy of the fluid element will therefore be increased. In the opposite case, it will be the fluid element that renders work to the adjacent fluid.

The next term on the right-hand side of Eq. (4.65)

⁹The *thermal conductivity* κ (SI unit: $\text{W m}^{-1} \text{K}^{-1}$) must be distinguished from the *thermal diffusivity* $\alpha = \kappa/(\rho c_v)$ (SI unit: $\text{m}^2 \text{s}^{-1}$), where ρ is the mass density (SI unit: kg m^{-3}) and c_v is the specific heat at constant volume (SI unit: $\text{J kg}^{-1} \text{K}^{-1}$).

$$\begin{aligned} \mathbf{v} \cdot (\nabla \tilde{\boldsymbol{\tau}}) \equiv & \frac{\partial(v_x \tau_{xx})}{\partial x} + \frac{\partial(v_x \tau_{xy})}{\partial y} + \frac{\partial(v_x \tau_{xz})}{\partial z} + \frac{\partial(v_y \tau_{yx})}{\partial x} \\ & + \frac{\partial(v_y \tau_{yy})}{\partial y} + \frac{\partial(v_y \tau_{yz})}{\partial z} + \frac{\partial(v_z \tau_{zx})}{\partial x} + \frac{\partial(v_z \tau_{zy})}{\partial y} + \frac{\partial(v_z \tau_{zz})}{\partial z} \end{aligned} \quad (4.68)$$

represents the volumetric work rate carried out by deviatoric stresses on the surfaces of the fluid element. The components of the deviatoric stress tensor are given in Eq. (4.64). As before, positive and negative signs indicate work transfer to or from the fluid element, respectively. This work contribution originates from the forces acting on the fluid element due to viscous drag of the adjacent fluid as outlined in Sect. 2.3.4.

The last term on the right-hand side of Eq. (4.65) comprises the work per unit volume and unit time done by body forces $\mathbf{f}$ such as gravity and electromagnetic interactions on the fluid element:

$$\rho \mathbf{f} \cdot \mathbf{v} \equiv \rho (f_x v_x + f_y v_y + f_z v_z) \quad (4.69)$$

4.8.1.4 The Heat Conduction Equation

In the absence of body and surface forces, the kinetic energy density will be constant, $\rho v^2/2 = \text{const.}$ The internal energy per unit mass is given by $\varepsilon_{\text{int}} = c_V T$, where c_V is the specific heat at constant volume. The internal energy per unit volume is consequently $\rho \varepsilon_{\text{int}} = \rho c_V T$. Furthermore, if there is no volumetric heat source or sink, that is, $\dot{q} = 0$, Eq. (4.65) can be cut back to

$$\frac{\partial}{\partial t}(\rho T) + \nabla \cdot (\rho \mathbf{v} T) = \nabla \cdot \left(\frac{\kappa}{c_V} \nabla T \right) \quad (4.70)$$

for the temperature field $T = T(\mathbf{R}, t)$ and the thermal conductivity κ . In the static case, that is, $\mathbf{v} = 0$, and for constant parameters ρ, c_V, κ , this reduces further to the ordinary *heat conduction equation*:

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T \quad (4.71)$$

where the *thermal diffusivity* is defined by $\alpha = \kappa/(\rho c_V)$. Note that Eq. (4.71) is analytically equivalent to the diffusion equation given in Eq. (4.60).

4.8.1.5 Generic Scalar Transport Equation

The conservation equations outlined in the previous sections can be expressed in a combined form with relatively general terms. This turned out to be of particular value for computational fluid dynamics purposes since corresponding software can be kept universal in this sense. In actual applications, merely the variables, parameters, and boundary and initial conditions need then to be specified [6].

Let us consider a dependent variable ϕ in a certain control volume. This variable is to be determined by a partial differential equation of the type we have established above. Accordingly, this variable can represent the density, the mass fraction of a chemical species, the temperature, the velocity component, the electric potential, etc. Analyzing the above conservation equations in terms of ϕ reveals that they are special cases of the following *generic scalar transport equation*:

$$\frac{\partial(\rho\phi)}{\partial t} + \nabla \cdot (\rho\mathbf{v}\phi) = \nabla \cdot (\Gamma\nabla\phi) + S \quad (4.72)$$

The first term on the left side, $\partial(\rho\phi)/\partial t$, is the *transient or unsteady term* accounting for the rate of change of ϕ . The second term is the *convection term* $\nabla \cdot (\rho\mathbf{v}\phi)$ referring to transport of ϕ by coherent flow. On the right-hand side, the first term $\nabla \cdot (\Gamma\nabla\phi)$ represents the dispersion of ϕ on a molecular level by *diffusion*¹⁰ along the gradient of ϕ , that is, $\nabla\phi$. The coefficient Γ characterizes the rate of this process and is specific for ϕ . Finally, the *source term* S is due to any surface and/or body forces acting on the control volume in the sense of sources or sinks of ϕ . That is, the quantity ϕ is either “created” or “annihilated” in the control volume.

Let us now verify the general character of Eq. (4.72) by deducing a number of special conservation equations on this basis: (1) Setting $\phi = 1$ means that the diffusion and source terms vanish, so that the ordinary continuity equation comes out as given in Eq. (4.57). (2) Replacing ϕ by the absolute temperature T reproduces the heat conduction equation in the form of Eq. (4.70), where we anticipate that no heat sources or sinks exist. (3) Conservation of momentum applies selectively to each Cartesian component of the momentum vector. Thus, equating ϕ with the velocity component v_x , for example, leads to

$$\frac{\partial(\rho v_x)}{\partial t} + \nabla \cdot (\rho\mathbf{v}v_x) = \nabla \cdot (\eta\nabla v_x) - \frac{\partial p}{\partial x} + \rho f_x + V_x \quad (4.73)$$

In this case, the source term consists of the last three terms on the right-hand side. The last contribution, V_x , stands for all terms of $(\nabla \cdot \tilde{\boldsymbol{\tau}})_x$ not comprised by $\nabla \cdot (\eta\nabla v_x)$. If the body forces refer to gravity, ρf_x must be replaced by ρg_x , where g_x is the x component of the gravitational acceleration. Eq. (4.73) is thus equivalent to the x component of Eq. (4.61) as well as of the Navier/Stokes equation in its original form given in Eq. (4.26).

¹⁰Turbulent fluctuations would also contribute to this process.

4.8.2 Principles of Numerical CFD Methods

The generic scalar transport equation given in Eq. (4.72) forms an umbrella scheme covering practically all relevant fluid dynamics problems after specifying the dependent variable ϕ , the parameters, and the boundary and initial conditions of the problem. As a partial differential equation, it cannot be solved analytically in most cases. One therefore seeks approximate solutions on a numerical basis. Typical techniques for this purpose are the *finite-element method* (FEM) and the *finite-volume method* (FVM) [5, 6].

Comprehensive and versatile software packages are commercially available for all sorts of applications and are in widespread use (see, e.g., Refs. [7, 8]). This user software is composed according to FEM and FVM principles or variants thereof. To give an idea how CFD methods basically work, let us restrict ourselves to the description of a typical FVM treatment of the generic scalar transport equation given in Eq. (4.72). For more detailed information, the reader is referred to the handbooks of the respective software packages.

Consider the dependent variable $\phi = \phi(\mathbf{R}, t)$ complying to Eq. (4.72) for a certain system with boundary conditions determined by the topology of the confining walls. Starting from a certain initial distribution, one is interested in the temporal and spatial evolution of this quantity. The volume occupied by the fluid is subdivided in a mesh of nonoverlapping but space-filling polyhedral cells acting as control volumes for further considerations. The cells are small enough (but anyway *finite* and not infinitesimally small) so that approximate solutions can be achieved on a local basis. The decisive feature of this approximation is to replace the distributions of the variable in the control volumes by *averages* and to allocate them in the centroids of the cells. The potentially varying sizes and shapes of the cells are adapted to the topology of the system according to boundary-fitting rules implemented in the software packages. Figure 4.6 schematically illustrates a number of space-filling cells.

Let V_i be the volume of the i -th cell which is to be considered in the following as the reference control volume. Forming the average $\langle \dots \rangle_i \equiv V_i^{-1} \int_{\text{cell}\#i} \dots dV$ over this control volume on both sides of Eq. (4.72) leads to the following *discretization approaches* for the individual terms (multiplied by V_i for the simplicity of representation).

4.8.2.1 Transient Term

Averaging and weighting the first term on the left side as described above suggests the approach

$$V_i \left\langle \frac{\partial(\rho\phi)}{\partial t} \right\rangle_i = \int_{\text{cell}\#i} \frac{\partial(\rho\phi)}{\partial t} dV \approx \frac{\bar{\rho}_i(t + \Delta t) \bar{\phi}_i(t + \Delta t) - \bar{\rho}_i(t) \bar{\phi}_i(t)}{\Delta t} V_i \quad (4.74)$$

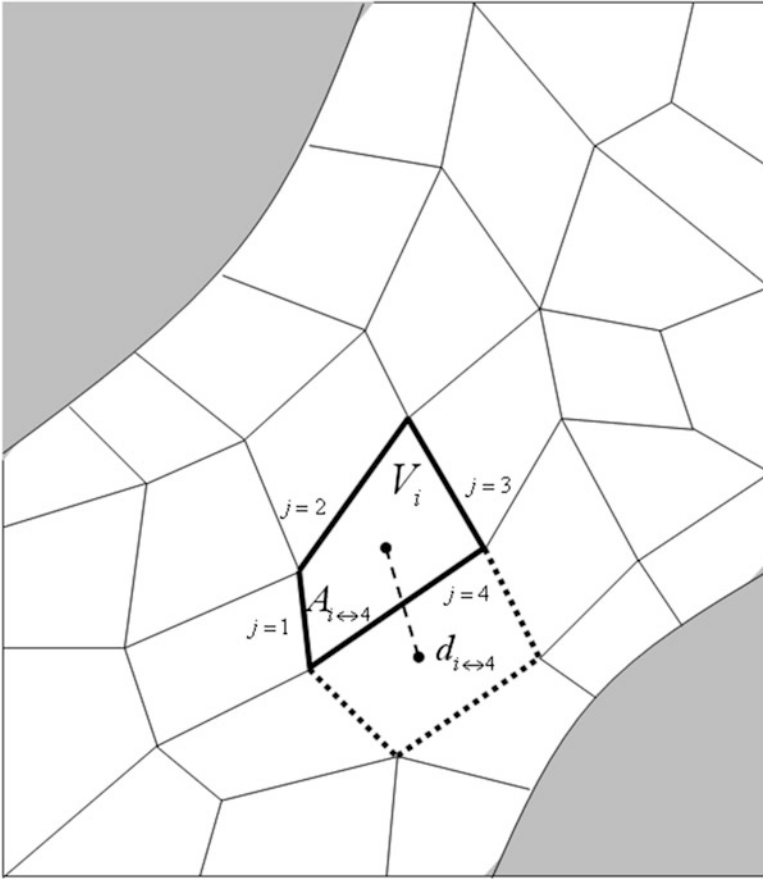


Fig. 4.6 Schematic representation of a mesh of control volumes in a fluid system in a confining matrix represented by *shaded areas*. The *reference cell* of volume V_i is enframed by *solid lines* and tagged by the subscript i . In this simplified representation for only two dimensions, the reference cell is surrounded by four adjacent cells, the interfaces to which are labeled by $j = 1, \dots, 4$. For example, the interface “area” to neighbor cell #4 is termed $A_{i \leftrightarrow 4}$. The centroid-to-centroid distance between the reference cell and neighbor cell #4 is designated by $d_{i \leftrightarrow 4}$.

where the quantities $\bar{\rho}, \bar{\phi}$ represent mean values in cell # i . The distributions of the variables, which are continuous in principle, are thus discretized by their cell averages and allocated to the centroids of the cells.

4.8.2.2 Convection Term

The second term on the left side of Eq. (4.72) can analogously be averaged and multiplied by V_i so that

$$\begin{aligned}
 V_i \langle \nabla \cdot (\rho \mathbf{v} \phi) \rangle_i &= \int_{\text{cell} \# i} \nabla \cdot (\rho \mathbf{v} \phi) dV \\
 &\stackrel{\text{Gauss' theorem}}{=} \int_{\text{cell} \# i} (\rho \mathbf{v} \phi) \cdot d\mathbf{A} \approx \sum_{j=1}^N \left(\rho \bar{\mathbf{v}}_{i \leftrightarrow j} \bar{\phi}_{i \leftrightarrow j} \right) \cdot \mathbf{A}_{i \leftrightarrow j} \quad (4.75)
 \end{aligned}$$

The volume integral is converted to an integral over the surface area of the i -th cell according to Gauss' theorem we have already made use of in Eq. (4.7). The vector $d\mathbf{A}$ is a surface area element aligned along the outward normal. The surface of the control volume V_i is assumed to have a polyhedral shape consisting of N planar interfaces to adjacent cells as illustrated in Fig. 4.6. The surface integral in Eq. (4.75) can therefore be approximated by a sum over the *mean* contributions across these planar faces numbered from $j = 1$ to N . The surface area vector $\mathbf{A}_{i \leftrightarrow j}$ is directed normal to the j -th planar interface of cell $\# i$. The quantity $\rho \bar{\mathbf{v}}_{i \leftrightarrow j} \bar{\phi}_{i \leftrightarrow j}$ is the *average* convective flux across the interface $i \leftrightarrow j$ between cell $\# i$ and the cell adjacent to its j -th interface. This mean value is established on the basis of the weighted average

$$\bar{\phi}_{i \leftrightarrow j} \approx \alpha_{i \leftrightarrow j} \bar{\phi}_i + (1 - \alpha_{i \leftrightarrow j}) \bar{\phi}_j^{(i)} \quad (4.76)$$

between the average values of the variable ϕ in the two adjacent cells separated by interface $i \leftrightarrow j$.

For the sake of clarity, let us specify the notation used in this expression a bit closer: $\bar{\phi}_i$ is the mean value of the variable ϕ averaged over the reference cell which we have tagged by the subscript i . Likewise, $\bar{\phi}_j^{(i)}$ is the mean value of the variable ϕ in the cell neighboring at the interface labeled by the subscript j . Reference cell and adjacent cell are schematically depicted in Fig. 4.6. The weighting factor $\alpha_{i \leftrightarrow j}$ can be chosen on the basis of different ansatz schemes depending on the Péclet number defined further down in Eq. (4.94). In the simplest case, it is just set equal to $\frac{1}{2}$ [5–8].

4.8.2.3 Diffusion Term

This is the first term on the right-hand side of Eq. (4.72). Carrying out the volume average and multiplying it by the volume give

$$\begin{aligned}
 V_i \langle \nabla \cdot (\Gamma \nabla \phi) \rangle_i &= \int_{\text{cell} \# i} \nabla \cdot (\Gamma \nabla \phi) dV \stackrel{\text{Gauss' theorem}}{=} \int_{\text{cell} \# i} (\Gamma \nabla \phi) \cdot d\mathbf{A} \\
 &\approx \sum_{j=1}^N (\Gamma \nabla \phi)_{i \leftrightarrow j} \cdot \mathbf{A}_{i \leftrightarrow j} \quad (4.77)
 \end{aligned}$$

where Gauss' theorem has been employed again. The approximation of the surface integral by a sum is analogous to the approach practiced in Eq. (4.75). The term $(\Gamma \nabla \phi)_{i \leftrightarrow j}$ is the diffusive flux averaged over the j -th planar interface of cell # i , that is, $j = 4$, in the example illustrated in Fig. 4.6.

The gradient $\nabla \phi$ of the variable ϕ can be further approximated by replacing it by a difference quotient. For this purpose, one refers again to the average values of ϕ in the two cells separated by the j -th planar interface. Allocating $\bar{\phi}_i$ and $\bar{\phi}_j^{(i)}$ to the respective centroids of the two cells and designating the distance between these centers by $d_{i \leftrightarrow j}$ lead to

$$V_i \langle \nabla \cdot (\Gamma \nabla \phi) \rangle_i \approx \sum_{j=1}^N \Gamma \frac{\bar{\phi}_i - \bar{\phi}_j^{(i)}}{d_{i \leftrightarrow j}} A_{i \leftrightarrow j} \quad (4.78)$$

The approximation of differential quotients by difference quotients works best for orthogonal meshes. Otherwise, it can be supplemented by correction terms.

4.8.2.4 Source Term

The average source term weighted by the volume V_i can be expanded in linear form

$$V_i \langle S \rangle_i = \int_{\text{cell} \# i} S dV \approx V_i (S_{i,0} + \bar{\phi}_i S_{i,1}) \quad (4.79)$$

with the coefficients $S_{i,0}$ and $S_{i,1}$.

Combining the approximate terms given in Eqs. (4.74), (4.75), (4.76), (4.77), (4.78), and (4.79) on the basis of Eq. (4.72) leads finally to a set of linear equations for the discrete values of the dependent variable ϕ in the centers of the cells as a function of discrete time moments:

$$\begin{aligned} \frac{\bar{\rho}_i(t + \Delta t) \bar{\phi}_i(t + \Delta t) - \bar{\rho}_i(t) \bar{\phi}_i(t)}{\Delta t} V_i + \sum_{j=1}^N \left[\rho \bar{v}_{i \leftrightarrow j} \left(\alpha_{i \leftrightarrow j} \bar{\phi}_i + (1 - \alpha_{i \leftrightarrow j}) \bar{\phi}_j^{(i)} \right) \right] \cdot \mathbf{A}_{i \leftrightarrow j} \\ = \sum_{j=1}^N \Gamma \frac{\bar{\phi}_i - \bar{\phi}_j^{(i)}}{d_{i \leftrightarrow j}} A_{i \leftrightarrow j} + V_i (S_{i,0} + \bar{\phi}_i S_{i,1}) \end{aligned} \quad (4.80)$$

Numerical solutions of this set can then be achieved in a series of iterative approaches.

Equation (4.80) is called the *discretization equation* of the problem. It is obvious that the conservation laws referred to above are satisfied for any control volume.

In particular, the integral balances among cells are exact in the solutions derived on this basis. Nevertheless, it must be emphasized that any such method remains an approximation procedure. All results obtained on this basis must be critically checked for their validity. It is therefore important to make use of experimental protocols permitting the one-to-one comparison of simulated and measured fluid dynamics data. Examples will be delineated in the subsequent section.

4.9 Transport Through Pipes, Pores, and Percolation Clusters: Theory, Simulations, and Experiments

In this section, a number of transport phenomena of entirely different nature will be compared. The problems to be examined refer to liquids in pipes and channel or pore networks. In this context, the term *transport* is considered not only in the sense of flow but also with respect to diffusion, electric current, or heat transport. As the most versatile set of experimental techniques, we will refer mainly to the NMR mapping methods described in Chap. 3.

After some basic considerations, applications to more complicated model objects will be juxtaposed to computational fluid dynamics simulations. Investigations of such systems can be found in Refs. [9–12], for instance. Illustrations of typical objects that can be classified as porous media are shown in Fig. 4.7. Apart from “classical” porous materials such as rock, brick, paper, and tissue, one may think of multichannel networks as they often occur in microsystem technology, for example. As an umbrella term, one may specify the materials and systems of interest here as *lacunar* in analogy to the practice in architecture and neurology.

Transport of fluids through porous rock is of major interest in particular for geology in the context of oil exploration or aquifers, for example. Other natural systems that could be circumscribed as complex channel networks are blood vessels in the body and tracheae in plants and invertebrate animals. Many more applications in chemical engineering and other technical fields can be attributed to this category. Recent developments such as *lab-on-a-chip* devices require detailed knowledge of the transport properties through the ramified network characteristic for such systems. As concerns NMR methods, descriptions of typical flow experiments of this category can be found in Refs. [10–12].

In all cases where analytical solutions of the hydrodynamic equations are not possible, the strategy will be to define artificial model pore or channel topologies for the systems confining the fluids under consideration. In this context, we will generally speak of *pore spaces* regardless of whether this refers to a porous medium in the proper sense or a technical channel or pipe device.

Model structures provide a detailed coordinate basis for the pore space that can be employed for numerical solutions with the aid of computational fluid dynamics. Irrespective of how elucidating such numerical approaches can be, a word of

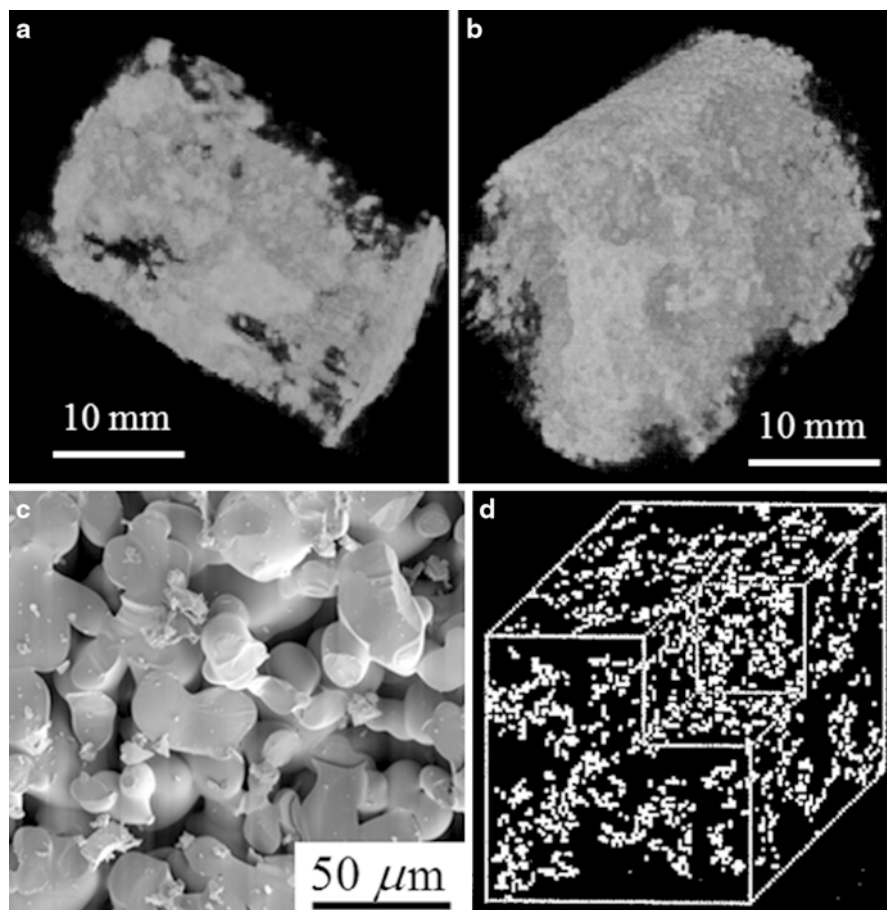


Fig. 4.7 Examples of porous media of interest in the present context. (a) Projected three-dimensional spin-density map of water filling the pore space of pumice (porosity 0.6). The map was acquired with the aid of the pulse sequence shown in Fig. 3.29b. (b) Projected three-dimensional spin-density map of water filling the pore space of natural sponge (porosity 0.8) recorded with the same technique. (c) Scanning electron micrograph of a porous silica glass (nominal pore size 10–16 μm , porosity about 0.25). (d) Computer-generated random-site percolation cluster as a model pore space. The picture shows a multisectonal view of the pore voxels at the surface, where the pore voxels are rendered in *white*. The base lattice size is $80 \times 80 \times 80$ lattice points. The porosity is 0.035 in comparison to the percolation threshold of 0.312 (Reproduced from Ref. [9] with kind permission from © APS 1997)

caution is deemed appropriate here. It may be tempting to put the results of computer simulations on the level of reality. However, any evaluation of this sort can be defective and of restricted accuracy. It is therefore essential to perform random checks by comparative experiments with real setups. For this purpose, model objects fabricated on the very same coordinate basis are ideal test systems. In the following sections, we will encounter a number of examples for this strategy.

4.9.1 Some Parameters Characterizing Porous Media

It may be a bit delicate to compare studies of different random porous materials because of the infinite variety of systems belonging to this class. Before examining features of transport through porous media, let us therefore define a number of parameters which help to specify the properties of pore spaces.

The simplest feature of a porous material is the fraction of free pore volume. The corresponding parameter is the *porosity*, that is, the ratio of the pore-space volume V_{pore} and the total sample volume V_{tot} :

$$\Pi = \frac{V_{\text{pore}}}{V_{\text{tot}}} \quad (4.81)$$

Permeable pore spaces of porous media are often modeled by mathematical constructs such as *percolation clusters* and *fractals*. Features of the artificial pore spaces generated on computers on this basis can also be employed for the comparative characterization of natural porous media. A percolation network [13, 14] is typically established on cubic base *lattices*. The lattice constant λ defines the spatial resolution of the pore topology to be generated. So-called *sites* are assigned to the lattice points. There are different types of directives for the construction of a percolation network. In the simplest case, the sites are occupied at random by voids with the volume of a lattice cell. The algorithm is based on random-number generators as they are available as standard computer software. The occupation probability is denoted by P . For pore spaces of percolation model objects fabricated on the basis of percolation networks, the occupation probability P coincides with the *porosity* Π . Since such model objects will be examined in more detail below, we prefer to speak of porosities in the present context.

Clusters are formed if voids happen to be located next to each other on the lattice so that a permeable network arises. Transport across the total object will be possible in clusters spanning the whole lattice while isolated clusters are irrelevant. Sample-spanning clusters will be designated as *percolation clusters* as such.

One of the most prominent predictions of percolation theory is that percolation clusters can exist only above the so-called percolation threshold Π_c . As a consequence, the porosity range that can be covered with percolation model objects is restricted to $\Pi \geq \Pi_c$ [13]. No transport across the object will be possible below this value. The threshold value Π_c depends on whether the base lattice is two- or three-dimensional, the particular occupation algorithm chosen, and on whether the occupation process is totally random or partly correlated [15]. In the case of *random-site percolation networks*, it is $\Pi_c \approx 0.5962$ in two dimensions and $\Pi_c \approx 0.312$ in the three-dimensional case. Other schemes for the generation of percolation networks, such as so-called *bond*, *swiss cheese*, and *inverse swiss cheese* variants, lead to somewhat different threshold values [13, 14].

The *correlation length* ξ in general characterizes the decay of the spatial density correlation function of the medium filling the pore space (see Eq. 7.4). In percolation

theory [13], the usual (and to some degree equivalent) definition is the mean size of pore space clusters *below* the percolation threshold. *Above* the percolation threshold, the correlation length indicates the length scale on which coarse-grain properties become homogeneous. This parameter also indicates the crossover from anomalous (short-scale) to normal (long-scale) diffusion behavior as discussed below in Sect. 4.9.3.2.

As concerns transport, the *tortuosity* reflects restrictions by the pore space (or percolation cluster) topology. A simple attempt to quantify this feature is the mean ratio

$$\tau = \left\langle \frac{\ell_{i,f}}{r_{i,f}} \right\rangle \quad (4.82)$$

where $r_{i,f} = |\mathbf{R}_f - \mathbf{R}_i| \gg \xi$ is the *Euclidean distance* between two positions $\mathbf{R}_f$ and $\mathbf{R}_i$ in the pore space. The *chemical distance* $\ell_{i,f}$ is the shortest transport path length in between (see Fig. 7.1). In free space, the tortuosity would thus be $\tau = 1$, whereas $\tau \gg 1$ in a random medium of very low porosity. Note that in the context of diffusion studies, an alternative definition is in use, the *diffusive tortuosity*:

$$\tau_{\text{diff}} = \frac{D_0}{D_{\text{eff}}} \quad (4.83)$$

This is the quotient of the diffusion coefficients effective in bulk, D_0 , and under pore space confinement, D_{eff} , in the limit of long diffusion times. Very roughly, Eq. (4.83) is the square of Eq. (4.82).

In a homogeneous medium of density $\rho = \text{const}$, the mass in a sphere of radius r scales as $m \propto r^{d_E}$, where $d_E = 3$ is the Euclidean dimension. This is in contrast to *fractal* or *fractal-like* media. In this case, the scaling law is

$$m \propto r^{d_f} \quad (4.84)$$

where $d_f < d_E$ is the *fractal dimension*. That is, the density probed in a spherical volume $V = \frac{4\pi}{3}r^3$ depends on the radius according to

$$\rho(r) = \frac{m}{V} \propto r^{d_f - d_E} \quad (4.85)$$

The average density in the probe volume *decays* for $d_E = 3$ with a negative exponent $(d_f - 3) < 0$ with increasing radius. The larger the probe volume, the larger are the empty holes in the fractal structure. With respect to porous media, the mass and the density refer to – notabene – the fluid with which the pore space is thought to be filled, whereas the matrix is not considered. The fractal dimension of random pore spaces thus characterizes their topologies.

Of course, one cannot expect that the power law in Eq. (4.85) applies to any arbitrary pore space and any size of the probe volume. As the crucial feature of

fractals, the randomness anticipated in this definition implies *self-similarity* of the pore space in a certain range. Self-similarity is predicted in the so-called *scaling window* $\lambda < r < \xi$, where ξ is the correlation length of the pore space and λ is the minimum pore diameter in general or the lattice constant of the base lattice in the case of percolation clusters in particular. Real systems often do not strictly comply with the self-similarity condition. The fractal concept may nevertheless be useful for approximate characterizations of sufficiently random and ramified pore spaces.

In the limit $r \gg \xi$, the volume-averaged pore space density approaches the constant value $\langle \rho \rangle$ independent of the probe volume radius r . It is related to the porosity, Eq. (4.81), by

$$\langle \rho \rangle = \rho_{\text{fluid}} \Pi \quad (4.86)$$

where ρ_{fluid} is the density of the fluid thought to be filling the pore space.

4.9.2 Laminar Flow

4.9.2.1 Flow Through a Pipe of Circular Cross Section

A simple scenario for transport by laminar flow is fluid transport in a pipe due to a steady pressure gradient. The pipe is assumed to be long enough to neglect any end effects. The cross section can be circular with a radius a_p . We are interested in the flow velocity profile across the pipe, $\mathbf{v} = \mathbf{v}(r)$, where r is the radial coordinate measured from the symmetry axis of the pipe as illustrated in Fig. 4.8. The problem can readily be treated on the basis of the Navier/Stokes equation, Eq. (4.26), by anticipating that there is no explicit time dependence and that gravitational forces do not matter. The former condition means stationarity, that is, $\partial \cdot \cdot \cdot / \partial t = 0$, the latter horizontal flow. For symmetry reasons, flow will be axial with constant velocity components along the streamlines. Radial components are zero. The convective acceleration consequently vanishes as well, that is, $(\mathbf{v} \cdot \nabla) \mathbf{v} = 0$. Under these circumstances, the Navier/Stokes equation is reduced to¹¹

$$\nabla p = \eta \nabla^2 \mathbf{v} \quad (4.87)$$

The nabla operators in this relation are best expressed in cylindrical polar coordinates r, ϕ, z as defined in Fig. 4.8. The somewhat lengthy expressions for the nabla operator in these coordinates can be found in Refs. [1, 4], for example. Owing to the symmetry of the problem, both pressure and flow velocity depend only on a single coordinate each. The pressure is a function of the distance along

¹¹ Equation (4.87) coincides with the equation of creeping motion, Eq. (4.43).

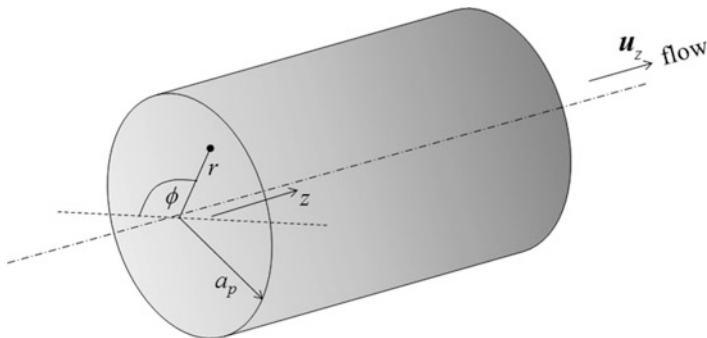


Fig. 4.8 Definition of cylindrical polar coordinates r, ϕ, z for the description of laminar flow through a pipe of circular cross section. The z -axis coincides with the axial symmetry axis

the pipe axis, whereas the flow velocity varies with the radial distance r from the pipe axis. As concerns pressure, all derivatives by ∂r and $\partial \phi$ vanish therefore. The remaining expression on the left side of Eq. (4.87) is $\nabla p = \mathbf{u}_z \partial p / \partial z$, where $\mathbf{u}_z$ is the unit vector along the flow direction. Likewise, all derivatives of the longitudinal velocity component v_z by ∂z and $\partial \phi$ disappear, and the radial and swirl velocity components v_r, v_ϕ are zero by definition. The Laplace operator term on the right-hand side of Eq. (4.87) thus becomes $\nabla^2 \mathbf{v} = \mathbf{u}_z \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v_z}{\partial r} \right)$, and the equation to be solved is reduced to

$$\frac{\partial p}{\partial z} = \eta \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v_z}{\partial r} \right) \quad (4.88)$$

Mathematically, the solution is

$$v_z = \frac{r^2}{4\eta} \frac{\partial p}{\partial z} + c_1 \ln \frac{r}{a_p} + c_2 \quad (4.89)$$

where c_1 and c_2 are constants to be determined with the aid of the boundary conditions. Physics requires that there is no singularity for $r = 0$. A necessary condition is therefore $c_1 = 0$. In the non-slipping case, one furthermore expects $v_z(r = a_p) = 0$ at the walls of the pipe, so that $c_2 = -\frac{a_p^2}{4\eta} \frac{\partial p}{\partial z}$. The velocity profile across the pipe thus takes the form

$$v_z(r) = -\frac{1}{4\eta} \frac{\partial p}{\partial z} (a_p^2 - r^2) \quad (4.90)$$

which is known as the *Hagen/Poiseuille velocity distribution*. The minus sign before the pressure gradient indicates a direction of flow opposite to that of the derivative.

The maximum of the velocity distribution arises at $r = 0$:

$$v_{z,\max} = -\frac{a_p^2}{4\eta} \frac{\partial p}{\partial z} \quad (4.91)$$

The mass flux, that is, the mass transported per unit time through the pipe, is

$$J = \int_0^{a_p} \rho v_z 2\pi r dr = \frac{\pi \rho a_p^4}{8\eta} \left| \frac{\partial p}{\partial z} \right| \quad (4.92)$$

where ρ is the mass density of the fluid. This version of Hagen/Poiseuille's law predicts a mass flux proportional to a_p^4 for laminar flow through a pipe of radius a_p . Reducing the pipe diameter by a factor of two, for instance, means a reduction of the mass flux by a factor of eight (if the pressure gradient is kept constant)! It is obvious how important this result is for fluid transport not only in technical applications. A demonstrative example often referred to is flow in blood vessels weakened by arterioscleroticly reduced diameters (although blood is a non-Newtonian fluid to which the above formalism strictly speaking does not exactly apply). In Fig. 4.9, the velocity profile predicted by Eq. (4.90) is compared with data recorded in a test experiment.

4.9.2.2 Flow Through Porous Media and Complex Channel Systems

In the light of the extremely wide variety and complexity of pore spaces for which microscopic transport features are of interest, it appears to be reasonable to define an artificial paradigm for microporous systems. This grants the option to design model pore spaces on a computer and to fabricate objects suitable for real experiments on this basis [9]. Microscopic transport laws can then be examined and compared under well-defined conditions. The ultimate objective of such investigations will be to relate *structural* parameters of the pore space with *dynamic* parameters of the transport processes. In the following, the model pore space to be taken as a paradigm will be deduced from numerically generated random-site percolation clusters.

The advantages of this investigative strategy are obvious: The pore space is of sufficient complexity to mimic the tortuous topology of typical natural or technical pore networks. Since the model objects are based on computer-generated clusters, the pore spaces are defined in the form of coordinate data sets. These data can directly be fed into finite-element or finite-volume computational fluid dynamics (CFD) programs in order to simulate transport properties [16]. On the other hand, the percolation cluster can be used as a template for the production of real model objects using milling or lithographic techniques (for the latter, see Refs. [17, 18], for instance). Spatial resolutions of the fabrication process as low as 50 μm have

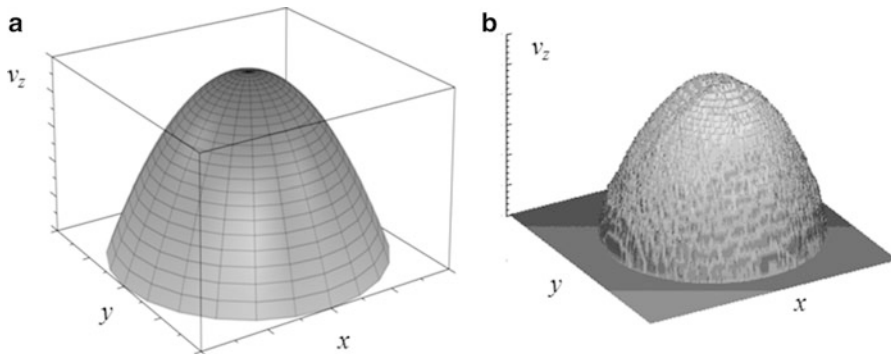


Fig. 4.9 Paraboloidal Hagen/Poiseuille velocity profiles in a tube with circular cross section. The data are plotted in arbitrary units. (a) Profile calculated on the basis of Eq. (4.90). (b) Experimental velocity data recorded with the aid of an NMR pulse sequence composed of the combined sequels shown in Fig. 3.29a, c. The diameter of the tube was 32 mm. The fluid was water flowing with a rate of 1 ml/s

been demonstrated in Ref. [17]. More recently, computer-controlled high-resolution 3D-printing (or prototyping) techniques have become available for setting up three-dimensional plastic objects. This is an alternative technique for the fabrication of porous model objects.

Figure 4.10 shows a typical model object fabricated using a two-dimensional random-site percolation cluster as template. Covering the grooves from above with a plate, filling the object with water, and applying a pressure gradient across the object as indicated in the figure lead to flow percolating through this quasi-two-dimensional channel network. The attribute “quasi-two-dimensional” indicates that practically no flow components perpendicular to the cluster plane exist.

Taking simulations and experiments together, this procedure permits one to test the validity of macroscopic transport theories on microscopic length scales, the reliability of experimental techniques, and, vice versa, the appropriateness of the CFD treatment. This strategy is demonstrated in Fig. 4.11 for water flowing through the percolation model object shown in Fig. 4.10. The maps Fig. 4.11a and b visualize the distributions of the magnitudes of the flow velocity, $v = \sqrt{v_x^2 + v_y^2}$, and of the acceleration, $a = \sqrt{a_x^2 + a_y^2}$, respectively. The data have been recorded with the NMR mapping techniques described in Sects. 3.3.3 and 3.3.4.

Before rendering these maps, all pixels with a velocity or an acceleration below the respective noise level, $v \leq v_n$ or $a \leq a_n$, were blackened. In this way, stagnant zones within the cluster can be identified, whereas pixels with brighter shades indicate finite velocities or accelerations.

The areas where flow acceleration is finite are obviously localized spots in contrast to the more continuous flow patterns visible in the velocity map. That is, acceleration maps specifically reveal the distribution of flow bottlenecks, changes of the flow resistance, and curved pathways of flow. They are therefore indicative for the restrictive topology elements of the pore space.

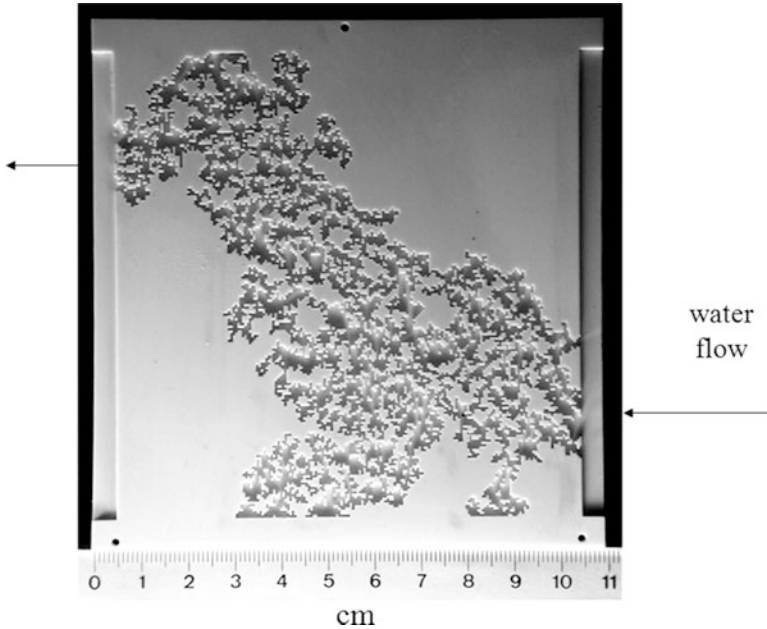


Fig. 4.10 Photograph of a quasi-two-dimensional model object for flow studies in porous media. “Quasi-two-dimensional” means that the pore space extension in the third space direction is negligible relative to those in the plane where the flow field to be examined evolves. The pore space was milled into a plastic plate using a random-site percolation cluster as template [16]. The numerically generated cluster is based on a square base lattice of 200×200 sites. The porosity is $\Pi = 0.6$ somewhat above the percolation threshold $\Pi_c \approx 0.5962$. The fractal dimension is $d_f = 1.9$, and the correlation length is $\xi = 1.95 \sim \text{mm}$. For flow studies, the pore space was filled with a liquid subjected to a pressure gradient (Reproduced from Ref. [19] with kind permission of © Elsevier 2002)

Based on the Navier/Stokes equation for incompressible fluids and steady flow,

$$\rho(\mathbf{v} \cdot \nabla)\mathbf{v} = -\nabla p + \rho\mathbf{g} + \eta\nabla^2\mathbf{v} \quad (4.93)$$

the flow field features in a pressure gradient ∇p can be evaluated also numerically for the non-slipping boundary conditions, $\mathbf{v}_{\text{wall}} = 0$, given by the topology of the pore space walls. The values for the density ρ and the viscosity η can be adapted to the fluid examined in the experiments. Results of such simulations are rendered in Fig. 4.11c, d in almost perfect accordance with the experimental data. In this way, the accuracies of the simulation method, of the fabrication procedure of the model objects, and of the NMR mapping technique are proven to be reliable and free of artifacts at the same time.

The flow maps in Fig. 4.11 refer to a (quasi) two-dimensional pore space. Therefore, only two velocity components and two acceleration components needed to be recorded in the experiments. Each of these can be examined with the aid of

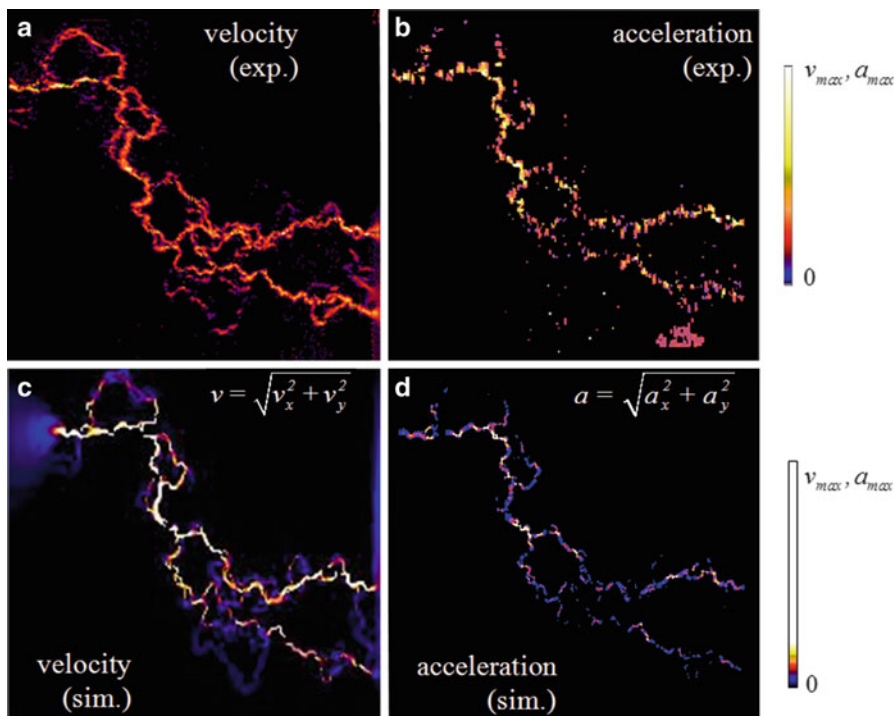


Fig. 4.11 Maps of water flowing through the percolation model object shown in Fig. 4.10. (a) *Experimental* map of the velocity magnitude. The NMR pulse sequence in use was a combination of the sequels shown in Fig. 3.29a, c. (b) *Experimental* map of the acceleration magnitude. The NMR pulse sequence was composed of the sequels shown in Fig. 3.29a, d. (c) Map of the velocity magnitude *simulated* with the aid of the finite-volume method. The boundary conditions are taken from the percolation cluster used for the fabrication of the model object. (d) Map of the acceleration magnitude *simulated* under the same conditions (Reproduced from Ref. [20] with kind permission of © Elsevier 2004)

three-dimensional NMR pulse sequences, where two dimensions refer to the spatial coordinates and one dimension is reserved for one of the two velocity or acceleration components. The respective pulse combination employed for the acquisition of the velocity and acceleration components is specified in Fig. 3.29a, c on the one hand and in Fig. 3.29a, d on the other.

The extension to three-dimensional objects in the sense that finite flow components exist in all three space directions is readily possible but requires often excessively time-consuming measurements. In this case, three four-dimensional data sets need to be acquired: Each velocity or acceleration component must be allocated to the three space coordinates.

An example where this option was exploited is represented by Fig. 4.12. The structure of the pore space of the model object used in that study is deduced from a so-called *inverse swiss cheese* percolation cluster [21]. The cluster was generated

by placing spherical voids at random with a certain probability in a semicontinuous matrix irrespective of any overlap. The cluster pore space consists then of the entity of the (partially overlapping) voids. “Semicontinuous” means that the void positions coincide with grid points of a square or cubic base lattice, whereas the voids are allowed to continuously overlap each other.

For the generation of the maps in Fig. 4.12, both spin-density and flow velocity maps have been recorded after filling the model object with water and exerting a pressure gradient. Suppressing all voxels of the three-dimensional velocity map corresponding to flow velocities below the noise level provides the so-called backbone of the percolation cluster represented by Fig. 4.12b. It is of interest since this is the structure on which transport by flow occurs effectively. As a quantitative parameter, complex pore space structures can be characterized by their *fractal dimensions* defined in the context of Eq. (4.85). Values for the example shown in Fig. 4.12 are given in the legend.

4.9.3 Hydrodynamic Dispersion in Porous Media

4.9.3.1 Classification by Limits of the Péclet Number

In the most general sense, hydrodynamic dispersion represents the combined action of coherent and incoherent displacements. This refers on the one hand to straight laminar shear flow as the paradigm of coherent transport. Coherent transport can be produced by pressure gradients applied to the sample or by exploiting the electro-osmotic effect [22]. On the other hand, molecular self-diffusion, turbulent flow, and tortuous streamlines in porous media tend to randomize the particle trajectories. As a consequence, the propagator will contain features both of self-diffusion and of coherent transport. The influence of the two phenomena relative to each other is weighted by the *Péclet number*,

$$P_e = \frac{\bar{v}\ell}{D}, \quad (4.94)$$

where ℓ is the length dimension on which the two transport processes are to be compared, $\bar{v}$ is the mean flow velocity on this length scale, and D is the self-diffusion coefficient. For example, in the case of hydrodynamic dispersion in a capillary [23], the length scale ℓ is identical to the radius of the capillary. In random porous media, the tortuosity of flow streamlines (see Eq. 4.82), the basis of the so-called *mechanical dispersion* [24], comes into play in addition to self-diffusion. Under such conditions, the characteristic length scale ℓ is defined in the macroscopic sense by the correlation length ξ . More detailed discussions of the Péclet number concept can be found in textbooks like Refs. [24, 25].

Based on the Péclet number, hydrodynamic dispersion can be classified into a number of different limits [24]. For $P_e \ll 1$, the so-called *diffusion regime*, all

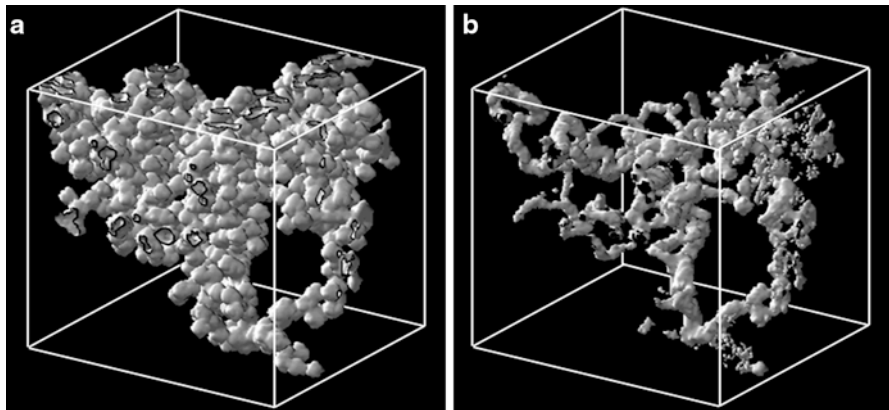


Fig. 4.12 Three-dimensional spin-density maps of water filled into a three-dimensional percolation model object. The object was fabricated on the basis of a sample-spanning percolation cluster generated on a computer using the inverse Swiss cheese variant of percolation networks. The object size is $3.2\text{cm} \times 3.2\text{cm} \times 3.2\text{cm}$. The size of the cubic lattice on which the cluster was generated is $64 \times 64 \times 64$ sites. The average porosity of the model object is $\Pi = 0.087$. (a) Spin-density map of the complete percolation cluster. The data were recorded with the NMR pulse scheme shown in Fig. 3.29b. The fractal dimension is $d_f = 2.29$ (evaluated from the spin-density map) or $d_f = 2.292$ (determined from the simulated cluster). (b) Percolation backbone derived with the aid of a three-dimensional flow velocity map recorded in the same object after application of a pressure gradient. The NMR pulse sequences employed for this purpose were composed of the schemes in Fig. 3.29b, c. After determining the spatial distribution of the magnitude of the velocity, $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$, voxels with velocities below the noise level $v < 0.85 \text{ mm/s}$ were attributed to stagnant water and therefore blackened. The remaining voxels form the backbone with a fractal dimension $d_f^{\text{bb}} = 1.98$. In this experiment, the maximum velocity was 16.65 mm/s , while the total flow rate was $59.3 \text{ mm}^3/\text{s}$ (Reproduced from Ref. [16] with kind permission of © APS 2001)

transport is dominated by molecular self-diffusion. In the regime $1 \ll P_e \ll 10^2$, laminar flow and molecular self-diffusion compete with each other with comparable contributions to the particle displacements. A special phenomenon relevant in this limit is the *Taylor/Aris dispersion* which refers to self-diffusion in a medium subject to shear flow [26, 27]. In Sect. 7.5.7, we will get back to this sort of scenario in the context of surface-related phenomena. Finally, in the limit $P_e \gg 10^2$, transport is dominated by displacements due to flow. As long as turbulence does not yet matter and flow is still laminar following tortuous streamlines through porous media, this regime is referred to as *mechanical dispersion* as already mentioned above.

4.9.3.2 Classification by Limits of the Root Mean Square Displacement

In Sect. 3.2.3, an NMR technique permitting the distinction of coherent and incoherent transport mechanisms has been described. The spin-echo experiments usually employed for the detection of transport phenomena are modified in such a way that coherent-displacement effects are compensated for. The spin echo to be recorded is then exclusively attenuated by incoherent processes. Analogous to the ordinary diffusion coefficient, a dispersion coefficient D_{disp} can be defined for the characterization of incoherent displacements including those due to hydrodynamic dispersion. It obeys the generalized law:

$$\langle r^2 \rangle = 6D_{\text{disp}}(t)t \quad (4.95)$$

Figure 3.28 shows typical RF and field-gradient pulse sequences suitable for the examination of Eq. (4.95) and measurements of D_{disp} . A number of investigations of this sort have been reported in Refs. [23, 28–30], for example.

With tortuous flow through randomly structured porous media, that is, mechanical dispersion, the question whether the velocity of a particle remains constant depends on the displacements probed in experiments and on the mean pore dimension b . For root mean square displacements obeying $\sqrt{\langle r^2 \rangle} < b$, laminar flow velocities tend to be constant so that the only incoherent displacement contribution can arise from Brownian diffusion and – in the presence of shear-flow fields – from Taylor/Aris dispersion. If the influence of the latter is minor, the dispersion coefficient approaches the ordinary Brownian diffusion coefficient:

$$D_{\text{disp}} \approx D_{\text{Brown}} = \text{const} \quad (4.96)$$

Root mean square displacements in the range $b < \sqrt{\langle r^2 \rangle} < \xi$ are connected with more or less random velocity changes. This is the *scaling window* for anomalous displacement behavior where a time-dependent dispersion coefficient is expected for large Péclet numbers, $P_e \gg 1$:

$$D_{\text{disp}} = D_{\text{disp}}(t) \propto t^f \quad (4.97)$$

The dispersion coefficient is then larger than the Brownian self-diffusion coefficient, $D_{\text{Brown}} < D_{\text{disp}}$. The range of the exponent f is between 0 and 1. The power-law character of Eq. (4.97) is a consequence of the randomness of the pore space anticipated here [31, 32]. According to the classification given in Sect. 2.5.2, this expression corresponds to a *superdiffusive* displacement law. That is, the mean square displacement of fluid particles obeys $\langle r^2 \rangle \propto t^\kappa$ where the exponent is *larger* than one: $\kappa = 1 + f > 1$.

Superdiffusive behavior is specific for the limit $P_e \gg 1$. In the opposite case, $P_e \ll 1$, that is, in the regime governed by diffusion, mean square displacements in the scaling window rather follow a *subdiffusive* law $\langle r^2 \rangle \propto t^\kappa$ with an exponent

smaller than one: $\kappa = 1 - f < 1$ [32]. Thus, gradually superimposing flow to Brownian diffusion actually leads to a crossover from sub- to superdiffusive displacement laws. Corresponding results have been reported in detail in Refs. [22, 29] for flow induced by pressure gradients as well as via electroosmosis.

Finally, beyond the scaling window, that is, for root mean square displacements in the limit $\sqrt{\langle r^2 \rangle} \gg \xi$, we have a superposition of a constant drift velocity and ramified displacements due to the tortuous topology of the pore space. As in the case of very short displacements, the dispersion coefficient will then adopt a stationary and *effective* value:

$$D_{\text{eff}} = \text{const} \gg D_{\text{Brown}} \quad (4.98)$$

4.9.3.3 Convective-Diffusion Equation

The two transport mechanisms contributing to hydrodynamic dispersion, namely, flow and molecular diffusion, can commonly be described by the *convective-diffusion equation* already explained in Eq. (4.59):

$$\frac{\partial P(\mathbf{r}, t)}{\partial t} + \nabla \cdot [P(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t)] - D \nabla^2 P(\mathbf{r}, t) = 0 \quad (4.99)$$

where D is the (spatially and temporally constant) self-diffusion coefficient and $\mathbf{v}$ is the flow velocity. The propagator $P(\mathbf{r}, t)$ depending on the displacement $\mathbf{r} = \mathbf{R} - \mathbf{R}_0$ and time t refers to an ensemble of particles or molecules in the fluid thought to be “tagged” and defined by the assumption that all of them start at the same initial position $\mathbf{R} = \mathbf{R}_0$ at time $t = 0$. The standard initial condition is therefore $P(\mathbf{r}, 0) \propto \delta(\mathbf{r})$. The boundary conditions are given by the structure of the pore space walls. An application will be described in Sect. 7.5.7.2.

4.9.3.4 Manifestation of Hydrodynamic Dispersion in Simulations

In the literature, numerous experimental studies of hydrodynamic dispersion can be found (see, e.g., Refs. [22, 23, 29]). Its nature becomes particularly evident in simulations as reported in Refs. [15, 33], for example. In any case, the crucial parameter determining how hydrodynamic dispersion manifests itself is the Péclet number Eq. (4.94). The crossover from diffusion-controlled to entirely flow-controlled displacements of fluid particles, that is, from very low to very high Péclet numbers, is illustrated in Fig. 4.13a by a series of typical trajectories. As a model pore space, a two-dimensional percolation cluster has been employed.¹²

¹² Actually, the pore space assumed here corresponds to an Ising-correlated percolation cluster with a porosity of 0.5672 which is above the percolation threshold. According to Ref. [15], the percolation threshold of this sort of network is somewhat lower than in ordinary random-site percolation clusters.

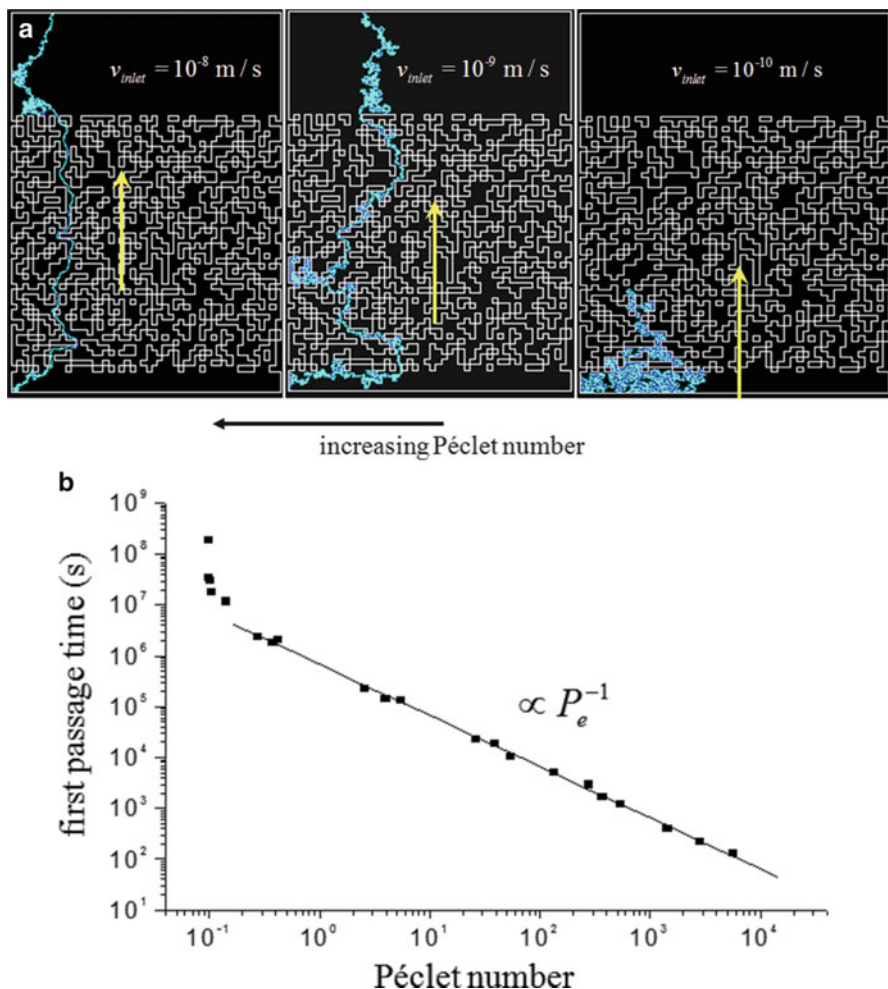


Fig. 4.13 Numerical simulations for the illustration and characterization of hydrodynamic dispersion in a porous medium for different Péclet numbers (realized by different inlet velocities v_{inlet} into the pore space). (a) Typical trajectories of a neutral tracer particle in a liquid percolating through a two-dimensional Ising-correlated site percolation cluster for Péclet numbers 0.09, 1.17, and 40.35 (right to left). The vertical arrows indicate the main flow direction. At the lowest Péclet number, Brownian diffusion is prevailing in contrast to the highest value. (b) First-passage time across the cluster as a function of the Péclet number (Reproduced from Ref. [15] with kind permission of © IOP 2005)

The figures show the numerically simulated trajectories of a tracer particle in a medium flowing through the cluster. Differences in the flow velocities obviously stipulate large changes in the tortuous trajectories. For low Péclet numbers, that is, relatively low flow velocities, the trajectory is diffusion controlled as shown in

Fig. 4.13a, right-hand graph. This is in contrast to the other extreme when flow-controlled displacements dominate as visualized in Fig. 4.13a, left graph [15].

The characteristics of transport can be quantified by evaluating the mean traveling time of a neutral tracer across the percolation cluster. In Fig. 4.13b, the mean first-passage travel time τ_t is plotted versus the Péclet number. Two regimes can be identified, namely, *isotropic dispersion* for the diffusion regime $P_e \ll 1$ and *mechanical dispersion* for $P_e \gg 1$. In the latter case, the data can be represented by a power law:

$$\tau_t \propto (P_e)^{-\chi} \quad (4.100)$$

in a range of about $10^0 < P_e < 10^4$. The exponent turned out to be $\chi \approx 1$. Evidently, it is coherent flow that determines transport under such conditions.

4.9.4 Heat Conduction and Thermal Convection

In the experiments and simulations described so far, hydrodynamic flow was induced by pressure gradients. Let us now turn to another driving force of coherent flow, namely, *thermal convection* in temperature gradients. This phenomenon is the result of the competitive action of the bulk forces arising due to buoyancy and gravity. The classical experiment for the demonstration of thermal convection is the situation established above the *Rayleigh/Bénard instability*.

4.9.4.1 The Rayleigh/Bénard Transition in Bulk Fluids

Figure 4.14a shows a cross section of a fluid-filled cell as it can be used for studies of thermal convection. This arrangement is referred to as *Rayleigh/Bénard configuration*. A temperature gradient from the top to the bottom is produced by cooling and heating compartments as indicated in the figure.

The instability at which pure heat conduction (in the absence of flow) suddenly turns into thermal convection is called the *Rayleigh/Bénard transition*. The cross-over from heat conduction to thermal convection takes place at a certain critical value of the so-called *Rayleigh number* R_a which essentially reflects the downward temperature gradient. This dimensionless quantity was introduced for the quantitative characterization of the convection tendency. It depends on various parameters as specified in the definition equation:

$$R_a = -\frac{g\rho\alpha_{\text{exp}}d^4}{\eta\alpha} \frac{\partial T}{\partial z} \quad (4.101)$$

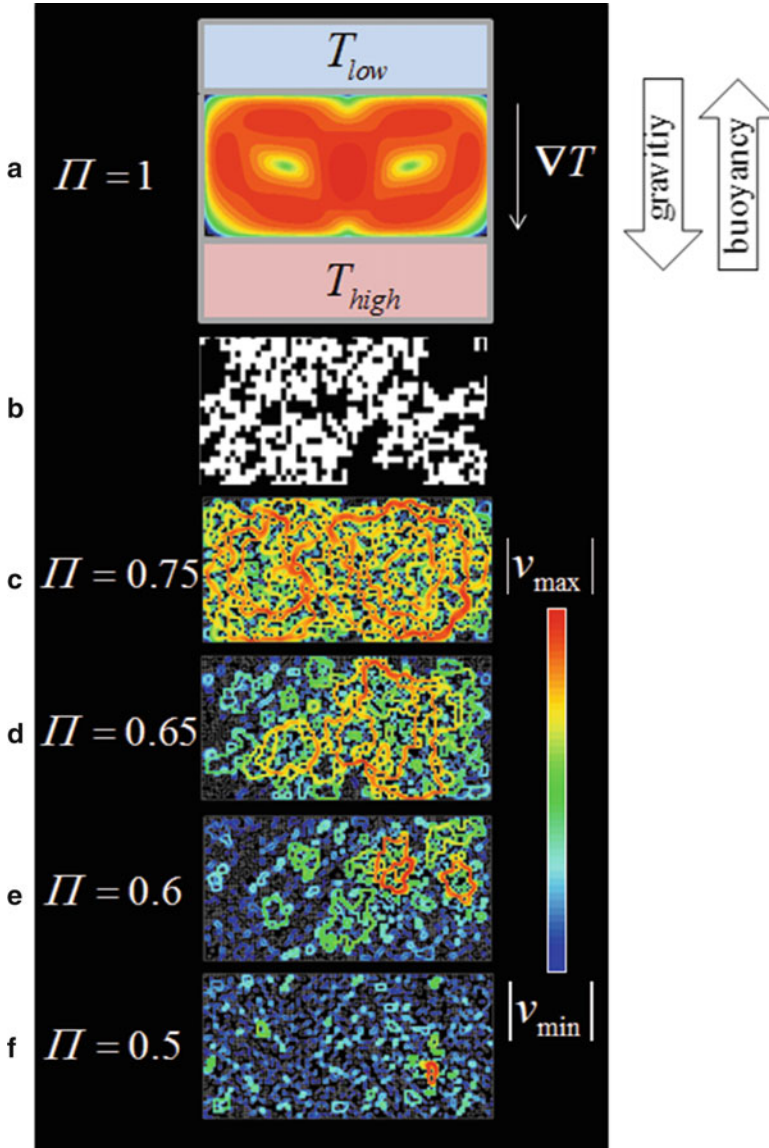


Fig. 4.14 Thermal convection in a cell in Rayleigh/Bénard configuration. **(a)** Schematic cross section of the cell. The cell is thought to be filled with a fluid in contact with a heating compartment at the *bottom* and a cooling device at the *top*. The typical convection rolls arising above the Rayleigh/Bénard transition in a free medium are exemplified by a numerical simulation of a velocity contour plot. **(b)** Two-dimensional random-site percolation cluster as a model for simulations of thermal convection restricted to the pore space (*rendered in white*). **(c)–(f)** Simulated velocity contour plots for porosities varying from $\Pi = 0.75$ (above the percolation threshold) to $\Pi = 0.5$ (below the threshold). All flow velocity maps were simulated with the aid of the finite-volume method [34] (Reproduced from Ref. [35] with kind permission of © APS 2002)

Apart from the temperature gradient $\partial T/\partial z$, the Rayleigh number depends on the following parameters: g , gravity acceleration; ρ , mass density; α_{exp} , thermal expansion coefficient of the fluid; d , vertical width of the fluid layer; η , (dynamic) viscosity of the fluid; α , thermal diffusivity. Note that the temperature gradient $\partial T/\partial z$, or more precisely the z component of the vectorial temperature gradient ∇T , is *negative* for a z direction pointing upward. This explains the minus sign in Eq. (4.101).

In experiments, the Rayleigh number can be varied continuously by adjusting the temperature gradient correspondingly. The Rayleigh/Bénard instability arises at the critical value $R_a^{\text{crit}} \approx 1,708$ [1, 36]. Above this value, the buoyancy of the hot, that is, low-density fluid, overwhelms the effect of gravity so that heat conduction becomes surpassed by coherent flow in the form of rolls as illustrated in Fig. 4.14a. Below this transition, heat transport occurs exclusively via heat conduction.

The sharp crossover at the Rayleigh/Bénard instability is demonstrated by the simulation shown in Fig. 4.15. These data are based on the finite-volume method (FVM). The results are rendered as maps of the spatial distribution of the convective flow velocity. The abrupt appearance of thermal convection at R_a^{crit} is quantified by the maximum magnitude of the flow velocity in the system as a function of the Rayleigh number (which is taken as a measure of the magnitude of the temperature gradient in this case).

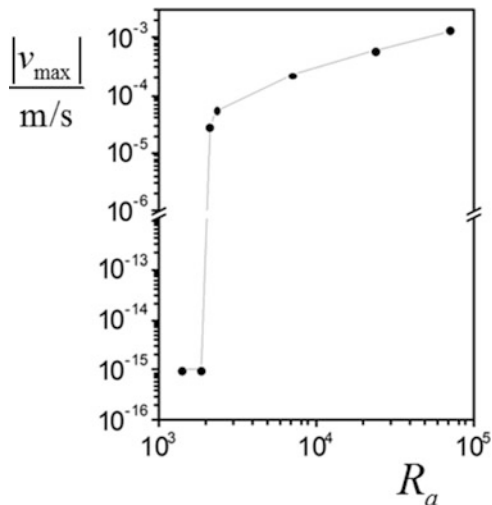
In the absence of flow obstacles, one expects symmetric convection rolls such as those depicted in Fig. 4.14a. These convection loops will be more or less strongly distorted if the pore space topology is more complex. Figure 4.14b shows a random-site percolation cluster as a model pore space restricting thermal convection. As a consequence, the extension of the convection loops is more and more reduced with decreasing porosity. In the series Fig. 4.14c–f, a number of corresponding simulations are demonstrated. In the following sections, thermal convection phenomena restricted in this way will be examined in more detail on a numerical as well as experimental basis.

4.9.4.2 Theoretical Background

Let us reconsider the theoretical framework needed for the treatment of heat conduction and convective flow in the special situation of a Rayleigh/Bénard cell. The problem will be to calculate the spatial distributions of the temperature and of the convective flow velocity. For theoretical considerations, the lateral width of the convection cell is often assumed to be “infinite” in order to be able to neglect side-wall effects. The Rayleigh/Bénard cell may contain a bulk fluid as assumed in the illustration Fig. 4.14a or a fluid-filled porous medium permitting only restricted convection rolls as visualized in the plots Fig. 4.14c–f.

Numerical simulations of thermal convection in fluids in bulk and confined in pore spaces are best performed with the aid of the FVM technique assuming the *Boussinesq approximation*. In this approach, all hydrodynamic parameters are kept

Fig. 4.15 FVM simulations of the Rayleigh/Bénard transition in a bulk fluid in a convection cell. The instability reveals itself by an abrupt increase of the maximum velocity $v_{\max}$ when the critical Rayleigh number is reached from *below*. The two lower data points correspond to the numerical accuracy achievable in the simulations (Reproduced from Ref. [35] with kind permission of © APS 2002)



fixed. Temperature-dependent density variations can be neglected in all terms of the Navier/Stokes relation, Eq. (4.26), other than the gravitational body force term. This implies that the continuity equation for incompressible fluids, $\nabla \cdot \mathbf{v} = 0$, is anticipated. It is furthermore assumed that the density varies *linearly* as a function of the absolute temperature T :

$$\rho = \rho_0 [1 - \alpha_{\text{exp}}(T - T_0)] \quad (4.102)$$

ρ_0 and T_0 are the fluid density and the temperature at the top cover, that is, at the cold surface, of the Rayleigh/Bénard cell, respectively (see Fig. 4.14a). The parameter α_{exp} is the thermal expansion coefficient of the fluid. The gravitational body force term can thus be replaced by $\rho_0 [1 - \alpha_{\text{exp}}(T - T_0)] \mathbf{g}$.

With these modifications, the Navier/Stokes relation, Eq. (4.26), can be approximated by the so-called *dynamic Boussinesq equation* [1, 36]:

$$\rho_0 \left[\frac{\partial}{\partial t} + (\mathbf{v} \cdot \nabla) \right] \mathbf{v} \approx -\nabla p + \eta \nabla^2 \mathbf{v} + \rho_0 [1 - \alpha_{\text{exp}}(T - T_0)] \mathbf{g} \quad (4.103)$$

$\mathbf{v} = \mathbf{v}(\mathbf{R})$ and $T = T(\mathbf{R})$ are functions of the location $\mathbf{R}$ in the cell. The time derivative vanishes in steady cases, of course. The fluid is assumed to comply with non-slipping boundary conditions at the confining walls so that the velocity vanishes at all surfaces: $\mathbf{v}_{\text{wall}} = 0$. The temperature boundary conditions at the top and bottom of the cell can be assumed to be isothermic with the heat reservoirs as illustrated in Fig. 4.14a. The side-wall conditions can be set adiabatic.

Within porous media, the solid matrix and the fluid in the pore space must be considered to be thermodynamically coupled according to the respective heat

conductivities (which can be extremely different). Eq. (4.103) is supplemented by the general heat conduction equation, Eq. (4.70):

$$\frac{\partial}{\partial t}(\rho T) + \nabla \cdot (\rho \mathbf{v} T) = \nabla \cdot \left(\frac{\kappa}{c_V} \nabla T \right) \quad (4.104)$$

The time derivative vanishes under steady-state conditions. Since $T = T(\mathbf{R})$ is a function of the position, the fluid density will vary with $\mathbf{R}$ as well according to Eq. (4.102): $\rho = \rho(\mathbf{R})$. The thermal conductivity κ and the specific heat at constant volume c_V can be taken as constant in each of the materials involved, that is, the fluid on the one hand and the matrix of the porous medium on the other:

$$\kappa = \begin{cases} \kappa_{\text{fluid}} & \text{for } \mathbf{R} \text{ in the pore space} \\ \kappa_{\text{matrix}} & \text{for } \mathbf{R} \text{ in the matrix} \end{cases} \quad (4.105)$$

and

$$c_V = \begin{cases} c_{V,\text{fluid}} & \text{for } \mathbf{R} \text{ in the pore space} \\ c_{V,\text{matrix}} & \text{for } \mathbf{R} \text{ in the matrix} \end{cases} \quad (4.106)$$

4.9.4.3 Experimental Convective Flow Velocity and Temperature Mapping

Like the flow fields examined so far, thermal convection is a further example where the NMR velocity mapping techniques described in Sect. 3.3.3 can favorably be employed. In the following, we will therefore refer again to the combined NMR pulse traces depicted in Fig. 3.29a–c. With the noninvasive character of these methods and a typical resolution of ≈ 0.01 mm/s for the record of flow velocities, such experiments permit the acquisition of all thermal-convection details of interest. This has been demonstrated in Ref. [37], for example, where three-dimensional convection rolls in a Rayleigh/Bénard have been visualized with the aid of three-dimensional flow velocity mapping. Let us now focus on the more complicated flow patterns to be expected for thermal convection in porous media [38].

In order to facilitate the comparison of experiments with computer simulations, we will refer again to model pore spaces formed by two-dimensional random-site percolation clusters like the example shown in Fig. 4.14b. The strategy is to use quasi-two-dimensional objects fabricated on this basis, to fill them with a suitable liquid, to expose this object to temperature gradients in a Rayleigh/Bénard cell, and to apply NMR velocity mapping techniques.

The first question to be dealt with in this context is as follows: What spatial distribution of the temperature gradient is effective under such circumstances? Unlike studies of bulk fluids, the gradient can no longer be anticipated to be spatially constant. The first experimental step must therefore be mapping of the

nonuniform temperature distribution expected in porous media. Although there is no direct encoding method like that for the flow velocity, temperature distributions can *indirectly* be mapped with the aid of temperature-dependent NMR parameters. Relaxation times, for example, tend to vary strongly with the temperature so that they can conveniently be calibrated in this respect [35, 39].

A typical temperature map acquired in this way is shown Fig. 4.16 at the top. It is based on measurements of the spin–lattice relaxation time T_1 in ethylene glycol as a liquid with a particularly pronounced sensitivity to temperature variations. The measurements have been carried out at a Larmor frequency of 200 MHz and in a temperature range between 293 and 353 K. Under such circumstances, T_1 of this particular liquid *increases* steeply with *increasing* temperature.

Varying the repetition time t_R of the transients of ordinary NMR imaging sequences (see Fig. 3.29a or b) from $t_R \ll T_1(\mathbf{R})$ to $t_R \gg T_1(\mathbf{R})$ reveals the crossover from more or less strong saturation of the local magnetization to fully relaxed magnetizations in analogy to the progressive saturation pulse sequence described in Sect. 3.1.4.3. In this way, the local spin–lattice relaxation time $T_1(\mathbf{R})$ can be mapped and then analyzed in terms of the local temperature. The local spin-echo amplitude $A(t_R, \mathbf{R})$ recorded in such experiments as a function of the repetition time t_R is attenuated by a factor:

$$A(t_R, \mathbf{R}) \sim 1 - c \exp\left\{-\frac{t_R}{T_1(\mathbf{R})}\right\} \quad (4.107)$$

where $c \approx 1$ is a numerical constant accounting for the modifications of the progressive saturation technique stipulated by the imaging sequence (compare Eq. 3.34).

Referring to protons in ethylene glycol at a magnetic field of 4.7 T in a temperature range $190 \text{ K} < T < 360 \text{ K}$, the calibration relation linking the absolute temperature T with the spin–lattice relaxation time T_1 is reported in Ref. [35] as

$$T(T_1) = 36.7 \ln\left(\frac{T_1}{0.18 \text{ ms}}\right) \text{ K} \pm 2 \text{ K} \quad (4.108)$$

On this basis, relaxation time maps $T_1 = T_1(\mathbf{R})$ can be converted to temperature maps $T = T(\mathbf{R})$. The results can be rendered in encoded form by gray shades or colors as depicted in the example in Fig. 4.16.

The top row shows experimental (left) and simulated (right) temperature maps in two-dimensional or quasi-two-dimensional random-site percolation clusters under steady-state conditions. The convectioal rolls arising in this temperature field are visualized by contour maps of the flow velocity components or magnitude. There are two reasons why the symmetry of thermal-convection rolls is distorted in nonuniform pore spaces. Perturbing factors are on the one hand topological constraints in the pore space and the nonuniform temperature gradient on the other. This is demonstrated by the maps of the vertical and horizontal velocity

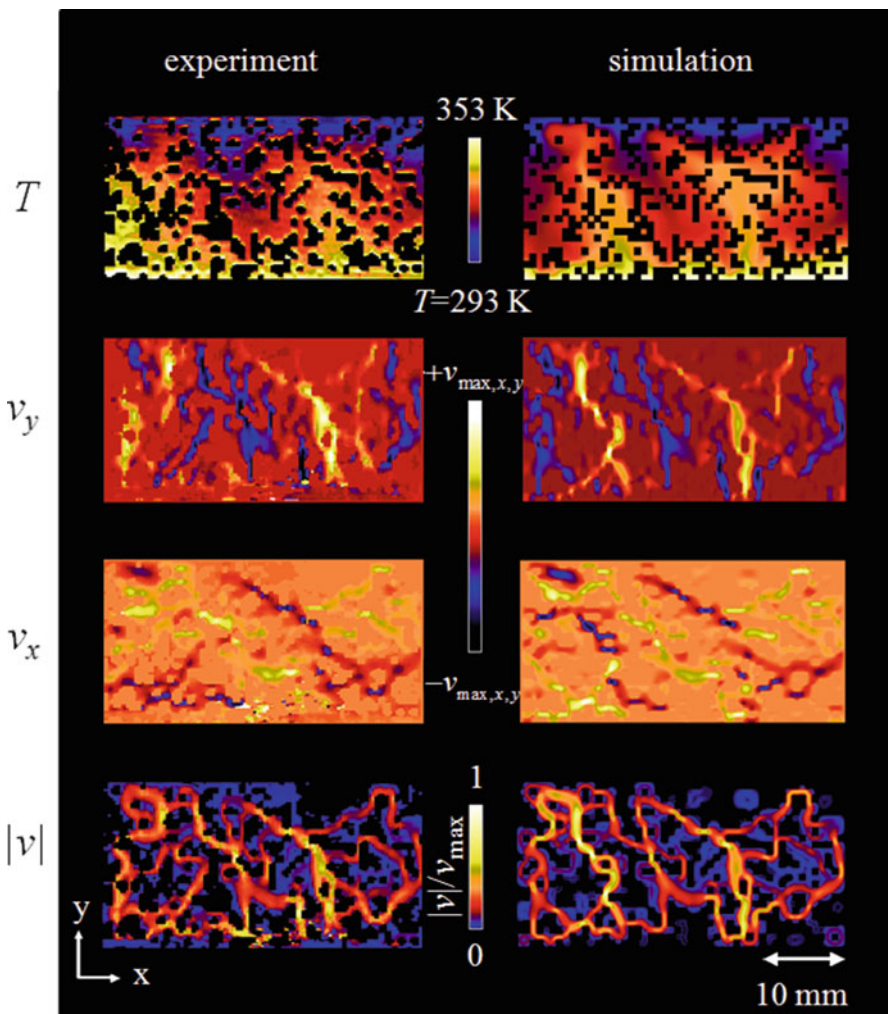


Fig. 4.16 Maps of the temperature and of the convective flow velocity in a (quasi) two-dimensional Rayleigh/Bénard cell of section $6 \times 4 \text{ cm}^2$. As model object for porous media, a random-site percolation cluster of porosity 0.7 such as the one shown in Fig. 4.14b has been investigated. The *left column* refers to NMR experiments, whereas the *right-hand side* represents data simulated with the finite-volume method under the same conditions. The maps in the first row show the temperature distribution $T(\mathbf{R})$ superimposed to the structure of the percolation cluster. The experiments have been carried out with an object filled with ethylene glycol (for the acquisition of temperature maps) or with silicon oil (for the record of velocity maps). The temperature of the *top* compartment of the Rayleigh/Bénard cell was 293 K and that of the *bottom* compartment 353 K. The experimental temperature map $T(\mathbf{R})$ was evaluated from a map of the spin-lattice relaxation time $T_1(\mathbf{R})$ at 200 MHz proton resonance frequency. The other experimental data refer to convective flow velocity components v_x , v_y , and the velocity magnitude $|\mathbf{v}| = \sqrt{v_x^2 + v_y^2}$ acquired with the aid of the combined pulse sequences Fig. 3.29b, c (Reproduced from Ref. [35] with kind permission of © APS 2002)

component and of the velocity magnitude evaluated from the component data. Such maps are shown in the second to fourth row of Fig. 4.16. As before, experimental and simulated maps closely match each other. This can be taken as a mutual validation of the reliability of the experimental and numerical procedures [34, 35].

Note that the third dimension perpendicular to the flow plane of real model objects was not taken into account in the simulations shown in the right-hand column of Fig. 4.16. Fortunately, it turned out that the neglect of friction at the bounding surfaces between which quasi-two-dimensional objects are sandwiched merely leads to simulated flow velocities globally increased by a factor of about four relative to the experimental data [34, 35]. More importantly, the good coincidence of the flow patterns found in both cases ratifies this inaccuracy.

The simulated and measured flow patterns revealed by the maps in Figs. 4.14 and 4.16 suggest that a certain interrelation of the loop size and the porosity of the percolation network exists. On the one hand, we have the Rayleigh/Bénard instability defined in Sect. 4.9.4.1. On the other hand, there is the percolation transition mentioned in Sect. 4.9.1. These are certainly two different categories of critical phenomena. The question nevertheless remains whether there is any interference. This will be examined in the following section.

4.9.4.4 The Rayleigh/Bénard Percolation Transition

The *Rayleigh/Bénard percolation transition* [34, 35] is a new phenomenon arising when the conditions of the *geometrical* phase transition at the percolation threshold [13] and of the *dynamic* Rayleigh/Bénard instability [1] coincide. It is expected to occur generally in random pore networks but can be demonstrated best with percolation clusters.

The percolation transition is characterized by the attribute *geometrical* since it manifests itself by the crossover from finite, that is, isolated, to sample-spanning (in principle “infinite”) percolation clusters. The critical porosities specified above refer to open systems where the fluid to be transported enters at one side and leaves the system at the other. The situation is different in systems that are closed like the cell illustrated in Fig. 4.14a. In this case, transport can only occur in cyclic form along loops instead of inflow at one side and outflow at another side.

If the fluid is furthermore restricted to the pore space of a percolation network, the number of possible loop pathways will strongly be reduced. In place of sample-spanning clusters, the critical porosities modified for such scenarios therefore refer to the minimum cluster size required for the particular loop under consideration. This is illustrated in the series of decreasing convection loops visualized in the simulated flow velocity maps in Fig. 4.14c–f.

The second point to which one should pay attention in this context is that the local temperature gradient will no longer be distributed uniformly in the system and will not necessarily be oriented in negative z direction as anticipated in the definition of the Rayleigh number Eq. (4.101). Inhomogeneous temperature distributions such as the one represented by Fig. 4.16 at the top even stipulate finite *horizontal* components of

the temperature gradient ∇T . That is, irrespective of the Rayleigh number, *uncritical* convection occurs whenever a closed-loop pathway of the porous matrix permits continuous flow. The critical onset of convection rolls induced by vertical-temperature gradients is then superimposed to convective flow due to horizontal temperature gradients.

The convective flow crossover at the Rayleigh/Bénard instability modified for porous media is demonstrated by the plot in Fig. 4.17. Thermal convection is quantified by the maximum velocity in the flow field as practiced already in Fig. 4.15. The plot shows maximum-velocity data for different temperature differences across the total system (top to bottom) as a function of the porosity of the percolation network. The Rayleigh/Bénard-like transitions observed under such conditions reveal themselves by more or less sharp steps of the flow velocity at certain porosities $\Pi = \Pi_{\text{RB}}$ specific for the different temperature gradients.

Convection loops are restricted to the extension of the percolation clusters as demonstrated in Fig. 4.14c–f. The dimension of the permitted loops, d_{eff} , corresponds to the distance d in Eq. (4.101) for the Rayleigh number. In analogy to Eq. (4.101), one can therefore define an effective Rayleigh number:

$$R_a^{\text{eff}} = -\frac{g\rho\alpha_{\text{exp}}d_{\text{eff}}^A}{\eta\alpha}\left\langle\frac{\partial T}{\partial z}\right\rangle \quad (4.109)$$

where $\langle\partial T/\partial z\rangle \propto \Delta T$ is the mean z component of the temperature gradient and ΔT is the overall temperature difference between the top and the bottom of the convection cell. Rayleigh/Bénard transitions of the fluid localized in percolation clusters are therefore expected at certain critical values $R_a^{\text{eff,crit}}(\Pi)$. The Rayleigh/Bénard criterion depends on the porosity Π because the size of the permitted convection loops depends on the porosity as well. Small values of the effective length scale d_{eff} of the clusters require large temperature gradients $|\langle\partial T/\partial z\rangle|$ to reach the critical value $R_a^{\text{eff,crit}}$ of the effective Rayleigh number. In Fig. 4.17, the effective Rayleigh/Bénard transitions are consequently shifted to *bigger* porosities $\Pi = \Pi_{\text{RB}}$ with *decreasing* overall temperature difference ΔT , and vice versa.

The geometrical percolation transition for closed loops in two-dimensional random-site percolation networks is expected at porosities Π_c^{eff} somewhat greater than the ordinary critical value $\Pi_c \approx 0.593$. While Π_c^{eff} is a fixed number characteristic for the percolation network under consideration, the porosities Π_{RB} , where the Rayleigh/Bénard transitions effectively take place, are functions of the local temperature gradient $\partial T/\partial z$ (or equivalently of the overall temperature difference ΔT). Π_{RB} can thus be varied by varying ΔT . When Π_{RB} matches Π_c^{eff} , both critical phenomena coincide: This is criterion for the *Rayleigh/Bénard percolation transition*.

To have an ad hoc definition, we assign the variable Π_{RB} to the porosity at which the maximum flow velocity $|v_{\text{max}}|$ is reached at the end of the transition. In the particular FVM simulation represented by Fig. 4.17, a maximum flow velocity of

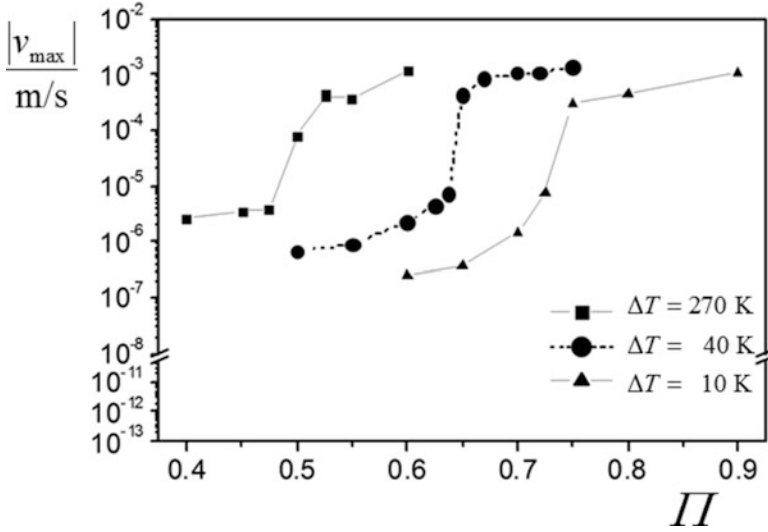


Fig. 4.17 Rayleigh/Bénard transitions in a fluid confined in two-dimensional random-site percolation clusters for different overall temperature differences ΔT . The data have been deduced from simulations using the finite-volume method [34]. The maximum convective flow velocity evaluated from flow velocity maps is plotted as a function of the porosity Π of the network. The abrupt changes of the maximum velocity indicate the Rayleigh/Bénard transitions modified for porous media. The finite flow velocities below the thresholds are due to pretransitional convection arising from horizontal temperature gradients (Reproduced from Ref. [35] with kind permission of © APS 2002)

$|v_{\max}| \approx 0.3$ mm/s corresponding to the upper edge of the transition steps is reached.

The two variables, namely, the overall temperature differences ΔT and the porosities Π_{RB} , where the Rayleigh/Bénard transitions take place can thus be correlated. A corresponding diagram is shown in Fig. 4.18. The kink appearing at $\Pi_{\text{RB}} \approx \Pi_{\text{c}}^{\text{eff}}$ indicates the combined effect of the hydro-thermodynamic Rayleigh/Bénard instability and the geometrical percolation transition, that is, the *Rayleigh/Bénard percolation transition* [34, 35].

4.9.5 Electroosmotic Flow

Electroosmotic flow (EOF) occurs in liquid electrolyte solutions confined between polar surfaces of a solid matrix in the presence of an externally applied potential difference [40, 25]. The prerequisite is the existence of so-called electric double layers along the polar walls. This scenario has already been described in Sect. 2.1.8 and is illustrated in Fig. 2.12. The point is that the double layer contains a net (usually positive) charge, whereas the concentrations of anions and cations in the

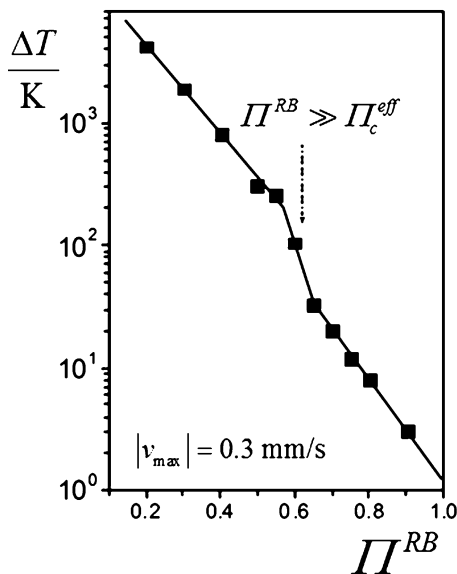


Fig. 4.18 Relationship between the overall temperature difference ΔT and the Rayleigh/Bénard transition. The latter is defined by the occurrence of the maximum convective flow velocity appearing in the particular FVM simulation on which the evaluation is based. In the present case, this is $v_{\max} = 0.3$ mm/s. The crossover at the Rayleigh/Bénard percolation threshold at $\Pi_{\text{RB}} \approx \Pi_c^{\text{eff}} \approx 0.6$ and $\Delta T \approx 110$ K indicates the coincidence of the Rayleigh/Bénard instability (modified for porous media) and the geometrical percolation transition (modified for closed loop flow pathways) (Reproduced from Ref. [35] with kind permission of © APS 2002)

central part of the electrolyte solution are balanced. If an electric-potential difference is applied to such a system by immersing electrode plates in the electrolyte solution, the electric field E_{ext} produced in this way drives the charged double layer toward the counter electrode. Friction between the drifting ions and the fluid leads in turn to flow of the whole electrolyte solution surrounded by the double layers. This results in a plateau-shaped velocity distribution with a mean value given by the *Helmholtz/Smoluchowski equation*:

$$\langle v_{\text{EOF}} \rangle \approx \frac{\varepsilon_r}{\eta} \zeta E_{\text{ext}} \quad (4.110)$$

η is the dynamic viscosity, ε_r is the relative dielectric permittivity, and ζ is the zeta potential we know already from Sect. 2.1.8. According to Eq. (4.110), the EOF velocity is expected to increase linearly with the voltage applied to the electrodes provided that the system is open and no dynamic counterpressure is established (see below).

4.9.5.1 Computational Fluid Dynamics of Electroosmotic Flow in Porous Media

Consider an electrolytic system with *open* electrodes. “Open” means that the electrodes are perfectly permeable for in- and outflow. As in the flow problems regarded above, computational fluid dynamics (CFD) is an appropriate tool also for the examination of electroosmotic flow patterns in complex channel systems. Taking the electrostatic force density $\rho_q \mathbf{E}_{\text{ext}}$ into account, the steady-state Navier/Stokes equation for the horizontal-flow velocity field, $\mathbf{v} = \mathbf{v}(\mathbf{R})$, can be extended as

$$\rho_m(\mathbf{v} \cdot \nabla)\mathbf{v} + \nabla p - \eta \nabla^2 \mathbf{v} = \rho_q \mathbf{E}_{\text{ext}} \quad (4.111)$$

Since we are dealing with a liquid system, the incompressibility condition $\nabla \cdot \mathbf{v} = 0$ applies. The quantities ρ_m and ρ_q are the mass and charge densities, respectively. In principle, non-slipping boundary conditions should be valid at the walls, that is, $\mathbf{v}_{\text{wall}} = 0$. However, the numerical treatment is considerably simplified by the following “coarse-grain” consideration: For technical reasons, the electric double layer cannot be resolved in the velocity mapping experiments to be described below. The external electrostatic force density in Eq. (4.111) can therefore be omitted while simultaneously replacing the non-slipping boundary conditions by an effective slipping variant. That is, the flow velocity at the confining walls is equated by the value predicted by the Helmholtz/Smoluchowski equation¹³:

$$\mathbf{v}_{\text{wall}} = \frac{\varepsilon_r}{\eta} \zeta E_{\text{ext}} \quad (4.112)$$

Effectively, we thus anticipate a pluglike displacement behavior of the bulk electrolyte solution outside of the double layer. In this phase, the flow velocity is essentially constant over the cross section of the pores or channels under consideration as schematically illustrated in Fig. 2.12. The dynamic equations for computational fluid dynamics are thus reduced to

$$\rho_m(\mathbf{v} \cdot \nabla)\mathbf{v} + \nabla p - \eta \nabla^2 \mathbf{v} = 0 \quad \text{and} \quad \nabla \cdot \mathbf{v} = 0 \quad (4.113)$$

Figure 4.19a shows simulated streamline patterns in a test structure consisting of a number of interconnected parallel channels of varying width. Since this is a closed system, electroosmotic flow from the cathode to the anode (as it is expected for negative zeta potential) must be accompanied by compensatory flow in the opposite direction. If narrow and broad channels compete in this respect, the narrow channels “win” by tendency because of the larger surface-to-volume ratio providing

¹³ Note, however, that the non-slipping boundary condition $\mathbf{v}_{\text{electrodes}} = 0$ must be assumed at the surfaces of the electrodes in *closed* systems blocking any in- and outflow. This is in contrast to *open* systems defined by unrestricted flow across the electrode boundaries.

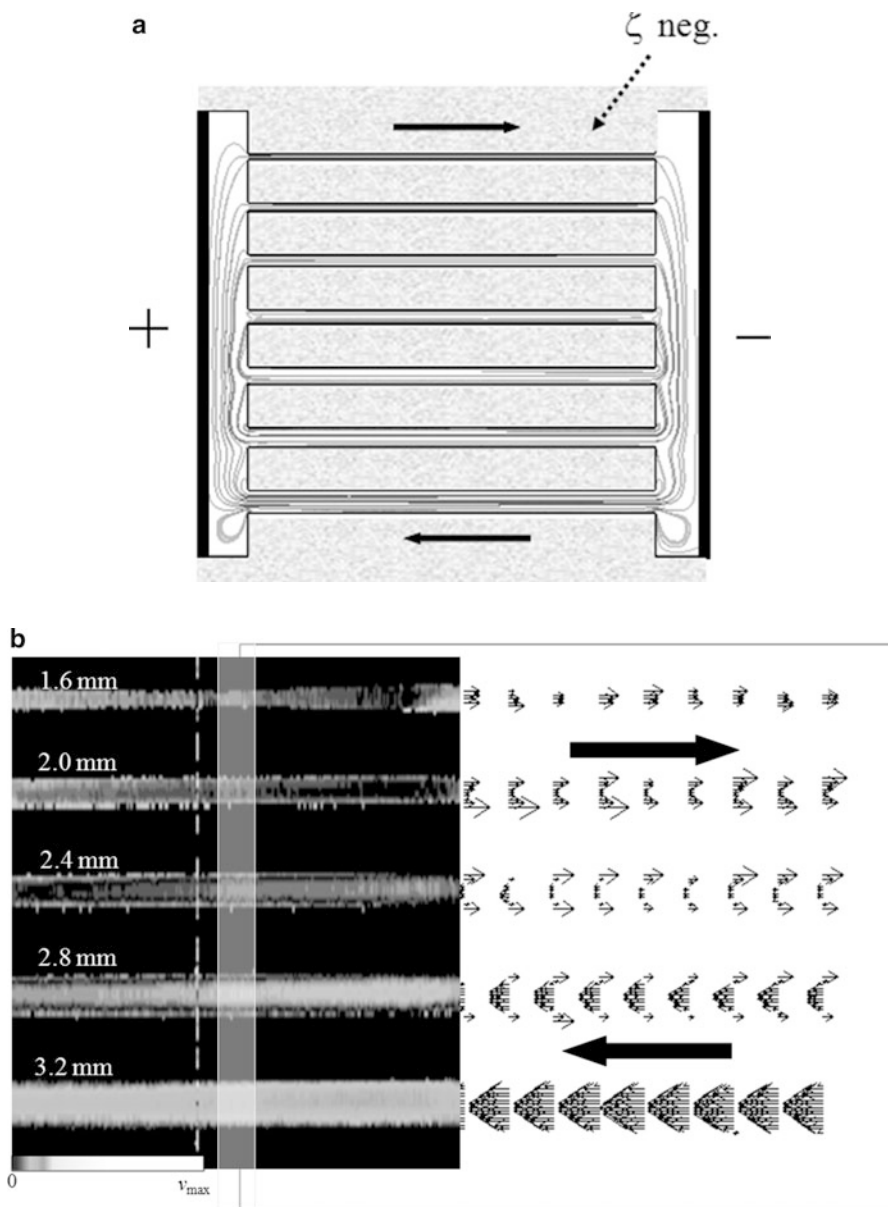


Fig. 4.19 Electroosmotic flow in closed systems of interconnected parallel channels filled with an electrolyte solution. **(a)** Two-dimensional CFD simulations of electroosmotic streamlines in a system of channels with increasing width from the *top to the bottom*. With negative zeta potential ζ and an electrode polarity as indicated, the primary electroosmotic flow direction is from plus to minus. This is the case in the thinnest channel, whereas the flow direction in the thickest channel is reversed, so that cyclic flow patterns arise. **(b)** Verification of the CFD simulations by NMR velocity mapping experiments using the combined pulse sequence shown in Fig. 3.31a–c. The (*quasi-two-dimensional*) channel structure was milled in a polar ceramic matrix. The channel diameters are indicated. Flow velocities are encoded according to the *grayscale bar* at the *bottom left*. The velocities in the central area (*shaded section*) are rendered also in vector form on the *right-hand side*. The main flow directions are marked by *bold arrows*. **(c)** CFD simulations of streamlines in a two-channel structure. The detail images on the *left* and *right* show the distribution of velocity vectors in the flow field. Note the opposite vector directions along the walls of the *thick* channel relative to the central section [41]

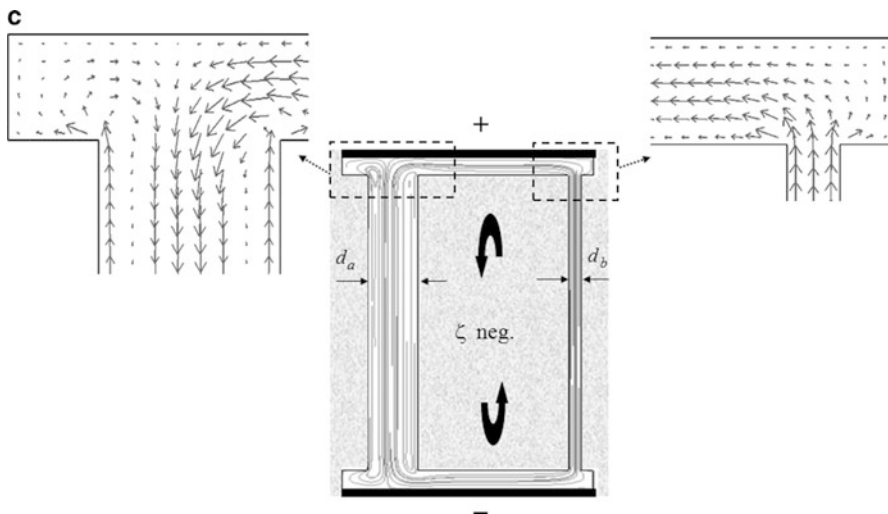


Fig. 4.19 (continued)

a stronger electroosmotic pressure. This favors transport loops from the narrower channels in direction to the anode and back through the wider channels as demonstrated in Fig. 4.19c for two interconnected channels of different widths.

4.9.5.2 Experimental Mapping of the Electroosmotic Flow Velocity

An NMR method suitable for EOF velocity mapping can be composed of the sequels shown in Fig. 3.31a–c. The flow velocity data visualized in Fig. 4.19b were recorded in a quasi-two-dimensional model object with the same lateral extensions as assumed in the simulations Fig. 4.19a [22, 41]. In order to ensure polar wall surfaces, a ceramic was chosen as matrix material.

The velocity vector representations in Fig. 4.19b, c visualize the influence of hydrodynamic backflow. This phenomenon leads on the one hand to cyclic flow in loops formed of thin and thick channels. On the other hand, in the 2.4 and 2.8 mm wide channels shown in Fig. 4.19b, both electroosmotic flow along the walls from left to right and hydrodynamic backflow in the middle of the channels from right to left occur at the same time. Likewise, both flow directions are obvious in the thick channel examined in Fig. 4.19c. In all cases, the velocity profile across the channels strongly deviates from the paraboloidal shape expected for pressure-induced Hagen/Poiseuille flow represented by Fig. 4.9. In a sense, it can even be reversed since the flow velocity near the walls can be larger than in the middle as demonstrated in the 2.0 mm thick channel depicted in Fig. 4.19b. The explanation lies in the different spatial distributions of the flow driving forces. While the forces due to pressure gradients are uniformly distributed across the channel section, those of electroosmotic flow are concentrated in the double layers along the walls.

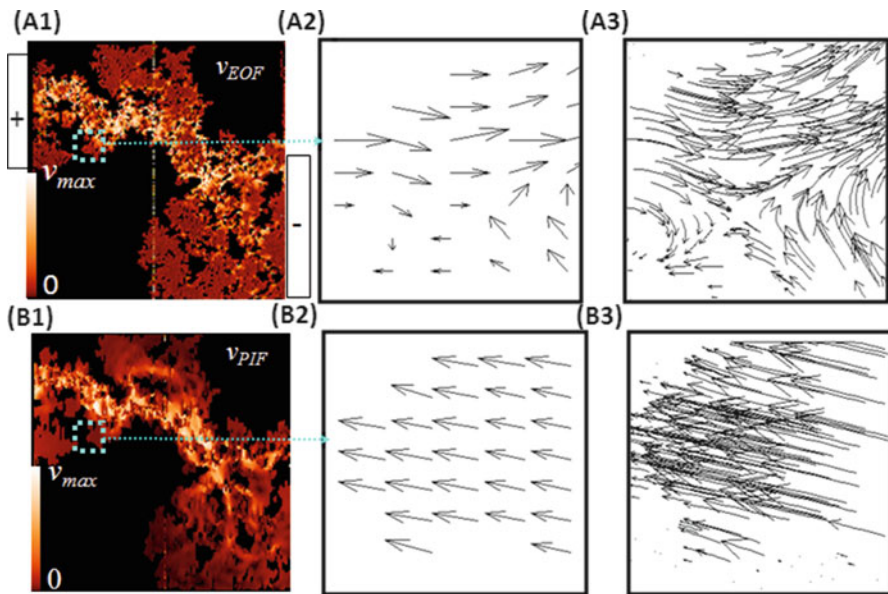


Fig. 4.20 Comparison of experimental maps of the flow velocity magnitude measured in quasi-two-dimensional percolation model objects of the type shown in Fig. 4.10. The material of the matrix is a polar ceramic. The field-of-view is $4\text{ cm} \times 4\text{ cm}$. The matrix is rendered in *black*. The velocity maps on the *left* are encoded according to the encoding bars displayed in the corners. The marked areas of $0.8\text{ mm} \times 0.8\text{ mm}$ are detailed on the *right-hand side* in velocity vector and in trajectory representation. The latter means that the local velocity vector *arrows* are bent along the streamlines. The length of these curvilinear vectors is proportional to the mean magnitude along the *arrow*. *Top row*: maps of the EOF velocity v_{EOF} . The positive and negative electrodes *encapsulating* the system are schematically indicated. The pulse sequence used is the combination shown in Fig. 3.31a–c. *Bottom row*: maps of the flow velocity v_{PIF} due to external pressure gradients in the *open* system. The measuring technique consisted of the combined sequels Fig. 3.31a, b [22, 41]

The different velocity distributions resulting from pressure-induced flow (PIF) and electroosmotic flow (EOF) become also obvious in more complex matrix geometries. Figure 4.20 shows experimental velocity maps recorded in ceramic model objects fabricated on the basis of random-site percolation clusters [22, 41, 42]. The vector and trajectory representations of the velocity distribution in the marked areas reveal remarkable differences. Both phenomena can again be reproduced very well by computational fluid dynamics.

The origin of the different patterns exhibited by the EOF and PIF velocity maps is not only due to the interplay of electroosmotic flow and hydrodynamic backflow missing in the PIF case. As a second source of distortions of EOF relative to PIF, a topology-dependent distribution of the ζ potential must be taken into account. This is demonstrated by the simulations shown in Fig. 4.21 for a simple channel structure with pronounced edges. In contrast to the scenario to which Fig. 4.20 refers, the

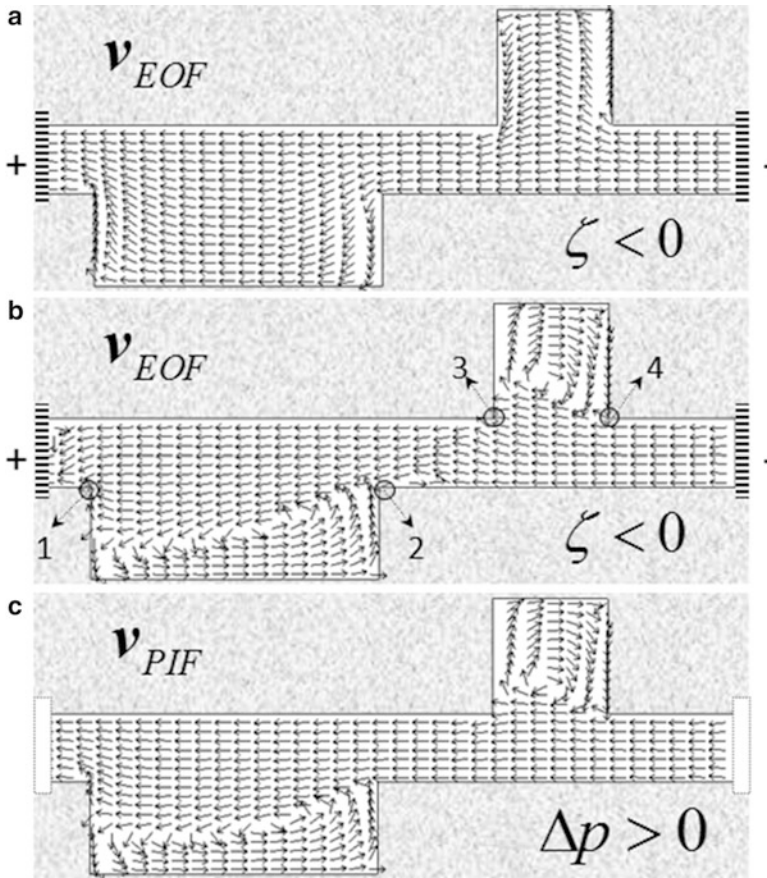


Fig. 4.21 Simulated velocity maps in vector representation in a two-dimensional channel with topological edges [22]. (a) EOF velocity v_{EOF} for a zeta potential, $\zeta = -100$ mV, uniformly distributed along the matrix surfaces. The voltage between the electrodes was assumed to be 600 V. (b) Distribution of the EOF velocity for a zeta potential $\zeta = -100$ mV at the flat parts of the surface and singular values $\zeta = -10$ V at the edge points 1–4. (c) Distribution of the pressure-induced flow velocity v_{PIF}

system has now been assumed to be open at the electrodes so that hydrodynamic backflow does not necessarily arise.

The EOF velocity distribution shown in Fig. 4.20a has been simulated by assuming a *uniform* distribution of the ζ potential along the surfaces. However, the edges marked by the numbers 1–4 form a kind of singularity, which is expected to modify the effective ζ potential relative to smooth surfaces. In the simulation Fig. 4.21b, this has been accounted for by abandoning the uniform distribution of the zeta potential along the channel walls. Instead, the zeta potential was assumed to adopt substantially different values of $\zeta = -10$ V just at those exposed edge positions in excess to the value $\zeta = -100$ mV taken otherwise. Under these conditions, the result Fig. 4.21b shows almost identical flow patterns as those found

in the PIF case Fig. 4.21c: In both cases, the topological surface edges act equivalently as singular points distorting flow. The values of the zeta potential at the edges assumed for this demonstration may appear a bit excessive. The simulation nevertheless reveals that the decisive origin of flow distortions is in both cases the nonuniformity of the conditions at the walls.

Qualitatively, these numerical findings could be reproduced by NMR mapping experiments with a model object of the same topology as reported in Ref. [22]. That is, the distribution of the ζ potential is indeed nonuniform in the presence of topological surface edges, and the singularities affect both EOF and PIF in an equivalent way as predicted by the simulations. In order to mimic the two-dimensionality of the above simulations in the experiments, the model objects were made in such a way that the fluid space was bounded at the top and the bottom by *nonpolar* polystyrene covers so that the EOF effect exclusively arose from the thin in-plane matrix material consisting of polar ceramics.

4.9.6 Ionic Currents

The applications of computational fluid dynamics and NMR mapping experiments described so far refer mainly to flow phenomena induced by various driving sources. It may be most elucidating to juxtapose material transport of this sort to other transport species not based on but possibly affected by hydrodynamic flow. An example already treated in previous sections is heat conduction. As a further non-flow transport phenomenon, we will now undertake a little side trip to electric currents. Referring especially to charge carriers in electrolyte solutions, we specify the quantity of interest in this context as *ionic current density* (ICD).

4.9.6.1 Numerical Simulations of Ionic Current Density Maps in Porous Media

The basic relation for the treatment of electrodynamic potential problems under steady-state conditions is *Laplace equation* for the electrostatic potential Φ :

$$\nabla^2 \Phi = 0 \quad (4.114)$$

Formally, we have encountered this relation already in Eq. (4.36) for the velocity potential in the context of irrotational flow. The boundary conditions for the electrolyte solution at the (impermeable) pore walls can be assumed to be of the Neumann type:

$$\frac{\partial \Phi}{\partial \mathbf{n}} = 0 \quad (4.115)$$

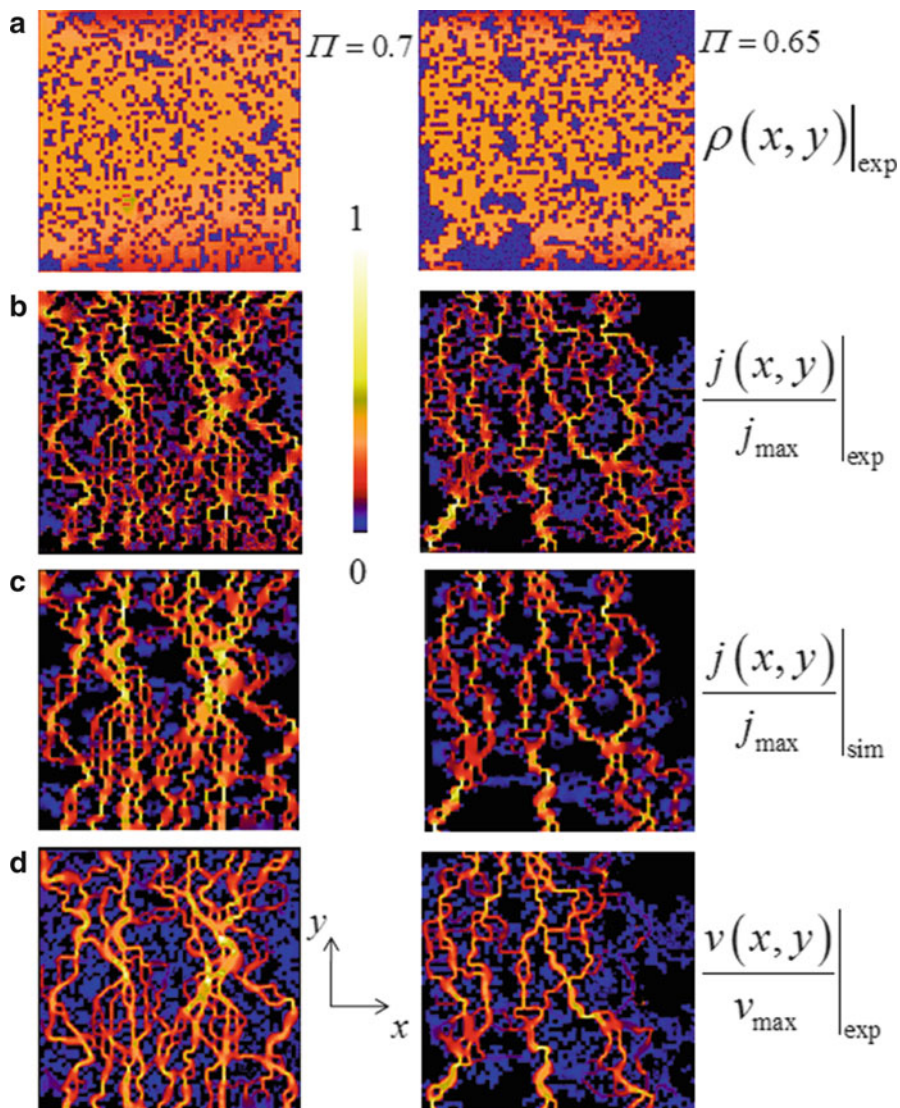


Fig. 4.22 Maps of diverse transport quantities in random-site percolation clusters. The simulations refer to two-dimensional clusters of different porosities generated on a computer. Using these clusters as templates, quasi-two-dimensional model objects have been fabricated similar to the one shown in Fig. 4.10. The porosities are $\Pi = 0.7$ (left column) and $\Pi = 0.65$ (right column). The pore spaces were milled in nonpolar plastic plates and then filled with an electrolyte solution. Row (a) experimental maps of the spin density ρ in the fluid-filled pore spaces. The (homogeneous) spin density in the fluid is represented by the *bright shade*. The data were recorded with the NMR pulse sequence shown in Fig. 3.31a. Row (b) experimental maps of the relative ionic current density j/j_{max} measured with the aid of the NMR sequel combination shown in Fig. 3.31a, d. In this case, the model objects were equipped with electrodes at the *top and bottom* and subjected to a DC potential difference. The current density is encoded according to the *color*

where the derivative by $\partial \dots / \partial \mathbf{n}$ addresses variations along the direction of the boundary normal $\mathbf{n}$. The (if necessary numerical) solution of Eq. (4.114), $\Phi = \Phi(\mathbf{R})$, straightforwardly leads to the distribution of the electric field strength in the pore space

$$\mathbf{E}(\mathbf{R}) = -\nabla\Phi(\mathbf{R}) \quad (4.116)$$

by forming the negative gradient of the potential (again numerically). *Ohm's law*

$$\mathbf{j}(\mathbf{R}) = \sigma \mathbf{E}(\mathbf{R}) \quad (4.117)$$

finally gives the spatial distribution of the current density $\mathbf{j}(\mathbf{R})$, where σ is the conductivity of the electrolyte solution.

Figure 4.22c shows typical current density maps simulated on this basis for electrolyte solutions in random-site percolation clusters subjected to a potential difference from top to bottom. The bright shades indicate the main transport pathways of the current.

4.9.6.2 Experimental Mapping of the Ionic Current Density

Maps of the electric current density in electrolyte solutions filled into pore spaces can be recorded with the NMR technique described in Sect. 3.3.5.2. It was argued there that the experimental protocol becomes particular simple if the current distribution is two-dimensional. The two-dimensionality can effectively be achieved by stacking a sufficient number of identical quasi-two-dimensional model objects¹⁴ so that the current density does not vary along the stacking axis. The component of the current density along this direction will furthermore be zero. The only finite current density components are thus coplanar to the layers of the electrolyte solution.

Typical results measured in percolation model objects composed in this way are shown in Fig. 4.22b. The good coincidence of these experimental data and the simulated transport patterns Fig. 4.22c mutually demonstrates the quality of



Fig. 4.22 (continued) bar indicated in the *middle. Row (c)* simulated maps of the ionic current density $j/j_{\max}$ in the same percolation clusters having served as templates for the fabrication of the model objects. *Row (d)* experimental maps of the relative flow velocity $v/v_{\max}$ induced by a pressure gradient applied across the objects. The NMR method employed for the record of these maps was composed of the sequels Fig. 3.31a, b. The magnitude of the flow velocity is encoded according to the same *color bar* as in the case of the current density (Reproduced from Ref. [43] with kind permission from © APS 2002)

¹⁴ As before, *quasi-two-dimensional* means that the pore space is restricted to a thin layer, the thickness of which is negligible relative to the lateral extension.

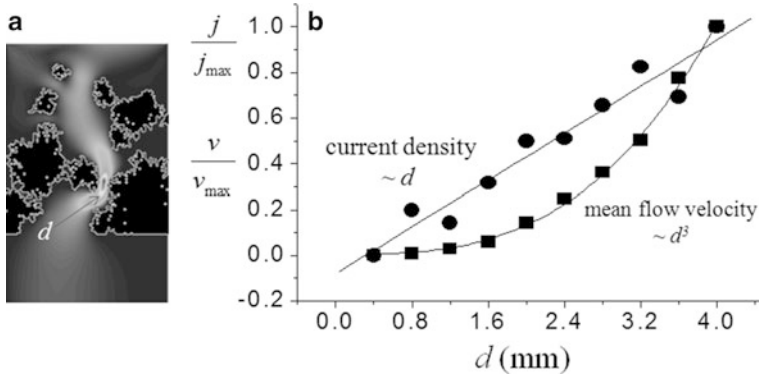


Fig. 4.23 (a) Simulated map of the flow velocity of a fluid percolating through a typical “bottleneck” in a percolation cluster. The velocity is encoded by *different shades of gray* and is particularly high at the narrowest pore passage. (b) Comparative simulations of the relative pressure-induced velocity and the relative ionic current density $v/v_{\max}$ and $j/j_{\max}$, respectively, in a two-dimensional test structure consisting of 10 parallel channels of varying widths d but identical thickness. A similar object is shown in Fig. 4.19a. The current density data can be described by a linear function of d , whereas the flow velocity data follow a d^3 law as suggested by the relevant transport resistances [41]

the techniques. This can also be corroborated quantitatively in terms of histograms evaluated from the maps as reported in Ref. [43].

Figure 4.22d shows comparative maps of the relative flow velocity recorded in the same objects after application of a pressure gradient. In both cases, the transport pathways appear to be remarkably similar. However, a closer look at the details reveals systematic differences of the patterns. Pressure-induced flow tends to follow pathways through wider pores in contrast to electric currents. The current patterns are more ramified than the flow transport ways. This is a consequence of the different dependences on the respective resistances.

Designating the lateral width of a pore by d and keeping the thickness of the (quasi-two-dimensional) pore-space layer fixed suggest a proportionality for the Ohmic resistance

$$R_{\text{Ohm}} \propto d^{-1} \quad (4.118)$$

since the cross-sectional layer area of a pore varies $\propto d$ in this case. On the other hand, the flow resistance is expected to follow

$$R_{\text{flow}} \propto d^{-3} \quad (4.119)$$

under the same conditions, that is, in a fluid layer of fixed thickness. Actually, this proportionality corresponds to the Hagen/Poiseuille law given in Eq. (4.92) if modified for constant layer thickness.

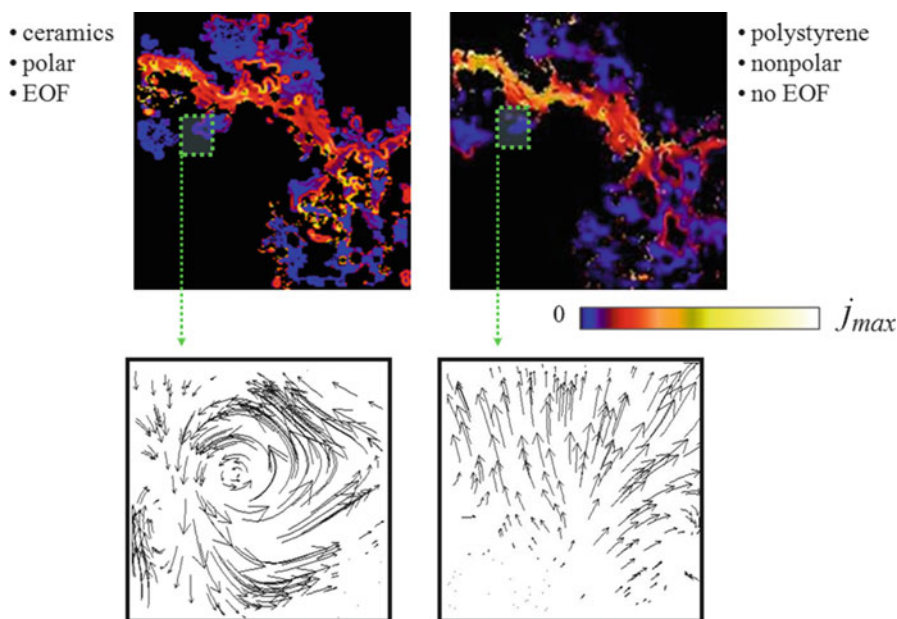


Fig. 4.24 Experimental ionic current density maps measured in percolation model objects made on the one hand of a polar ceramic (*left*) and of a nonpolar plastic on the other. The model object is based on the same percolation cluster as that used in the flow study represented by Fig. 4.20. As a consequence of the different matrix materials, the current density was recorded in the presence (*left*) and in the absence (*right*) of electroosmotic flow, respectively [41]. The NMR pulse sequence used for these experiments is represented by the combination of the sequels Fig. 3.31a, d. The magnitude of the current density is encoded according to the *color bar* on the *right-hand side*. The marked areas are detailed at the *bottom* in trajectory representation. The velocity vector arrows are bent along the local streamlines, and the length of the curvilinear vectors is proportional to the mean magnitude along the *arrow*

The different transport resistances matter particularly at bottlenecks of the pore space as illustrated in Fig. 4.23a. The relationships Eqs. (4.118) and (4.119) can be verified in numerical simulations of transport through a test structure of interconnected channels of varying width as demonstrated in Fig. 4.23b.

It may also be of interest to compare current density maps with maps rendering the distribution of electroosmotic flow. In this context, an intriguing question arises: Electroosmotic flow and ionic currents are both electric phenomena based on an electrostatic potential difference applied to electrolyte solutions. Whenever electroosmotic flow occurs, ionic currents are intrinsically present as well. This suggests that there might be some influence of electroosmotic flow on the spatial distribution of the current density. Experimentally, this problem can be studied by measuring the distributions of the ionic current density both in polar and nonpolar, but otherwise identical matrices. That is, the respective maps of the ionic current density are acquired in the presence and in the absence of electroosmotic flow. Typical results of such experiments are depicted in Fig. 4.24.

As a matter of fact, there is a substantial interference of hydrodynamic flow on the spatial distribution of the electric currents. This is exemplified by the detail streamline pictures in the bottom row of Fig. 4.24. The main finding is that eddies of the electric current density are observed in the presence of electroosmotic flow, but not in the static case. Clearly, recirculation patterns of hydrodynamic flow are not unlikely in complex pore spaces. On the other hand, cyclic electric currents appear to contradict the static conditions of the experiments at first sight. The explanation of this apparent discrepancy is that both hydro- and electrodynamic laws must commonly be taken into account if flow and electric currents coexist. Ionic charge carriers driven by hydrodynamic flow through an inhomogeneous electrostatic field effectively experience a *time-dependent* electric field strength, $\mathbf{E} = \mathbf{E}(t)$, in spite of steady flow and electrostatic conditions. Therefore, the basic electrostatic relation $\nabla \times \mathbf{E} = 0$ does not apply in the presence of electroosmotic flow. This problem is also referred to as *dissimilitude* between flow velocity and ionic current density (see Refs. [44, 45]).

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Chapter 5

Molecular Dynamics in Polymers

Abstract Suitably modified versions of the Langevin equation introduced in Chap. 2 will be taken as a general basis for analytical explanations of macromolecular-chain motions. The reader will straightforwardly be led from the dynamics of freely draining polymer chains as the simplest case to entangled-chain phenomena and finally to mesoscopic confinement effects. The Langevin equation-based treatments will be supplemented step by step by additional force terms specific for the diverse model scenarios. The restriction to this equation-of-motion strategy is expected to favor the comprehensibility of this demanding field. The relaxation-mode solutions will be expressed in the form of predictions for diverse experimental techniques outlined in Chap. 3. This in particular refers to spin–lattice relaxation, coherent and incoherent neutron scattering, and mechanical relaxation.

The main feature of fluid dynamics treated in the previous chapter was *coherence*, the more or less uniform transport of molecular entities. With polymer dynamics, we are also dealing with coherent processes in a sense. However, the coherence does not refer to whole molecules in this case but to polymer segments as a consequence of chain connectivity. One therefore speaks better of *collective* phenomena referring largely (but not exclusively) to intramolecular effects. As will be shown in subsequent sections, the key to our understanding of polymer-chain dynamics is the superposition of *relaxation modes* describing just these collective segment motions. Before outlining the corresponding concepts, it may be useful to clarify a number of basic definitions and laws specific and crucial for the polymer field.

5.1 Terminology

Macromolecules consist of covalently bound *monomers* which in turn may be composed of several *chemical segments*. A monomer is the chemical unit linked in the polymerization process in the form of a chain. A number of examples will be

specified further down. By contrast, the term *chemical segment* addresses the smallest physical unit being able to contribute to thermal motions. This is normally the chemical group between two adjacent and saturated main-chain bonds. In later sections of this chapter, another type of segment will also be referred to, namely, the *Kuhn* or *statistical segment* and the *Rouse subchain* or *Rouse segment*. These entities are understood as groups of a certain number of ordinary, that is, chemical, segments subdividing a polymer in such a way that they form a model chain with the degrees of freedom needed for formal treatments. Definitions will be provided below in the context of the model theories for polymer dynamics to be presented here.

Macromolecules are primarily characterized by their length and by their mass. Let the number of monomers be N . Beginning with $N = 2$, a dimer, $N = 3$, a trimer, and so on until about $N \approx 30$, one speaks of *oligomers*. For larger numbers, the term *polymer* is adequate. Due to the different chemical synthesis methods, the molar mass of polymers is normally not as well defined as with oligomers. They are no longer *monodisperse* but subject to a distribution of the number of monomers per chain depending on the polymerization method. As a consequence, the molar mass must be specified in the form of an average. One distinguishes the empirical *weight* (or more correctly mass) *average* defined by

$$M_w = \frac{\sum_i (f_i M_i) M_i}{\sum_i (f_i M_i)} = \frac{\sum_i f_i M_i^2}{\sum_i f_i M_i} \quad (5.1)$$

from the *number average*

$$M_N = \frac{\sum_i f_i M_i}{\sum_i f_i} = \sum_i f_i M_i \quad (5.2)$$

where f_i is the number fraction of molecules of molar mass M_i . In principle, the sums in Eqs. (5.1) and (5.2) are approximations replacing integrals. Since the fractions are determined experimentally and refer therefore to finite molecular-mass intervals, the representation by sums is nevertheless appropriate.

Unless the polymer is monodisperse, the so-called *polydispersity index* or plainly *polydispersity*, that is, the ratio of the weight and number averages, will be larger than 1, $M_w/M_N \geq 1$. This parameter is often taken as a measure of the width of the molecular-mass distribution. The smaller the polydispersity, the narrower is the molecular-mass distribution. Typical values for particularly narrowly distributed polymers are in the range $1.0 < M_w/M_N < 1.1$. On the other hand, polymers in plastic materials used for practical applications may have polydispersities up to 20 or even more. Experimentally, weight- and number-average molecular masses and, hence, polydispersities can be determined with the aid of *gel permeation chromatography*.

If the monomers a polymer consists of are identical, one speaks of *homopolymers*. Typical examples are polyethylene, $-\text{[CH}_2\text{--CH}_2\text{]}_v-$, poly(ethylene oxide), $-\text{[CH}_2\text{--CH}_2\text{--O]}_v-$, and polybutadiene, $-\text{[CH=CH--CH}_2\text{--CH}_2\text{]}_v-$, where v is the number of repeat units. Of course, unless closed ring chains are formed, the end groups of a polymer must be of a somewhat different composition so that no open valence bonds remain.

Asymmetric monomers can in principle be linked in sequences *head-to-tail*, *head-to-head*, or *tail-to-tail* although head-to-tail sequences are more likely for energetic reasons. If stereoisomers of monomers exist, the question of the so-called *tacticity* arises. An example is polystyrene, $-\text{[CH}_2\text{--CH(C}_6\text{H}_5\text{)]}_v-$, where the phenyl ring C_6H_5 can be located on either side bond of the skeletal carbon to which it is bound. If only one stereoisomer is used for the synthesis, *isotactic* polystyrene is produced. This is in contrast to *atactic* polystyrene where the two stereoisomers are sequenced at random. In the case of an alternating sequence, the term *syndiotactic* is in use.

Polymers can also be composed of chemically different monomers. In this case, one speaks of *copolymers*. In particular, almost all biopolymers such as polysaccharides, proteins, and DNA are of a copolymeric composition as manifested by their primary structure. An example of a synthetic copolymer of practical importance is ABS plastic which is composed of acrylonitrile, butadiene, and styrene monomers. If the different monomer species are arranged block by block (as it is partly the case with ABS plastic), the compound is called *block copolymer*.

In contrast to linear polymers, copolymers containing multifunctional monomer units can form branched macromolecules or in special cases even stars and dendrimers [1]. Systematic crosslinking between different polymer chains leads to *networks* composed of meshes. In the case of rubber (i.e., essentially polyisoprene), this process is initiated with the aid of a sulfur additive and is called vulcanization. Cross-linking within the same polymer leads to globular, fibrillar, or sheet structures. Typical examples are the secondary and tertiary structures of proteins and nucleic acids based on intersegment hydrogen bonds.

Polymers containing *mesogenic* groups, that is, rodlike units normally formed by some aromatic compounds, tend to form *liquid crystalline* (LC) phases. One distinguishes between main-chain and side-chain LC polymers depending on the position of the mesogenic groups. At the extreme, if the whole polymer has the form of a rigid rod as it is the case with poly- γ -benzyl-L-glutamate (PBLG) in its α -helical phase, for example, liquid crystalline order is principally unavoidable.

While the ordered phases of mesogenic molecules can be explained by the energetics of molecular packing, there is another form of polymers which are totally flexible but nevertheless form mesophases for different reasons. Examples are poly(diethylsiloxane) (PDES) and higher homologues of poly(dialkylsiloxanes) [2]. We will get back to this species in Sect. 6.9.

The term *polymer* is sometimes attributed also to chain- or wormlike aggregates of molecules in the sense of supramolecular chemistry. In this case, the “monomers” may themselves be macromolecules which are non-covalently bound to each other by much weaker interactions such as hydrogen bonds, van

der Waals couplings, hydrophobic interactions, and electrostatic attraction. Prominent examples are the muscle filaments actin and myosin. Surfactants forming worm-like micellar structures with polymer properties also belong to this category.

From the physicist's point of view, analytical treatments of polymer-chain dynamics appear to be hopeless at first sight even in the case of the simplest homopolymers. The excessive number of internal degrees of motional freedom on the one hand and conformational restrictions due to valence bond constraints and sterical hindrances on the other are seemingly unsurmountable difficulties. How could one solve a system of equations of motion under such conditions? As the way out of this dilemma, *coarse-grain modeling* turned out to be the key for analytical treatments. It will be shown that the results for – in this sense – macroscopic material properties are of an amazing accuracy in spite of the substantial simplification inherent to this sort of analysis.

Historically, a couple of truly ingenious steps can be identified as landmarks of modern theory of polymer dynamics. Outstanding examples are: the *Kuhn (or statistical) segment* description [3], the *Rouse bead-and-spring chain* model [4, 5], Flory's *chain statistics* [6], and Edwards' and de Gennes' concept to illustrate entanglements by a *fictitious tube* [7, 8]. In the following, we will delineate these ideas in more detail one after the other.

5.2 Microstructure

Figure 5.1 shows a schematic representation of the paradigm of linear polymers: polyethylene in its simplest conformation, the all-trans structure. Under real conditions, all degrees of motional freedom will be activated as far as compatible with thermal equilibrium. This in particular means that isomeric conformations will be adopted by rotations of the chemical segments about the valence bonds as indicated by the bent double arrows in Fig. 5.1. The degrees of motional freedom are constrained by the practically fixed valence bond lengths and angles between adjacent backbone valence bonds illustrated in Fig. 5.2. Furthermore, there is some hindrance due to potential barriers that must be overcome for rotations about backbone valence bonds. A plot of such a *rotation potential* is shown in Fig. 5.3 for butane as a function of the dihedral rotation angle φ .

Valence bond lengths are often specified as distances between the centers of mass of the electron orbitals as they are measured in X-ray diffraction experiments. To be precise, this definition should be distinguished from the somewhat different internuclear distances that are relevant for neutron scattering and nuclear dipole–dipole coupling. Mean valence bond lengths are furthermore affected by asymmetric vibrations to some minor degree.

Rotational degrees of freedom about skeletal valence bonds can be activated by thermal energy. The equilibrium population p_g of the two gauche conformers relative to that of the trans-alignment p_t is given by the Boltzmann factor

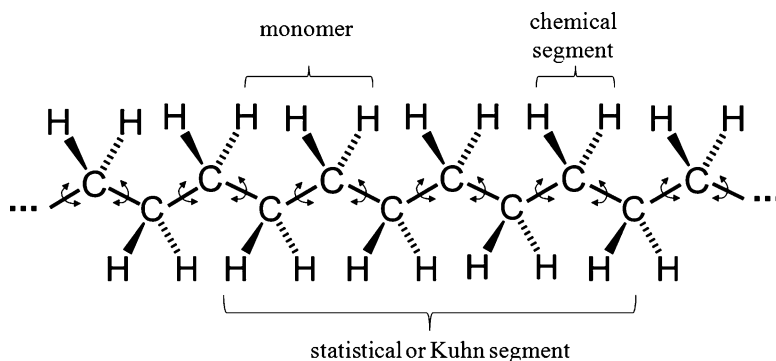
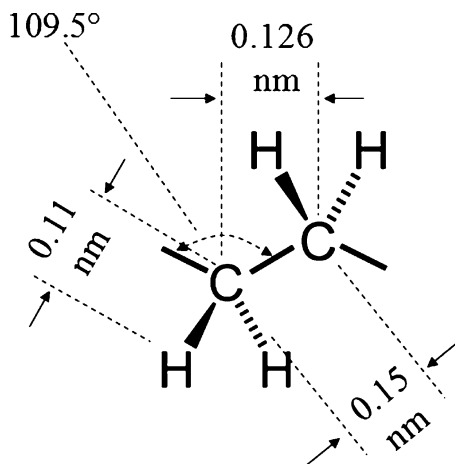


Fig. 5.1 Structural formula of polyethylene as a typical polymer in all-trans (i.e., planar) conformation. Rotational degrees of freedom about the backbone valence bonds are indicated by bent *double arrows*. As elements forming chains, one distinguishes *monomers* ($-\text{[CH}_2\text{-CH}_2\text{-]}$), *chemical segments* ($-\text{[CH}_2\text{-}]$), and *statistical or Kuhn segments* ($-\text{[CH}_2\text{]}_{6...8}-$)

Fig. 5.2 Bond length and valence angle for polyethylene (and more generally for vinyl polymers)



$$\frac{p_g}{p_t} = 2 \exp \left\{ -\frac{U_{tg}}{RT} \right\} \quad (5.3)$$

where U_{tg} is the molar potential difference between gauche and trans states. R is the gas constant and T the absolute temperature. The factor of two on the right-hand side represents the twofold degeneracy of the gauche state (see Fig. 5.3). The total gauche population can thus be expressed by

$$p_g = \frac{2 \exp \left\{ -\frac{U_{tg}}{RT} \right\}}{1 + 2 \exp \left\{ -\frac{U_{tg}}{RT} \right\}} \quad (5.4)$$

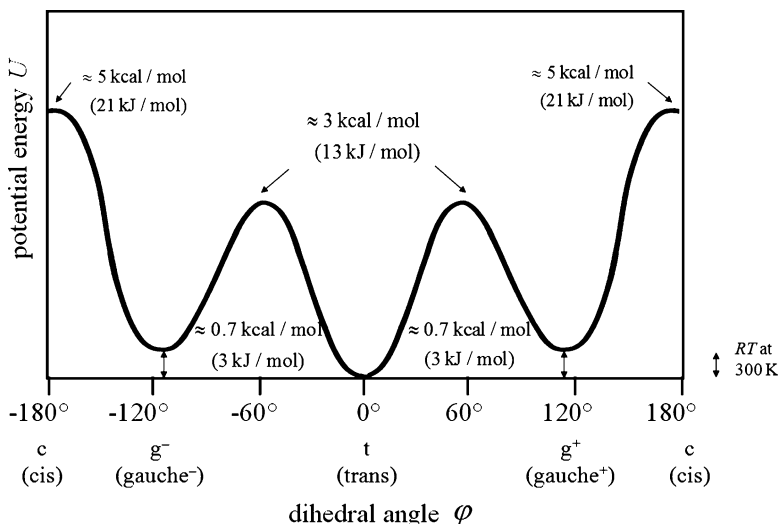


Fig. 5.3 Values for the (molar) potential energy U as a function of the dihedral rotation angle φ about the central bond of butane $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_3$. For a definition of this angle, see Fig. 5.4. The value of RT at 300 K is visualized at the right-hand side. Very roughly, it is of the same value as the molar potential elevation of the gauche positions relative to the trans conformation, $U_{\text{tg}} \approx RT$. That is, gauche conformations are well populated in thermal equilibrium near room temperature

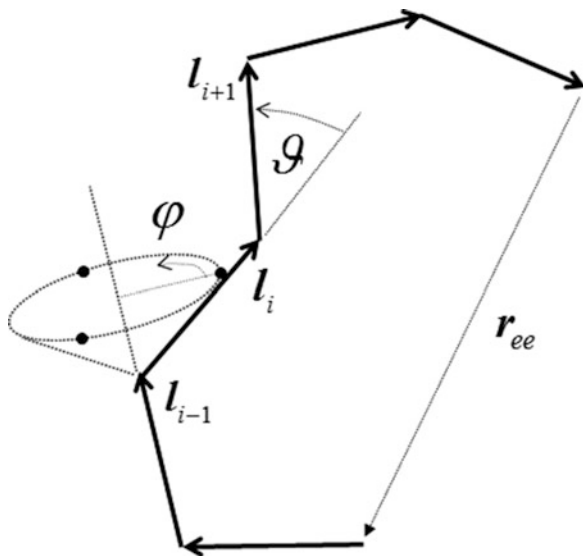
In the case of alkanes and vinyl polymers, U_{tg} is of the same order as the mean thermal energy at room temperature as indicated in Fig. 5.3. This suggests that the gauche and trans populations are similar. As a consequence, one expects that polymers with this property are rather flexible and subject to random coiling.

5.2.1 Chain End-to-End Distance

As illustrated in Fig. 5.4, a valence-angle chain is thought to consist of N chemical segments with main-chain bonds inclined relative to each other by the fixed valence angle ϑ . In the figure, this is exemplified by the bond vectors $\mathbf{l}_i$ and $\mathbf{l}_{i+1}$. The second microstructural variable, the dihedral angle φ , indicates twists about a bond relative to the trans sequence of consecutive chemical segments. In Fig. 5.4, this is schematically depicted by the rotation of segment number i about the axis of bond number $i - 1$. The end-to-end distance vector of such a valence-angle chain is given by

$$\mathbf{r}_{\text{ee}} = \sum_{i=1}^N \mathbf{l}_i \quad (5.5)$$

Fig. 5.4 Definition of the dihedral angle φ and the valence bond angle ϑ of a so-called *valence-angle chain*. The dihedral angles for the trans, gauche⁻, and gauche⁺ conformers (see Fig. 5.3) are indicated by dots. The bonds are symbolized by the vectors $\mathbf{l}_i$, where the subscript i is the number of the chemical segment. The bond length $|\mathbf{l}_i| = l$ is the same for all subscripts i . The distance $\mathbf{r}_{ee}$ is the end-to-end vector of the chain. Characteristic parameters of polyethylene chains are $\vartheta = 70.5^\circ$ and $l = 0.15$ nm (compare Fig. 5.2)



where the bond vectors are assumed to have a fixed length l . The mean-square end-to-end distance of the chain, that is, the ensemble average over all chain conformations, can then be expressed as

$$\langle r_{ee}^2 \rangle = \left\langle \left(\sum_{i=1}^N \mathbf{l}_i \right) \cdot \left(\sum_{j=1}^N \mathbf{l}_j \right) \right\rangle = Nl^2 + 2 \sum_{0 < i < j \leq N} \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle \quad (5.6)$$

The evaluation of the scalar products $\mathbf{l}_i \cdot \mathbf{l}_j$ in Eq. (5.6) stipulates that both factors are expressed relative to the same coordinate system. For each chemical segment, a local orthogonal Cartesian frame can be defined with the x -axis aligned along its bond vector, while the y -axis lies in the plane spanned by this bond vector and the adjacent neighbor bond. For example, the coordinates of a bond vector $\mathbf{l}_{i+1}$ relative to its own frame are given by the components of the column vector

$$(\mathbf{l}_{i+1})_{(i+1)} = \begin{pmatrix} l \\ 0 \\ 0 \end{pmatrix}_{(i+1)} \quad (5.7)$$

The subscript of the parentheses, $(\dots)_{(i+1)}$, indicates the reference frame to which the representation refers. That is, in the case of Eq. (5.7), the reference frame is the same as that of bond number $i + 1$. If a bond vector is to be expressed relative to the frame of the preceding bond, a coordinate transformation is required according to

$$(\mathbf{l}_{i+1})_{(i)} = \mathbf{T}_{\sim i} \begin{pmatrix} l \\ 0 \\ 0 \end{pmatrix}_{(i+1)} \quad (5.8)$$

Equation (5.8) gives the bond vector $\mathbf{l}_{i+1}$ in coordinates of the frame defined by the adjacent bond vector $\mathbf{l}_i$. The transformation matrix generating coordinates of bond vector $\mathbf{l}_{i+1}$ relative to frame i is given by [6, 9]

$$\mathbf{T}_{\sim i} = \begin{Bmatrix} \cos \vartheta & \sin \vartheta & 0 \\ \sin \vartheta \cos \varphi_i & -\cos \vartheta \cos \varphi_i & \sin \varphi_i \\ \sin \vartheta \sin \varphi_i & -\cos \vartheta \sin \varphi_i & -\cos \varphi_i \end{Bmatrix} \quad (5.9)$$

The valence angle ϑ is the same for all segments in the polymer and therefore need not be specified by bond numbers.

With these definitions, the scalar product $\mathbf{l}_i \cdot \mathbf{l}_j$ in Eq. (5.6) can be rewritten in matrix form as

$$\mathbf{l}_i \cdot \mathbf{l}_j = (\mathbf{l}'_i)_{(i)} (\mathbf{l}_j)_{(i)} \quad (5.10)$$

Since the right-hand side is interpreted as a matrix product, there is no multiplication dot. We are rather dealing with a product of the column matrix $(\mathbf{l}_j)_{(i)}$ with the line matrix $(\mathbf{l}'_i)_{(i)} = (l_{ix}, l_{iy}, l_{iz})_{(i)}$ as the transposed form of the column matrix $(\mathbf{l}_i)_{(i)}$. Using the above transformation matrix, the bond matrix $(\mathbf{l}_j)_{(j)}$ relative to the reference frame j can be expressed in coordinates relative to the system of bond vector i :

$$\mathbf{l}_i \cdot \mathbf{l}_j = (\mathbf{l}'_i)_{(i)} (\mathbf{l}_j)_{(i)} = (\mathbf{l}'_i)_{(i)} \left\{ \mathbf{T}_{\sim i} \cdots \mathbf{T}_{\sim j-2} \quad \mathbf{T}_{\sim j-1} \right\} (\mathbf{l}_j)_{(j)} \quad (5.11)$$

The bond column matrix $(\mathbf{l}_j)_{(i)}$ is the result of successively applying the transformation matrix from bond number i to bond number $j-1$ according to $(\mathbf{l}_j)_{(i)} = \{\mathbf{T}_{\sim i} \cdots \mathbf{T}_{\sim j-2} \quad \mathbf{T}_{\sim j-1}\} (\mathbf{l}_j)_{(j)}$. In this way, it is ensured that the bond vectors $\mathbf{l}_i$ and $\mathbf{l}_j$ linked by the scalar product in Eq. (5.11) refer to the same reference frame.

The only variables of the system concerning the ensemble average $\langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle$ in Eq. (5.6) are the dihedral angles φ_v of the bonds involved in the chain section under consideration. The calculation of this average is based on Boltzmann factors

$$\langle \cdots \rangle = \frac{\int_0^{2\pi} \cdots \exp\left(-\frac{U(\varphi_v)}{RT}\right) d\varphi_v}{\int_0^{2\pi} \exp\left(-\frac{U(\varphi_v)}{RT}\right) d\varphi_v} \quad (5.12)$$

for the rotational potential energy $U(\varphi_v)$ (for an example, see Fig. 5.3). Anticipating that the dihedral angles of different bonds are independent of each other so that the same fixed rotational potential distribution applies, Eq. (5.11) can be averaged according to

$$\begin{aligned}\langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle &= (\mathbf{l}'_i)_{(i)} \left\langle T_{\sim i} \cdots T_{\sim j-2} T_{\sim j-1} \right\rangle (\mathbf{l}_j)_{(j)} \\ &= (\mathbf{l}'_i)_{(i)} \left\langle T_{\sim i} \right\rangle \cdots \left\langle T_{\sim j-2} \right\rangle \left\langle T_{\sim j-1} \right\rangle (\mathbf{l}_j)_{(j)}\end{aligned}\quad (5.13)$$

The two bond vectors linked by this relation can be expressed in components as

$$(\mathbf{l}'_i)_{(i)} = (l, 0, 0)_{(i)} = l(1, 0, 0)_{(i)} \quad \text{and} \quad (\mathbf{l}_j)_{(j)} = \begin{pmatrix} l \\ 0 \\ 0 \end{pmatrix}_{(j)} = l \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}_{(j)} \quad (5.14)$$

Normally, the rotational potential distribution is symmetric as assumed in Fig. 5.3, so that $U(\varphi_v) = U(-\varphi_v)$. The mean sine of the dihedral angle therefore vanishes for all bonds: $\langle \sin \varphi_v \rangle = 0$. For fixed valence bond angle ϑ and variable dihedral angle φ , the ensemble average of the transformation matrix in Eq. (5.9) thus adopts the form

$$\left\langle T_{\sim v} \right\rangle = \left\langle T_{\sim} \right\rangle = \begin{Bmatrix} \cos \vartheta & \sin \vartheta & 0 \\ \sin \vartheta \langle \cos \varphi \rangle & -\cos \vartheta \langle \cos \varphi \rangle & 0 \\ 0 & 0 & \langle -\cos \varphi \rangle \end{Bmatrix} \quad (5.15)$$

Note that this expression is *independent* of the subscript number v since all chemical segments are considered to be identical. No reference to individual bonds is needed.

Combining Eqs. (5.6) and (5.13), (5.14), (5.15) leads for long chains to the result

$$\langle r_{ee}^2 \rangle = Nl^2 \left(\frac{1 + \cos \vartheta}{1 - \cos \vartheta} \right) \left(\frac{1 + \langle \cos \varphi \rangle}{1 - \langle \cos \varphi \rangle} \right) \quad (5.16)$$

In summary, the conditions for the validity of this relation are as follows: (1) The valence bond angle ϑ , is fixed; (2) the distribution of the rotational potential is fixed, symmetric, and independent of other chemical segments; (3) any long-range steric or excluded-volume interactions are absent; and (4) the numbers of chemical segments are large, $N \gg 1$. In the case of vinyl polymers, “large” practically means more than 40–50 skeletal bonds per chain.

The last term on the right-hand side of Eq. (5.16),

$$\left(\frac{1 + \langle \cos \varphi \rangle}{1 - \langle \cos \varphi \rangle} \right) \equiv \sigma^2 \geq 1 \quad (5.17)$$

is a measure for the dihedral rotation hindrance. The quantity σ is therefore called (sterical) *hindrance parameter* ranging between 1.5 and 2.5 for typical polymers [9–13]. For free rotation about the bond axes, it is equal to 1.

Since the valence bond angle ϑ and the average of the cosine of the dihedral angle $\langle \cos \varphi \rangle$ are characteristic for the polymer species, the quotient

$$\frac{\langle r_{ee}^2 \rangle}{Nl^2} = \left(\frac{1 + \cos \vartheta}{1 - \cos \vartheta} \right) \left(\frac{1 + \langle \cos \varphi \rangle}{1 - \langle \cos \varphi \rangle} \right) \equiv C_{\infty} \quad (5.18)$$

is termed the *characteristic ratio*, where the subscript ∞ reminds of the large-number limit. C_{∞} relates the mean-square end-to-end distance of a real chain to the value expected for a freely jointed chain with the same number of segments and the same segment length. Numerical values of C_{∞} lie between 4 and 12 for typical polymers [10]. Note that the ensemble average $\langle \cos \varphi \rangle$ implies Boltzmann factors according to Eq. (5.12). In principle, it is therefore a function of temperature.

5.2.2 From the Valence-Angle Chain to the Freely Jointed Segment Chain

Figure 5.5 illustrates different models for polymer chains as they are in use for theoretical and numerical treatments or just for supporting our imagination. In the course of the present chapter, we will frequently get back to these chain representations. One of the models is the *freely jointed segment chain*. It consists of *Kuhn* or *statistical segments*. These segmental entities consist of sequels of a sufficient number of chemical segments of the valence-angle chain as illustrated in Fig. 5.6. If the number of chemical segments forming a Kuhn segment is large enough, the rotational degrees of freedom of the involved main-chain bonds taken together permit free rotation of Kuhn segments relative to each other. Actually, this is the most fundamental measure for *coarse-graining* treatments one typically employs in polymer science [3]. The *Kuhn length* is defined by

$$b = \frac{\langle r_{ee}^2 \rangle}{L} \quad (5.19)$$

where $\langle r_{ee}^2 \rangle$ is the mean-square end-to-end distance of the chain and L is the *contour length*

$$L = Nl' \equiv r_{ee}^{\max} \quad (5.20)$$

As before, N is the number of skeletal bonds per chain. The length from chemical segment to chemical segment projected on the main-chain axis is l' . The prime



Fig. 5.5 Different versions of model chains for polymers. *Middle section*: Space-filling atom model of polyethylene. The hydrogen atoms are represented in *white* as hemispheres with a radius equal to the van der Waals radius. This is the radius that would determine nearest atom distances in crystalline structures. *Left*: Freely jointed model chain. *Right*: Bead-and-spring polymer model. (Reproduced from Ref. [14] with kind permission of © Elsevier 1988)

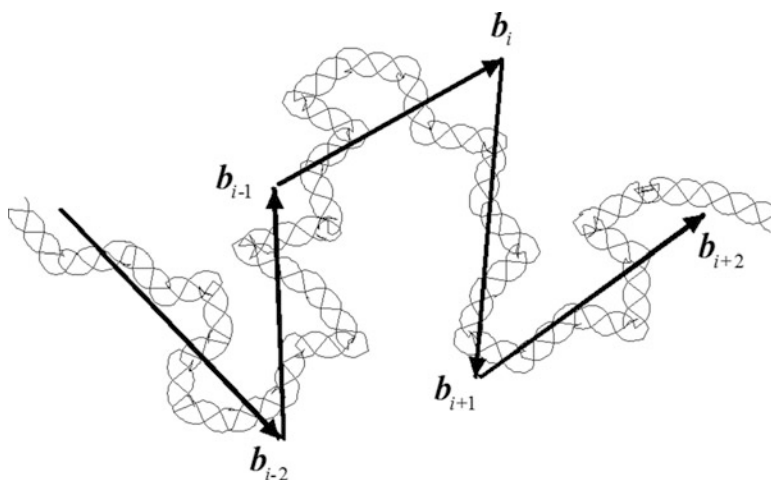


Fig. 5.6 Schematic representation of Kuhn segment vectors $\mathbf{b}_i$ containing a sufficient number of main-chain valence bonds. The orientations of the Kuhn segment vectors drawn as *solid arrows* are uncorrelated relative to each other. On this understanding, the Kuhn segments effectively form a freely jointed chain. The sequel of Kuhn segments is also called *primitive path* of the polymer with the step length b (not to be confused with the primitive path of the so-called *tube* with the step length a defined in the frame of the tube/reptation model in Sect. 5.4.6)

Table 5.1 Kuhn lengths b (in units of the monomer length projected on the chain axis, l'_{monomer}) for typical polymer species [1]

Polymer species	Acronym	Monomer	b/l'_{monomer}
Poly(ethylene oxide)	PEO	$-\text{[CH}_2\text{--CH}_2\text{--O]}-$	2.5
Polypropylene	PP	$-\text{[CH}_2\text{--CH(CH}_3\text{)]}-$	3.0
Polyethylene	PE	$-\text{[CH}_2\text{--CH}_2\text{]}-$	3.5
Poly(methyl methacrylate)	PMMA	$-\text{[CH}_2\text{--C(CO\{OCH}_3\})(CH_3)]-$	4.0
Poly(vinyl chloride)	PVC	$-\text{[CH}_2\text{--CHCl]}-$	4.0
Polystyrene	PS	$-\text{[CH}_2\text{--CH(C}_6\text{H}_5\text{)]}-$	5.0
Polyacrylamide	PAM	$-\text{[CH}_2\text{--CH(CO--NH}_2\text{)]}-$	6.5
Deoxyribonucleic acid (as double helix)	DNA	Different nucleotide base pairs	300
Poly(γ -benzyl-L-glutamate) (as α -helix)	PBLG	$-\text{[NH--CH(CH}_2\text{--CH}_2\text{--CO--O--CH}_2\text{\{C}_6\text{H}_5\})--CO]}-$	500

In the chemical formulas of the monomers, main (or side)-chain valence bonds are indicated by *dashes*. Side groups other than hydrogen, oxygen, or chlorine atoms are specified in *parenthesis* (or *curly braces* in the case of secondary side groups) and refer to the preceding main (or side)-chain atom. The elements are then typed in *italics*

indicates that this length is to be distinguished from the real bond length l introduced in Eq. (5.6). For the polymer example represented by Fig. 5.2, the projected length is $l' = 0.126$ nm, while $l = 0.15$ nm. $r_{\text{ee}}^{\text{max}}$ is the maximum end-to-end distance corresponding to a fully stretched chain in all-trans conformation.

The Kuhn length b obviously implies the characteristic ratio:

$$b = \frac{\langle r_{\text{ee}}^2 \rangle}{Nl'} = C_{\infty} \frac{l^2}{l'} \quad (5.21)$$

The number z of skeletal bonds needed per Kuhn segment to establish the free-joint property therefore depends on factors like the rotational potential distribution, the valence bond angle, and the sterical interactions between chemical segments and side groups. In Table 5.1, a number of typical values for b are listed.

The ingenious idea behind the Kuhn segment concept is that *all* sterical properties and all degrees of motional freedom of the monomer compound are packed into a single parameter, the Kuhn length b . This characteristic quantity will be particularly short if there are no bulky side groups and if there is little hindrance of rotational rearrangements about the skeletal valence bonds. On the other hand, it takes excessive values if strong intra-molecular interactions such as the hydrogen bonds in DNA and poly(γ -benzyl-L-glutamate) lead to inflexible, rodlike conformations. The shorter the Kuhn length, the more flexible the polymer will be.

In terms of the rotational potential exemplified in Fig. 5.3, chain conformations near room temperatures can be represented by more or less *random* sequences of *gauche*[−], *trans*, and *gauche*⁺ states about which torsional vibrations (or librations [15]) are activated. The consequence is that the polymer is much less extended than for the rectilinear case. The conformation of a Kuhn segment chain is often referred to as *random coil*. In the next section, we will deal with the statistics connected with the randomness of such coils.

5.2.3 Random-Coil Statistics

5.2.3.1 Gaussian Distribution of the Chain End-to-End Distance

The crucial property of random-coil conformations is that orientational correlations between any pair of Kuhn segments vanish, that is, $\langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle = b^2 \delta_{ij}$, where the Kronecker symbol is defined by $\delta_{ij} = 1$ for $i = j$ and $\delta_{ij} = 0$ for $i \neq j$. As usual, the angle brackets indicate an ensemble average. For N_K Kuhn segments per chain, the statistics of chain conformations is equivalent to that of a random walk of N_K steps of fixed step length b . In the long-chain limit, $N_K \gg 1$, the distribution function of the *random-walk displacement*, that is, the probability density for the chain end-to-end distance vector $\mathbf{r}_{ee}$, is given by a Gaussian function:

$$W(\mathbf{r}_{ee}) = \left(\frac{3}{2\pi N_K b^2} \right)^{3/2} \exp \left\{ -\frac{3r_{ee}^2}{2N_K b^2} \right\} \quad (5.22)$$

$W(\mathbf{r}_{ee})d^3r_{ee}$ is the probability to find a chain end in the volume element d^3r_{ee} in a distance r_{ee} from the other one. Equation (5.22) is also called *normal distribution* [16, 17]. Note that this expression formally coincides with the Gaussian propagator given in Eq. (2.168), the solution of Fick's second law for self-diffusion, after replacing Dt by $6^{-1}N_K b^2$ and the displacement $\mathbf{r}$ by the end-to-end distance $\mathbf{r}_{ee}$. In terms of statistical physics, the Gaussian distribution function in Eq. (5.22) is a consequence of the *central-limit theorem* for large numbers of random steps [18]. As a quantity characterizing the extension of a random coil, the *Flory radius* is defined as the root-mean-square end-to-end distance

$$R_F \equiv \sqrt{\langle r_{ee}^2 \rangle} = \sqrt{\int r_{ee}^2 W(\mathbf{r}_{ee}) d^3r_{ee}} = bN_K^{1/2} \quad (5.23)$$

where the integration covers the whole space around a chain end.

The Gaussian distribution function in Eq. (5.22) adopts a maximum for $r_{ee} = 0$. This fact must however not be interpreted in the sense that the most likely chain-end distance in an ensemble were zero. The actual distribution of chain end-to-end distances in the sense of *magnitudes* is rather obtained by integration over a spherical shell between the radii r_{ee} and $r_{ee} + \delta r_{ee}$. The result, that is, the probability for a chain-end distance between r_{ee} and $r_{ee} + \delta r_{ee}$, is $W(\mathbf{r}_{ee})4\pi r_{ee}^2 \delta r_{ee}$. Figure 5.7 illustrates the two functional relationships. On this basis, the most probable chain end-to-end distance R_p is calculated as

$$R_p = \sqrt{\frac{2\langle r_{ee}^2 \rangle}{3}} = b\sqrt{\frac{2N_K}{3}} \quad (5.24)$$

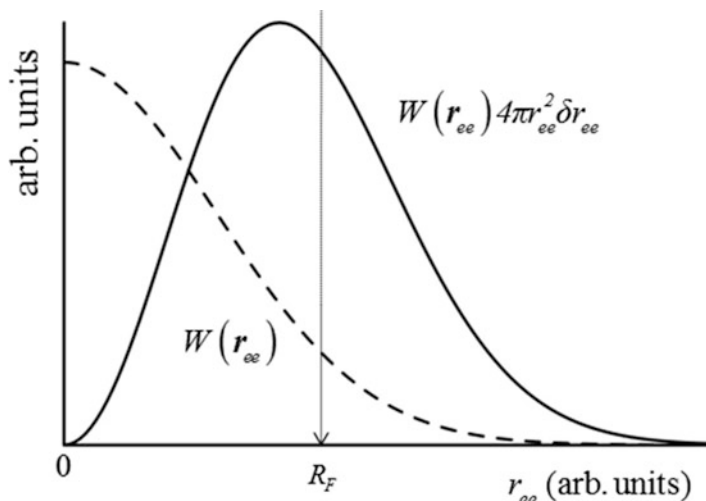


Fig. 5.7 Probability density $W(r_{ee})$ for the chain end-to-end distance vector $\mathbf{r}_{ee}$, and probability $W(r_{ee})4\pi r_{ee}^2 \delta r_{ee}$ for an end-to-end distance (magnitude) between r_{ee} and $r_{ee} + \delta r_{ee}$ as functions of r_{ee} . The Flory radius $R_F = \sqrt{\langle r_{ee}^2 \rangle}$ is indicated

which is somewhat less than the Flory radius $R_F = \sqrt{\langle r_{ee}^2 \rangle} = b\sqrt{N_K}$.

Having a closer look at the Gaussian function in Eq. (5.22), one might wonder whether a small but anyway finite probability density of finding an end-to-end distance *larger* than the chain length is predicted, that is a distance $r_{ee} > N_K b$, where $N_K b$ is the chain length. Strictly speaking, this of course cannot be. The origin of this problem is that the Gaussian distribution function in Eq. (5.22) is normalized in the range $0 \leq r_{ee} < \infty$ instead of the real limits $0 \leq r_{ee} \leq N_K b$. There are more precise approaches remedying this problem [19, 20], but these formalisms tend to be somewhat complicated. Fortunately, the deviations of the Gaussian distribution from the exact finite random-walk end-to-end distance probability density turn out to be extremely small as demonstrated by the comparison in Fig. 5.8. The rule is as follows: The larger the number of Kuhn segments per chain is, so much better the accuracy.

There is a rather general and attractive aspect of Gaussian distributions which will turn out to be most important for the treatments in later sections. Assume that the Kuhn segment length is no longer fixed as suggested by the derivation of Eq. (5.22). Rather, it can itself be thought to be subject to a Gaussian distribution. The end-to-end distance of a chain formed of such Kuhn segments of fluctuating length is then distributed in the very same way for *any* number of Kuhn segments. The Gaussian approximation is transferred to the segment level, while the distribution of the end-to-end distances of the whole chain is Gaussian in any case, not only for large Kuhn segment numbers [16]. The Kuhn length can be interpreted as the root-mean-square end-to-

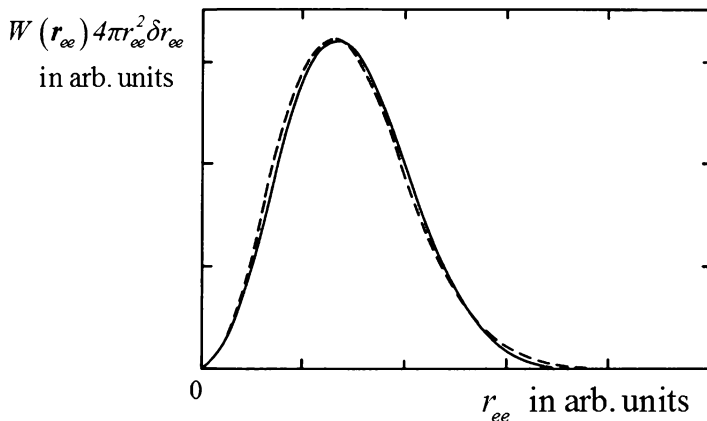


Fig. 5.8 Probability to find a chain end in a spherical shell between radii r_{ee} and $r_{ee} + \delta r_{ee}$, while the other end is fixed at the origin. The *broken line* corresponds to the Gaussian distribution in Eq. (5.22), while the *solid curve* renders the exact finite random-walk expression for a freely jointed chain of 10 Kuhn segments of fixed length. The small deviations underline the accuracy of the Gaussian approximation. (Adapted from Ref. [20])

end distance of the z chemical segments of bond length l forming the Kuhn segment. That is,¹

$$b = \sqrt{\left\langle \left(\sum_{i=1}^z l_i \right)^2 \right\rangle} \equiv \sqrt{\langle b_{ee}^2 \rangle} \quad (5.25)$$

The accordingly modified distribution function of the end-to-end vector of the whole chain is

$$W(\mathbf{r}_{ee}) = \left(\frac{3}{2\pi N_K \langle b_{ee}^2 \rangle} \right)^{3/2} \exp \left\{ -\frac{3r_{ee}^2}{2N_K \langle b_{ee}^2 \rangle} \right\} \quad (5.26)$$

and holds for any number of Kuhn segments N_K . This property of random coils is referred to as *scale invariance*: Any section of a Gaussian random coil is again subject to a Gaussian distribution [6]. For example, the distribution function of the distance $|\mathbf{R}_i - \mathbf{R}_j|$ between two Kuhn segments i and j of a random coil is given by

¹ In this context, the following remark appears to be appropriate: In the frame of the Rouse model to be described in Sect. 5.4.3, one often speaks of *subchains* having Gaussian end-to-end statistics by definition. Kuhn segments by contrast are defined primarily with regard to freely-jointed chain properties not stringently requiring a Gaussian end-to-end distribution. The above statement should therefore be taken cum grano salis. This point will be discussed further in the context of models for chain dynamics.

$$W(\mathbf{R}_i - \mathbf{R}_j) = \left(\frac{3}{2\pi N_{ij} \langle b_{ee}^2 \rangle} \right)^{3/2} \exp \left\{ -\frac{3(\mathbf{R}_i - \mathbf{R}_j)^2}{2N_{ij} \langle b_{ee}^2 \rangle} \right\} \quad (5.27)$$

where $N_{ij} = |j - i|$ is the number of Kuhn segments linking the two Kuhn segments.

A number of additional relations valid for Gaussian distributions can be established in the following way. For symmetry reasons, the *mean end-to-end distance* (or the first moment of the Gaussian distribution) vanishes. That is,

$$\langle \mathbf{r}_{ee} \rangle = \int \mathbf{r}_{ee} W(\mathbf{r}_{ee}) d^3 r_{ee} = 0 \quad (5.28)$$

Expressing $\mathbf{r}_{ee}$ by Cartesian components, x_{ee}, y_{ee}, z_{ee} likewise leads to

$$\langle x_{ee} \rangle = \langle y_{ee} \rangle = \langle z_{ee} \rangle = 0 \quad (5.29)$$

where the averages must be formed with the one-dimensional versions of the distribution function. $W(\mathbf{r}_{ee})$ can be factorized according to

$$W(\mathbf{r}_{ee}) = W_1(x_{ee})W_1(y_{ee})W_1(z_{ee}) \quad (5.30)$$

where

$$W_1(x_{ee}) = \left(\frac{3}{2\pi N_K b^2} \right)^{1/2} \exp \left\{ -\frac{3x_{ee}^2}{2N_K b^2} \right\} \quad (5.31)$$

etc.

On the other hand, the *mean-square end-to-end distance* (or the second moment of the Gaussian distribution) results in²

$$\langle r_{ee}^2 \rangle = \int r_{ee}^2 W(\mathbf{r}_{ee}) d^3 r_{ee} = N_K b^2 = L_f b \quad (5.32)$$

where the length of the freely jointed chain measured along its curvilinear contour is given by

$$L_f = N_K b \quad (5.33)$$

²The same findings can be concluded directly from the fact that the Kuhn segment vectors $\mathbf{b}_i$ of the freely jointed chain are *uncorrelated* by definition as already mentioned above. That is, $\mathbf{R}_{ee} = \sum_{i=1}^{N_K} \mathbf{b}_i$, $\langle \mathbf{R}_{ee} \rangle = \sum_{i=1}^{N_K} \langle \mathbf{b}_i \rangle = 0$, and $\langle R_{ee}^2 \rangle = \left\langle \left(\sum_{i=1}^{N_K} \mathbf{b}_i \right)^2 \right\rangle = \sum_{i,j=1}^{N_K} \langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle = \sum_{i=j=1}^{N_K} \langle b_i^2 \rangle = N_K \langle b_i^2 \rangle = N_K b^2$.

5.2.3.2 The Polymer Radius of Gyration

Instead of the root-mean-square end-to-end distance, the Flory radius, the extension of random coils can also be characterized by the *polymer radius of gyration*, which can directly be determined in light, X-ray, or neutron scattering experiments. Moreover, the polymer radius of gyration can favorably be applied for the characterization of branched polymers where end-to-end distances are ill-defined.

In classical mechanics, the conventional radius of gyration refers to a certain axis of rotation unless the object is of spherical symmetry with the center located on the rotation axis. The radius of gyration of a body is conventionally defined by

$$R_g^{\text{conv}} = \frac{I}{M} = \frac{\int r_{\perp}^2 \rho dV}{\int \rho dV} \quad (5.34)$$

where I is the (scalar) moment of inertia for rotation about an axis through the center of the mass distribution, ρ is the local mean mass density, M is the total mass of the molecule, and $r_{\perp}$ is the distance of the volume element dV from the rotation axis.

The problem is that this definition is not directly applicable to flexible polymers for two reasons. First of all, the conformation of a polymer coil is fluctuating and can adopt practically infinitely many spatial mass distributions. A definition is therefore only possible in the form of a root-mean-square value representing the ensemble average over all molecules in a sample. Secondly, there is no symmetry axis relative to which one could define a moment of inertia as it is sometimes possible with small molecules. For a given conformation of a homopolymer, one therefore refers to the center of mass the position vector of which is given by

$$\mathbf{R}_{\text{cm}} = \frac{1}{N} \sum_{i=1}^N \mathbf{R}_i \quad (5.35)$$

The vector $\mathbf{R}_i$ defines the position of the i th chemical segment, and N is the number of chemical segments per chain. In contrast to Eq. (5.34), the *polymer radius of gyration* is then defined by the root-mean-square

$$R_g = \sqrt{\frac{1}{N} \sum_{i=1}^N \langle (\mathbf{R}_i - \mathbf{R}_{\text{cm}})^2 \rangle} \quad (5.36)$$

The angle brackets indicate the ensemble average. A more adequate but less common terminology would be that R_g^2 is the *second moment of the mass distribution about the center of mass*.

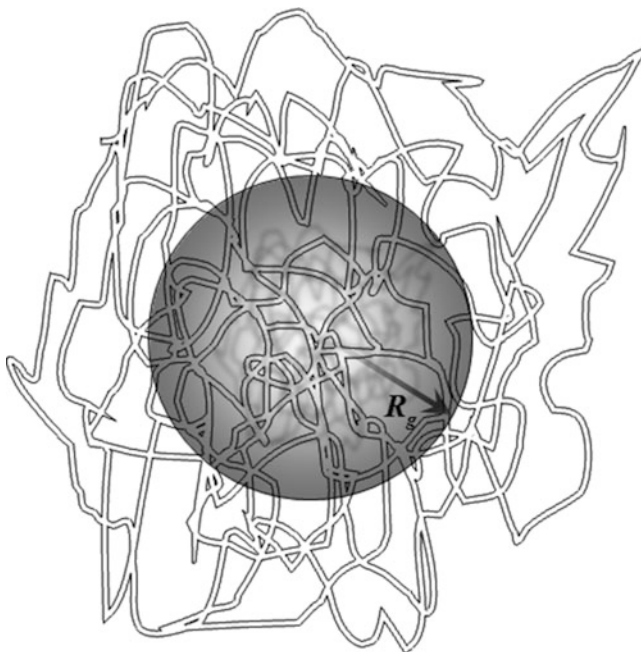


Fig. 5.9 Schematic illustration of the polymer radius of gyration R_g of a random coil. The spatial mass distribution of the polymer is considered as an average over all possible conformations. The polymer radius of gyration, Eq. (5.36), is the radius of a representative *thin spherical shell* about the center of mass in which the whole mass is thought to be concentrated

While the conventional definition, Eq. (5.34), is based on distances $r_\perp$ perpendicular to a given axis preferably reflecting some symmetry of the object, the polymer radius of gyration is not formed relative to an axis but relative to a point, namely, the center of mass. The average mass distribution in space is taken to be equivalent to a thin spherical shell of radius R_g about the center of mass. The total mass of the polymer is thought to be concentrated in this shell as illustrated in Fig. 5.9. In this sense, the symmetry underlying this definition is spherical.

Inserting Eq. (5.35), the expression in Eq. (5.36) can be reformulated as

$$R_g = \sqrt{\frac{1}{2N^2} \sum_{i,j=1}^N \langle (\mathbf{R}_i - \mathbf{R}_j)^2 \rangle} \quad (5.37)$$

The equivalence of Eqs. (5.36) and (5.37) can be shown by the following conversions. Let us first consider Eq. (5.36). Disregarding the angle brackets and the square root for the moment, the sum term can be reformulated as

$$\begin{aligned}
\frac{1}{N} \sum_{i=1}^N (\mathbf{R}_i - \mathbf{R}_{\text{cm}})^2 &= \frac{1}{N} \sum_{i=1}^N (\mathbf{R}_i \cdot \mathbf{R}_i + \mathbf{R}_{\text{cm}} \cdot \mathbf{R}_{\text{cm}} - 2\mathbf{R}_i \cdot \mathbf{R}_{\text{cm}}) \\
&= \frac{1}{N} \left(\sum_{i=1}^N (\mathbf{R}_i \cdot \mathbf{R}_i) + \sum_{i=1}^N (\mathbf{R}_{\text{cm}} \cdot \mathbf{R}_{\text{cm}}) - \sum_{i=1}^N (2\mathbf{R}_i \cdot \mathbf{R}_{\text{cm}}) \right) \\
&= \frac{1}{N} \left(\sum_{i=1}^N (\mathbf{R}_i \cdot \mathbf{R}_i) + N(\mathbf{R}_{\text{cm}} \cdot \mathbf{R}_{\text{cm}}) - 2N(\mathbf{R}_{\text{cm}} \cdot \mathbf{R}_{\text{cm}}) \right) \\
&= \frac{1}{N} \left(\sum_{i=1}^N (\mathbf{R}_i \cdot \mathbf{R}_i) - N(\mathbf{R}_{\text{cm}} \cdot \mathbf{R}_{\text{cm}}) \right) \tag{5.38}
\end{aligned}$$

where we have employed Eq. (5.35). Likewise, the sum term in Eq. (5.37) can be rewritten as

$$\begin{aligned}
\frac{1}{2N^2} \sum_{i,j=1}^N (\mathbf{R}_i - \mathbf{R}_j)^2 &= \frac{1}{2N^2} \sum_{i,j=1}^N (\mathbf{R}_i \cdot \mathbf{R}_i + \mathbf{R}_j \cdot \mathbf{R}_j - 2\mathbf{R}_i \cdot \mathbf{R}_j) \\
&= \frac{1}{2N^2} \sum_{i,j=1}^N (\mathbf{R}_i \cdot \mathbf{R}_i + \mathbf{R}_j \cdot \mathbf{R}_j) - \left(\frac{1}{N} \sum_{i=1}^N \mathbf{R}_i \right) \cdot \left(\frac{1}{N} \sum_{j=1}^N \mathbf{R}_j \right) \\
&= \frac{1}{N} \left(\sum_{i=1}^N (\mathbf{R}_i \cdot \mathbf{R}_i) - N(\mathbf{R}_{\text{cm}} \cdot \mathbf{R}_{\text{cm}}) \right) \tag{5.39}
\end{aligned}$$

The last lines of Eqs. (5.38) and (5.39) are obviously identical. Reintroducing the angle brackets and the square roots thus demonstrates that the two expressions for R_g in Eqs. (5.36) and (5.37) are equal.

Recalling the scale-invariance property, namely, that any section of sufficient length of a freely jointed chain is subject to a Gaussian distribution of the end-to-end distance, suggests

$$\left\langle (\mathbf{R}_i - \mathbf{R}_j)^2 \right\rangle = \left\langle \mathbf{r}_{ij}^2 \right\rangle = N_{ij} b^2 \tag{5.40}$$

where b is the Kuhn length. $N_{ij} = |j - i|$ is the number of Kuhn segments in the chain section under consideration with the end-to-end distance $\mathbf{r}_{ij} = \mathbf{R}_i - \mathbf{R}_j$. Equation (5.37) thus becomes

$$R_g = \sqrt{\frac{1}{2N_K^2} \sum_{i,j=1}^{N_K} \left\langle (\mathbf{R}_i - \mathbf{R}_j)^2 \right\rangle} = \sqrt{\frac{b^2}{2N_K^2} \sum_{i,j=1}^{N_K} N_{ij}} \tag{5.41}$$

In the limit $N_K \gg 1$, the sum in the square root can be approximated by $\sum_{i,j=1}^{N_K} N_{ij}$
 $= \sum_{i,j=1}^{N_K} |j - i| = \frac{N_K^3}{3} - \frac{N_K}{3} \approx \frac{N_K^3}{3}$, so that

$$R_g \approx b \sqrt{\frac{N_K}{6}} = \sqrt{\frac{\langle r_{ce}^2 \rangle}{6}} \quad (5.42)$$

for sufficiently long chains with Gaussian end-to-end statistics. The polymer radius of gyration of a random coil is smaller than the Flory radius by a factor of $1/\sqrt{6}$. The Gaussian chain statistics anticipated in the derivation of Eqs. (5.32) and (5.42) is an idealization not taking into account long-range interactions between Kuhn segments. An example is the so-called *excluded-volume effect*. This problem will be discussed in more detail in the section after next.

5.2.4 Worm-Like Chain Model and Persistence Length

As an alternative to the Kuhn segment chain, Kratky and Porod suggested the worm-like chain model [21, 22]. Consider two (chemical) chain segments at positions $\mathbf{R}(s_0)$ and $\mathbf{R}(s_1)$, where s_0 and s_1 are curvilinear coordinates along the chain as schematically shown in Fig. 5.10. The correlation function of the tangential unit vector $\mathbf{u}(s) = \partial \mathbf{R}(s)/\partial s$ at these positions is defined by

$$G(s_0, s_1) \equiv \langle \mathbf{u}(s_1) \cdot \mathbf{u}(s_0) \rangle \quad (5.43)$$

Designating the angle between the two tangential unit vectors by $\vartheta_{\Delta s}$, the correlation function can be expressed as

$$G(s_0, s_1) = \langle \mathbf{u}(s_0 + \Delta s) \cdot \mathbf{u}(s_0) \rangle = \langle \cos \vartheta_{\Delta s} \rangle \quad (5.44)$$

Let the number of chemical segments in the relevant chain section of length $\Delta s = s_1 - s_0$ be k . For a valence-angle chain like the one depicted in Fig. 5.4, the cosine of the angle $\vartheta_{\Delta s}$ can then be replaced by k -fold application of the projection cosine of the valence angle ϑ :

$$G(s_0, s_1) = \langle \cos^k \vartheta \rangle \quad (5.45)$$

Since the valence angle ϑ is fixed due to the structural restraints of chemical segments, the ensemble average represented by the angle brackets is irrelevant here, and the brackets can be omitted. Equation (5.45) can then be expressed as

$$G(s_0, s_1) = \cos^k \vartheta \equiv \exp\{k \ln(\cos \vartheta)\} \equiv \exp\{-k |\ln(\cos \vartheta)|\} \quad (5.46)$$

As a matter of course, the valence angle is restricted to the range $0 \leq \vartheta \leq \pi/2$.

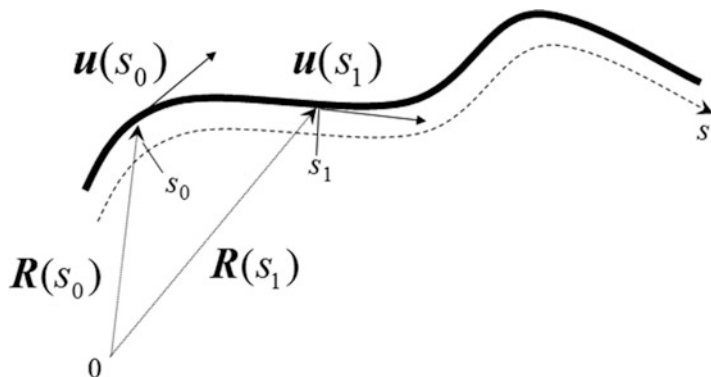


Fig. 5.10 Illustration of the wormlike chain model. The curvilinear coordinates s (*dashed line*) follow the contour of the chain (*fat line*). This concept refers to tangential unit vectors $\mathbf{u}(s_0)$ and $\mathbf{u}(s_1)$ at the positions defined either by the respective curvilinear coordinates s_0 and s_1 or the position vectors $\mathbf{R}(s_0)$ and $\mathbf{R}(s_1)$

Auto correlation functions of Markovian systems are even and depend merely on the magnitude of the variable difference. In the present case, the curvilinear coordinates s_0 and s_1 can therefore be replaced by the curvilinear contour-length distance $|\Delta s| = |s_1 - s_0| = kl'$, where l' is the projection of the skeletal bond length on the main-chain axis (compare Eq. 5.20). The absolute value of the curvilinear coordinate s_0 of the chemical segment is insignificant, so that $G(s_0, s_1) = G(|\Delta s|)$. With the substitution $k = l'/|\Delta s|$, Eq. (5.46) can be reformulated as

$$G(|\Delta s|) = \exp \left\{ -\frac{|\Delta s|}{l_p} \right\} \quad (5.47)$$

where the *persistence length* is defined by

$$l_p \equiv \frac{l'}{|\ln \cos \vartheta|} \quad (5.48)$$

This parameter characterizes the *rigidity* of the chain (or, in inverse form, its *flexibility*). Since the correlation function in Eq. (5.47) refers to the orientation of chemical segments, the persistence length may synonymously be termed *orientation correlation length*. Long persistence lengths lead to more extended chain conformations, while short values indicate that chains are tightly coiled. For small valence angles, $\vartheta \rightarrow 0$, the persistence length becomes correspondingly long, $l_p \rightarrow \infty$. The chain adopts a rectilinear conformation in this limit.

The above derivation of the correlation function in Eq. (5.47) is based on fixed valence angles ϑ . In the case of a freely jointed chain consisting of Kuhn segments $\mathbf{b}_v = b\mathbf{u}_v$, no orientation correlation can be expected for curvilinear distances $s > b$ by definition. The parameters l_p and b of the wormlike and freely jointed chain

models, respectively, are nevertheless related with each other in the long-chain limit. This can be shown in the following way.

The mean-square end-to-end distance of a freely jointed (Kuhn) chain can be expressed as

$$\langle \mathbf{r}_{ee}^2 \rangle \equiv \langle \mathbf{r}_{ee} \cdot \mathbf{r}_{ee} \rangle = \sum_{i,j=1}^{N_K} \langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle \quad (5.49)$$

where N_K is the number of Kuhn segments per chain (see footnote 2). In the limit of long contour lengths ($L \gg b$), that is, large numbers of Kuhn segments ($N_K \gg 1$), a continuous-variable approach becomes adequate. The sums can then be replaced by integrals over curvilinear coordinates of the Kuhn segments in the sense of the definition illustrated in Fig. 5.10. With the tangential unit vector $\mathbf{u}(s) = \partial \mathbf{R}(s)/\partial s$ at the curvilinear position s , the end-to-end vector can be represented in integral form as

$$\mathbf{r}_{ee} = \int_0^L \mathbf{u}(s) ds \quad (5.50)$$

The mean-square end-to-end distance consequently obeys

$$\langle \mathbf{r}_{ee}^2 \rangle \equiv \langle \mathbf{r}_{ee} \cdot \mathbf{r}_{ee} \rangle = \int_0^L ds' \int_0^L ds'' \langle \mathbf{u}(s') \cdot \mathbf{u}(s'') \rangle = \int_0^L ds' \int_0^L ds'' G(|\Delta s|) \quad (5.51)$$

where the correlation function $G(|\Delta s|)$ is defined in Eq. (5.43).

Substituting the variables s' and s'' by the new set $\Delta s = s'' - s'$ and s' , and integrating over all possible combinations of these variables, gives

$$\langle \mathbf{r}_{ee}^2 \rangle = \underbrace{\int_0^L d\Delta s \left[G(|\Delta s|) \int_0^{L-\Delta s} ds' \right]}_{\Delta s > 0} + \underbrace{\int_{-L}^0 d\Delta s \left[G(|\Delta s|) \int_{-\Delta s}^L ds' \right]}_{\Delta s < 0} \quad (5.52)$$

The first term on the right-hand side refers to *positive* values of Δs . The inner integration therefore ranges from $s' = 0$ to $s' = L - \Delta s$, while the limits of the outer integral refers to the whole chain length from 0 to L . The second term on the right-hand side is valid for *negative* Δs , so that the inner integration extends from $s' = -\Delta s = |\Delta s|$ to $s' = L$ and the outer integral covers the range from $\Delta s = -L$ to $\Delta s = 0$. Both terms obviously yield identical results, so that the sum can be replaced by twice the first term. Inserting the expression for the correlation function $G(|\Delta s|)$ given in Eq. (5.47) and carrying out the integrations give

$$\langle r_{ee}^2 \rangle = 2 \left[Ll_p + l_p^2 \left(e^{-\frac{L}{l_p}} - 1 \right) \right] \quad (5.53)$$

In the (extreme) limit $L \gg l_p$, the second term in the brackets can be neglected so that

$$\langle r_{ee}^2 \rangle \approx 2Ll_p = 2N_K b l_p \quad (5.54)$$

On the other hand, the mean-square end-to-end distance of a freely jointed chain was found to be

$$\langle r_{ee}^2 \rangle = N_K b^2 \quad (5.55)$$

The comparison of the last two equations provides the result to be demonstrated:

$$b = 2l_p \quad (5.56)$$

In the long-chain limit, the Kuhn length is twice the persistence length.

5.2.5 *The Real-World Polymer, Excluded-Volume Effect, and Θ -Conditions*

As noted above, the freely jointed, infinitely thin polymer-chain model is an idealization under several aspects. The situation becomes more realistic if the so-called excluded-volume effect and interactions in the presence of solvent molecules in solutions are taken into account. The excluded-volume effect arises if distant chemical segments of the same chain approach each other on a subnanometer length scale. Van der Waals attraction and Coulomb and Pauli repulsion by orbital overlap will then be effective. If measured in curvilinear coordinates along the polymer chain, one can speak of long-distance interactions of segments. However, relative to Euclidean space, the distances must be short enough to ensure perceptible attraction or repulsion. Long-range forces across Euclidean space are only relevant with charged groups such as in polyelectrolytes which are subject to Coulomb interaction on length scales far beyond van der Waals radii.

Note that steric hindrance of rotations about main-chain valence bonds due to bulky side groups of neighboring chemical segments is not meant when we refer to excluded-volume effects. Sterical obstruction of rotational isomerism is rather implied in the definitions of the Kuhn segment or the persistence length. Provided a polymer is long enough, steric side group hindrance is not a source of deviations from ideal coil statistics. Merely the Kuhn length varies as demonstrated by the values for different polymer species listed in Table 5.1.

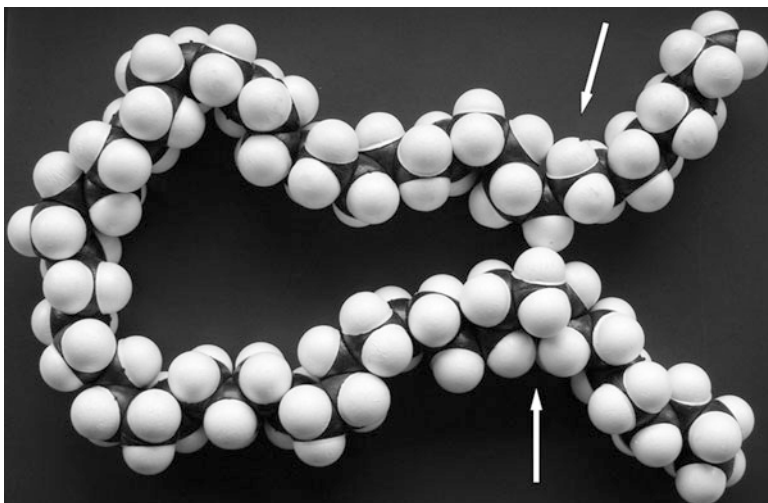


Fig. 5.11 Space-filling atom model of a polyethylene chain (white $\rightarrow$ hydrogen, black $\rightarrow$ carbon). The arrows indicate a situation where the excluded-volume effect of remote segments restricts possible conformations

Excluded-volume effects and polymer–solvent interactions will have an impact on the variety of possible chain conformations. The mean extension of coiled conformations will largely depend on such factors. A quantity specifying this is the *characteristic ratio* which we know already from Eq. (5.18):

$$C_{\infty} = \frac{\langle r_{ee}^2 \rangle}{Nl^2} \geq 1 \quad (N \gg 1) \quad (5.57)$$

l is the length of a chemical segment, and N is the number of chemical segments per chain. The characteristic ratio ranges from the value 1 for freely jointed chains to 4–12 in the case of real polymers. A number of representative examples are listed in Ref. [6] (Chapter II, Table 1).

5.2.5.1 Consequences of the Excluded-Volume Effect

Figure 5.11 illustrates the repulsion of chemical segments due to Pauli's exclusion principle, prohibiting interpenetration of electron orbitals of different segments, and due to Coulomb interaction of charged bodies of the same polarity. The consequence is that random-coil conformations tend to be more extended than they would be in the ideal-chain case. Excluded volume is therefore expected to affect the scaling of the end-to-end distance. An approximate treatment of this effect was originally suggested by Flory [23]. The principle is to formulate an expression for the *conformational Helmholtz free energy* (in the terminology of

statistical physics: *configurational Helmholtz free energy*) of a chain, ΔA_H , as a function of the end-to-end distance r_{ee} :

$$\Delta A_H = \Delta U - T\Delta S_{\text{conf}} = f(r_{ee}) \quad (5.58)$$

ΔU is the internal energy, and ΔS_{conf} is the entropy contribution connected with the conformation of the chain. The equilibrium end-to-end distance, that is, the root-mean-square end-to-end distance $\sqrt{\langle r_{ee}^2 \rangle}$, corresponds to the minimum of ΔA_H which can be found as follows.

The *conformational entropy* of a chain can be expressed with the aid of Boltzmann's formula

$$\Delta S_{\text{conf}} = k_B \ln \{ \Omega(r_{ee}) \} \quad (5.59)$$

$\Omega(r_{ee})$ is the number of conformations³ compatible with an end-to-end distance vector $\mathbf{r}_{ee}$. Boltzmann's constant is denoted by k_B . Note that this contribution selectively addresses the possible chain conformations, but does not include phase-space entropy which is not of interest in the present context.⁴

Assuming Gaussian chain statistics again, that is, the validity of Eq. (5.22) for the distribution function $W(\mathbf{r}_{ee})$ of the end-to-end vector $\mathbf{r}_{ee}$, the number of conformations compatible with a certain vector $\mathbf{r}_{ee}$ will be proportional to the probability that this vector points in the volume element dV (see Fig. 5.12):

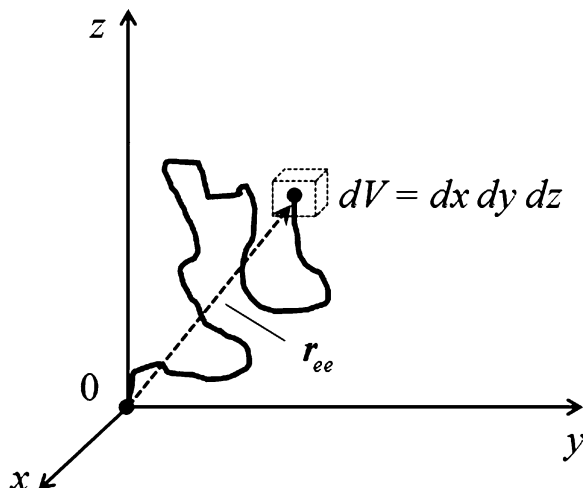
$$\begin{aligned} \Omega(\mathbf{r}_{ee}) &\propto W(\mathbf{r}_{ee})dV = \left(\frac{3}{2\pi N_K b^2} \right)^{3/2} \exp \left\{ -\frac{3r_{ee}^2}{2N_K b^2} \right\} dV \\ &\propto \exp \left\{ -\frac{3r_{ee}^2}{2N_K b^2} \right\} \end{aligned} \quad (5.60)$$

Combining Eqs. (5.59) and (5.60) leads to

³ The use of the term “number” is a bit delicate here but anyway justified: The quantity $\Omega(\mathbf{r}_{ee})$ actually numbers the *microstates* compatible with a certain *macro-state*. In the present case, a macrostate is defined by a certain end-to-end distance vector $\mathbf{r}_{ee}$. In principle, this number is not infinite, as one might suspect, since micro-states must be considered as quantum states. That is, the position and the momentum of a segment can only be defined with an accuracy limited by Heisenberg's uncertainty relation on the basis of Planck's finite constant h . One thus differentiates the classical approach of a *continuous* distribution of polymer conformations and the *discrete* quantum mechanical set of micro-states.

⁴ A well-known example of *phase-space entropy* is the volume-dependent expression for ideal gases. This sort of entropy contribution will be considered in Sect. 5.4.2.2 in the context of entropy-elastic forces.

Fig. 5.12 End-to-end distance vector between one chain end fixed at the origin and the other in a volume element dV . The configurational entropy contribution represents all chain conformations compatible with these end points



$$\Delta S_{\text{conf}} = k_B \ln\{\Omega(r_{ee})\} = \text{const} - k_B \frac{3r_{ee}^2}{2N_K b^2} \quad (5.61)$$

The first term contributing to the Helmholtz free energy in Eq. (5.58), the *internal energy* ΔU of a chain, reflects inter-segmental interactions. In principle, these interactions are a matter of the molecular orbitals, that is, of chemical segments. Since the approach on which Eq. (5.61) is based refers to the Gaussian statistics of freely jointed chains, we will nevertheless speak somewhat loosely of Kuhn segments in the following. Actually, this mild imprecision pays tribute to the approximative character of the current treatment.

The internal energy can be estimated with the aid of a probability consideration. The interaction is assumed to be effective if two Kuhn segments approach each other in a volume element δV small enough to accommodate just two of such elements (compare Fig. 5.11). The probability that a *single* Kuhn segment of the chain under consideration is found in that volume element is $w_1 = N_K \delta V / V$, where $V = \gamma r_{ee}^3$ is the effective volume of the random coil and γ is a numerical factor. The probability that *two* Kuhn segments are located simultaneously in that volume element is consequently $w_2 = (N_K \delta V / V)^2$, where we ignore the influence of chain connectivity for simplicity. With the number $N_{\delta V} = V / \delta V$ of volume elements δV in the total volume of the chain, V , we can thus calculate the number of interacting Kuhn segment pairs per chain as

$$w_2 N_{\delta V} = N_K^2 \frac{\delta V}{V} \quad (5.62)$$

The mean interaction energy contributing to the internal energy is provided by thermal energy, that is, $\alpha k_B T$ per interacting segment pair, where α is a numerical factor. Taking the internal energy of all Kuhn segment pairs interacting in a chain together gives

$$\Delta U = \alpha k_B T N_{\delta V} = \alpha k_B T \frac{N_K^2}{V} \delta V = \alpha k_B T \frac{N_K^2}{\gamma r_{ee}^3} \delta V \quad (5.63)$$

Substituting Eqs. (5.61) and (5.63) into Eq. (5.58) results in the following expression of the conformational Helmholtz free energy:

$$\Delta A_H = k_B T \left(\frac{\alpha N_K^2 \delta V}{\gamma r_{ee}^3} + \frac{3 r_{ee}^2}{2 N_K b^2} - \text{const} \right) \quad (5.64)$$

The minimum of this function complies with the condition

$$\frac{\partial(\Delta A_H)}{\partial r_{ee}} = k_B T \left(-3 \frac{\alpha N_K^2 \delta V}{\gamma r_{ee}^4} + 3 \frac{r_{ee}}{N_K b^2} \right) = 0 \quad (5.65)$$

The end-to-end distance for minimum Helmholtz free energy consequently obeys

$$(r_{ee})_{\min} = \sqrt{\langle r_{ee}^2 \rangle} \propto N_K^{3/5} \quad (5.66)$$

instead of the proportionality $\propto N_K^{1/2}$ valid in the absence of the excluded-volume effect (see Eq. 5.23). The value of the exponent 3/5 of this elementary estimation is very well reproduced by less simplistic Monte Carlo simulations and renormalization group studies [1, 7, 9], so that the presuppositions made in the derivation can thus be considered to be sanctioned.

5.2.5.2 Solutions Under Θ -Conditions

In solutions of polymers in (low-molecular) solvents, polymer–solvent interactions will specifically contribute to thermodynamic potentials. In particular, the distribution of chain conformations depends on whether segment–segment or segment–solvent interactions are energetically and entropically more favorable. In this sense, one distinguishes good solvents from poor solvents.

In a *good solvent*, polymer–solvent contacts are thermodynamically more advantageous than solvent–solvent or segment–segment contacts. The polymer molecules consequently tend to be surrounded by more or less tightly bound solvation shells. The extension of the polymer coil is therefore *increased* relative to the pure polymer melt. Instead of the linear relation in Eq. (5.32) for an ideal random coil, the mean-square end-to-end distance then scales with the number of Kuhn segments as

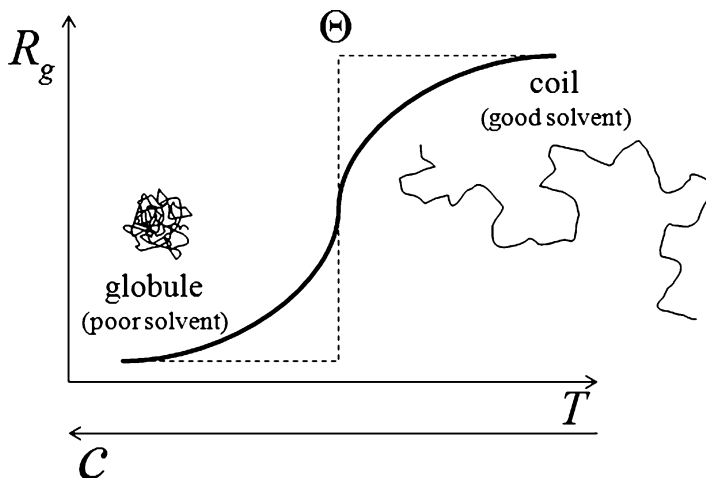


Fig. 5.13 Schematic representation of the globule–coil transition at the Θ -point upon variation of the temperature T or of the polymer concentration c [25–27]

$$\langle r_{ee}^2 \rangle \propto N_K^{1+\varepsilon} \quad (5.67)$$

The empirical exponent $\varepsilon = 0 \dots 0.2$ depends on the species in the solute–solvent pair and on experimental parameters such as the temperature and the concentration.

The opposite effect arises in *poor solvents*. Segment–segment and solvent–solvent interactions are then more beneficial with respect to potential energy and entropy. The polymer coil dimension will consequently be reduced in equilibrium. Even some tendency to counteract and compensate the expansion by the excluded-volume effect may arise on these grounds. Note that the concentration range of solutions in poor solvents will be limited by a certain tendency of precipitation.

If the excluded-volume expansion is completely compensated by solution in a poor solvent, the system is said to be at the Θ -point, the *theta* or *Flory temperature*, characteristic for the polymer–solvent pair, the concentration, and possibly also depending on the molecular mass. Under Θ -conditions, chain conformations are governed by Gaussian end-to-end statistics so that $\varepsilon = 0$ in Eq. (5.67). Empirical values of the Θ -temperature for numerous polymer–solvent systems can be found in Ref. [1], for instance.

Varying the temperature or the concentration across the Θ -point leads to the so-called *coil–globule* (or *globule–coil*) *transition* [24] as illustrated in Fig. 5.13. “Globule” means that the coil collapses to a compact object exposing minimal interaction surface to the solvent. As a consequence of crossing the Θ -point by variation of temperature or concentration, the character of the solvent will change from “good” to “poor” or vice versa. The rather abrupt crossover of the coil dimensions upon variation of the temperature or the concentration can be measured in terms of the polymer radius of gyration with the aid of *static light scattering* [25–27].

5.3 Elastic Modules of Permanent Polymer Networks

Many polymer species can be cross-linked covalently so that they form three-dimensional networks consisting of more or less tight meshes. A schematic illustration is shown in Fig. 5.14a. The best known example is rubber which essentially consists of vulcanized polyisoprene. This sort of material is of practical interest because of its *entropy-elastic properties* sometimes referred to as rubber elasticity. The purpose of the present section is to derive corresponding expressions for Young's modulus E_0 and for the shear modulus G_0 . In contrast to *dynamic* deformation phenomena to be discussed later in Sect. 5.4.3.9, for instance, we will refer first to *static* deformations of permanently cross-linked materials. The following treatment is restricted to the Hookean limit, that is, small deformations where linear stress/strain relations can be expected as introduced in Sect. 2.3.3.

In the following, the section between two neighboring cross-links will be termed *mesh chain*. In the simplest case, the network consists of mesh chains of equal contour length L . Each mesh chain is assumed to be composed of $N_K \gg 1$ freely jointed (Kuhn) segments of length b . The end-to-end distance r_{ee} can then be taken to be distributed according to Gaussian statistics. Straining such a network will deform each of the mesh chains. The end-to-end distance vector $\mathbf{r}_{ee}$ of a certain mesh chain with the Cartesian components x_{ee}, y_{ee}, z_{ee} will be converted to the vector $\mathbf{r}'_{ee}$ with the components

$$x'_{ee} = \lambda_x x_{ee}, \quad y'_{ee} = \lambda_y y_{ee}, \quad z'_{ee} = \lambda_z z_{ee} \quad (5.68)$$

$\lambda_x, \lambda_y, \lambda_z$ are the *affine deformation factors* for the three space directions (see Fig. 5.14b).

As the denomination “entropy elasticity” suggests, the entropy of the system changes upon deformation. Let us therefore begin with the statistics of mesh chains in a network. The probability that the magnitude of the end-to-end distance of an undeformed mesh chain is found between r_{ee} and $r_{ee} + dr_{ee}$, that is, that the vector $\mathbf{r}_{ee}$ points in a spherical shell of volume $4\pi r_{ee}^2 dr_{ee}$, is given by the Gaussian expression

$$W(\mathbf{r}_{ee}) 4\pi r_{ee}^2 dr_{ee} = \left(\frac{3}{2\pi N_K b^2} \right)^{3/2} \exp \left\{ -\frac{3}{2N_K b^2} r_{ee}^2 \right\} 4\pi r_{ee}^2 dr_{ee} \quad (5.69)$$

as suggested by Eq. (5.22). On this basis, each mesh chain contributes an amount

$$S_{\text{mesh}} = \text{const} - k_B \frac{3r_{ee}^2}{2N_K b^2} \quad (5.70)$$

to the conformational entropy (see Eq. 5.61). Likewise, in the *deformed* state, the conformational entropy contribution is

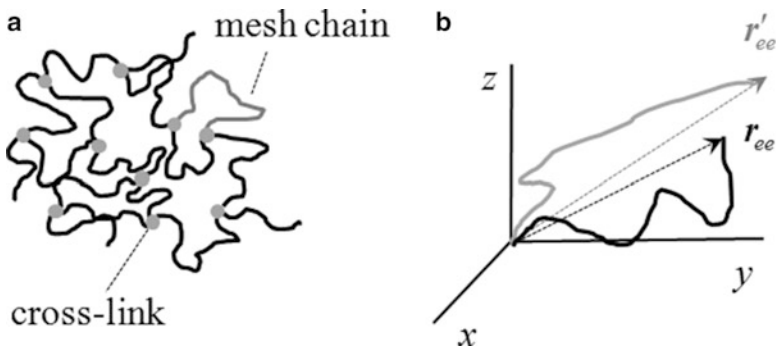


Fig. 5.14 (a) Schematic representation of a polymer network formed of permanently cross-linked mesh chains of equal length. (b) End-to-end vectors r_{ee} and r'_{ee} of representative mesh chain conformations as they could occur before and after deformation, respectively

$$S'_{\text{mesh}} = \text{const} - k_B \frac{3}{2N_K b^2} \left(\lambda_x^2 x_{ee}^2 + \lambda_y^2 y_{ee}^2 + \lambda_z^2 z_{ee}^2 \right) \quad (5.71)$$

The entropy change per mesh chain upon deformation is consequently

$$\begin{aligned} \delta S_{\text{mesh}} &= S'_{\text{mesh}} - S_{\text{mesh}} \\ &= -k_B \frac{3}{2N_K b^2} \left\{ (\lambda_x^2 - 1) x_{ee}^2 + (\lambda_y^2 - 1) y_{ee}^2 + (\lambda_z^2 - 1) z_{ee}^2 \right\} \end{aligned} \quad (5.72)$$

Summing up over all N mesh chains in a volume V gives the total entropy change per unit volume

$$\begin{aligned} \frac{\delta S_N}{V} &= \frac{1}{V} \sum_1^N \delta S_{\text{mesh}} \\ &= -\frac{3k_B}{2N_K b^2 V} \\ &\quad \times \left\{ (\lambda_x^2 - 1) \sum_1^N x_{ee}^2 + (\lambda_y^2 - 1) \sum_1^N y_{ee}^2 + (\lambda_z^2 - 1) \sum_1^N z_{ee}^2 \right\} \end{aligned} \quad (5.73)$$

In the undeformed state, the mesh chains can be assumed to be isotropically distributed, so that

$$\sum_1^N x_{ee}^2 = \sum_1^N y_{ee}^2 = \sum_1^N z_{ee}^2 = \frac{1}{3} \sum_1^N r_{ee}^2 = \frac{1}{3} N \langle r_{ee}^2 \rangle = \frac{1}{3} N N_K b^2 \quad (5.74)$$

where the last expression on the right-hand side implies Eq. (5.32). Inserting Eq. (5.74) into Eq. (5.73) gives

$$\frac{\delta S_N}{V} = -\frac{1}{2} \frac{Nk_B}{V} \left\{ \lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 \right\} \quad (5.75)$$

As a condensed material, the system can be taken to be practically incompressible. That is, a volume element $\Delta x \Delta y \Delta z$ of the undeformed material does not change during deformation:

$$\Delta x' \Delta y' \Delta z' = \lambda_x \Delta x \lambda_y \Delta y \lambda_z \Delta z = \Delta x \Delta y \Delta z \quad (5.76)$$

The affine deformation factors consequently obey the condition

$$\lambda_x \lambda_y \lambda_z = 1 \quad (5.77)$$

Consider now an elongation λ_x of the sample exclusively along the x -axis, for example. From Eq. (5.77), one can then infer that the other two affine deformation factors, that is, λ_y and λ_z , must be equal owing to the isotropy anticipated for the undeformed system. Therefore,

$$\lambda_y = \lambda_z = \lambda_x^{-1/2} = \lambda^{-1/2} \quad (5.78)$$

where we have replaced λ_x by the unspecified elongation λ for the sake of generalization. On this basis, Eq. (5.75) can be converted into

$$\frac{\delta S_N}{V} = -\frac{1}{2} \frac{Nk_B}{V} \left\{ \lambda^2 + \frac{2}{\lambda} - 3 \right\} \quad (5.79)$$

Deformations are the consequence of work exerted on the material. In this respect, let us now consider the first law of thermodynamics. The change of the internal energy per unit volume, $\delta U_N/V$, in the system is given by the sum of the elastic work per unit volume, $\delta W_N^{\text{elast}}/V$, and the change of heat per unit volume, $\delta Q_N/V$:

$$\frac{\delta U_N}{V} = \frac{\delta W_N^{\text{elast}}}{V} + \frac{\delta Q_N}{V} \quad (5.80)$$

For further treatment, we assume that the deformation process is carried out reversibly. That is, the deformation is performed in such a way that the system practically stays in permanent thermal equilibrium, or, in other terms, that the elongation is thought to be carried out infinitely slowly. In this limit, the heat variation can be quantified as

$$\frac{\delta Q_N}{V} = T \frac{\delta S_N}{V} \quad (5.81)$$

Furthermore, free joints of the mesh chains stipulate that the internal energy remains constant, that is, $\delta U_N = 0$. The elastic work per unit volume applied to the material thus becomes

$$\frac{\delta W_N^{\text{elast}}}{V} = -\frac{\delta Q_N}{V} = -T \frac{\delta S_N}{V} = -\frac{1}{2} \frac{Nk_B T}{V} \left\{ \lambda^2 + \frac{2}{\lambda} - 3 \right\} \quad (5.82)$$

Since the elongation considered here is assumed to be aligned along the x -axis, the stress acting on the N mesh chains in the volume V is calculated via the negative derivative of the elastic work along this coordinate axis with respect to λ :

$$\sigma_{xx} = -\frac{1}{V} \frac{\partial \delta W_N^{\text{elast}}}{\partial \lambda} = \frac{Nk_B T}{V} \left\{ \lambda - \frac{1}{\lambda^2} \right\} \quad (5.83)$$

This is the normal stress component defined as the force per unit area acting in x direction on a surface with the normal aligned in x direction as well (see Eq. 2.78). In terms of the affine deformation factors defined in Eqs. (5.68) and (5.78), the mesh chains are deformed along the x -axis according to

$$x'_{ee} = x_{ee} + \delta x_{ee} = \left(1 + \frac{\delta x_{ee}}{x_{ee}} \right) x_{ee} = \lambda x_{ee} \quad (5.84)$$

With the isochore and isothermal elongation $\varepsilon_{xx} = \delta x_{ee}/x_{ee}$, this equation can be represented by

$$\lambda = 1 + \varepsilon_{xx} \quad (5.85)$$

Combining Eq. (5.85) with Eq. (5.83) results in the first-order approximation

$$\sigma_{xx} \approx \frac{3Nk_B T}{V} \varepsilon_{xx} \quad (5.86)$$

in the limit $\varepsilon_{xx} \ll 1$. Comparing this with Eq. (2.117) leads to the relation

$$E = \frac{3Nk_B T}{V} = 3 \frac{\rho N_A k_B T}{M_{\text{mesh}}} \quad (5.87)$$

for *Young's modulus* of the network, where ρ is the density of the material, N_A is Avogadro's number, and M_{mesh} is the molecular mass of a mesh chain. Recalling that we have assumed an incompressible material, we can use Eq. (2.126) to obtain an expression for the *shear modulus* from Eq. (5.87):

$$G = \frac{Nk_B T}{V} = \frac{\rho N_A k_B T}{M_{\text{mesh}}} = \frac{\rho RT}{M_{\text{mesh}}} \quad (5.88)$$

$R = N_A k_B$ is the universal gas constant. Remarkably, both moduli *increase* linearly with the temperature. That is, the material gets *stiffer* upon heating it up. This directly manifests the entropic nature of the elasticity of polymer networks.

5.4 Dynamic Features

5.4.1 Classification and Terminology

As far as will be needed in the following, we have dealt up to now with static properties of polymers as a basis for the actual topic of the present chapter, chain dynamics. The starting point of most analytical treatments of polymer dynamics is the Langevin equation given in Eq. (2.157). In that version, the effects of intramolecular interactions are not yet detailed. The problem is that the number of internal degrees of motional freedom is prohibitively large to be directly accounted for. A better strategy is – and this is an approach typical for modern polymer science – the introduction of thermodynamic potentials for “coarse-grained” considerations. As already mentioned in Sect. 5.1, the two fundamental steps of theories warranting analytical tractability are (1) reference to *freely jointed Kuhn* and *Rouse* segment chains and (2) further abstracting the polymer by a *bead-and-spring* chain.

A fascinating aspect of the model formalisms founded on these abstractions is that they predict *universal* features of chain dynamics for all polymer species, while the polymer-*specific* properties are packed into some more or less empirical parameter values. A by-product of this strategy is furthermore that the time scales of molecular-dynamics computer simulations can be extended in this way to account for practically relevant dynamic features (see, e.g., Ref. [28], for example).

Coarse-grained chain dynamics refers to *collective segment motions* on length and time scales which are long relative to atomistic or segmental dimensions and processes. Typical model treatments of this sort will be delineated in Sects. 5.4.3, 5.4.5, and 5.4.6. By contrast, on the scales of atoms and segments, structural details must be taken into account, so that analytical treatments are hardly feasible. As concerns model descriptions, *local dynamics* is therefore studied preferably with the aid of computer simulations. We will get back to this point in Sect. 5.4.7.

Depending on the impact of interchain interactions, collective motions can be subdivided into the limits *freely draining* and *entangled-chain* dynamics referring to particularly short and particularly long polymers, respectively. The attributes “freely draining” and “entangled” mean that the respective interchain interactions fluctuate fast and slow relative to the chain relaxation times. The crossover from the freely draining to the entangled-chain limit of polymer dynamics as a function of the chain length is phenomenologically characterized by the critical molecular mass M_c . Its value is predominantly determined by the polymer species and the concentration as will be specified below.

The term “entanglement” means interchain interactions causing temporary interchain correlations. Motions of neighboring chains are then no longer independent of each other. This is in contrast to the more collision-like chain contacts anticipated in the case of freely draining polymers. The time scale on which interchain correlations become perceptible, that is, how long neighboring chains stay in contact with each other as a whole, depends on how long neighboring random polymer coils remain overlapped before they get separated by translational diffusion. This is certainly a matter of the chain length as relativized by the critical molecular mass M_c . As a consequence, chain modes with long “wave” lengths are expected to be modified qualitatively and slowed down quantitatively, whereas short-range modes will be less susceptible to entanglements: Interchain constraints need some space to build up. A principal objective of the model theories to be outlined in the following will be to explain and quantify the effects arising on these grounds.

5.4.1.1 Critical Molecular Mass

Historically, the critical molecular mass M_c was introduced to characterize a rheological phenomenon observed in liquids of numerous polymer species: Well below M_c , the zero-shear viscosity (corrected for chain-end free-volume effects according to the empirical *William/Landel/Ferry equation*⁵) obeys the linear relationship $\eta_0 \propto M$, while the molecular-mass dependence far above M_c follows a power law $\eta_0 \propto M^{3.4 \cdots 3.5}$. The critical molecular mass is then defined as the midpoint of the crossover region as illustrated in Fig. 5.15. In melts, it is typically equivalent to 100 to 300 monomers. Values for a series of flexible linear polymers are listed in Table 5.2.

Diluting a polymer liquid by a solvent increases the critical molecular mass. Empirically, it varies with the concentration according to [29]

$$M'_c \approx f_v^{-1} M_c \quad (5.89)$$

where f_v is the volume fraction of the polymer in the solution and M_c is the value for the undiluted polymer. The critical molecular mass also grows with rising temperatures. This effect is however relatively weak unless the temperature is varied excessively ($>100^\circ$ centigrade). By contrast, mesoscopic confinement has a substantial effect as will be discussed in Sect. 5.4.8.

5.4.1.2 Entanglements

As concerns the crossover from freely draining to entangled-polymer dynamics, another quantity intimately related to M_c is in alternative use, namely, the

⁵ For details, the interested reader is referred to Ref. [1], Chapter 26 by K.L. Ngai, D. J. Plazek, and Refs [29], [30].

Fig. 5.15 Schematic double-logarithmic graph of the zero-shear viscosity η_0 in polymer liquids as a function of the molecular mass M (*dashed curve*). Two power-law limits (*solid lines*) have been identified empirically. The critical molecular mass M_c specifies the crossover region between the two limits

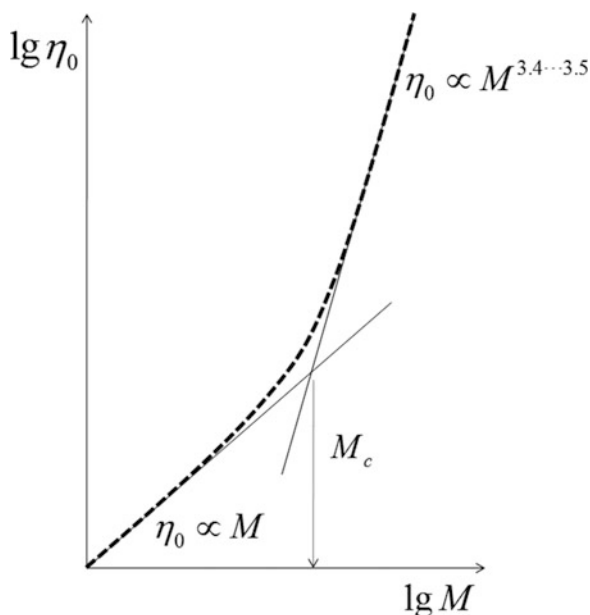


Table 5.2 Typical values for the critical molecular mass M_c of a series of linear polymer species. m_0 designates the molecular mass of monomers

Polymer species	Acronym	Monomer	m_0	M_c
Polyethylene	PE	$-\text{[CH}_2\text{--CH}_2\text{]}-$	28	4,000
Poly(ethylene oxide)	PEO	$-\text{[CH}_2\text{--CH}_2\text{--O]}-$	44	5,000
1,4-Polybutadiene	PB	$-\text{[CH=CH--CH}_2\text{--CH}_2\text{]}-$	54	5,900
Poly(vinyl chloride)	PVC	$-\text{[CH}_2\text{--CHCl]}-$	62.5	6,500
Polypropylene	PP	$-\text{[CH}_2\text{--CH(CH}_3\text{)]}-$	42	7,000
cis-1,4-polyisoprene	cis-PI	$-\text{[CH}_2\text{--CH=C(CH}_3\text{)--CH}_2\text{]}-$	68	10,000
Polytetrahydrofuran	PTHF	$-\text{[CH}_2\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{--O]}-$	72	10,000
Polyisobutylene	PIB	$-\text{[CH}_2\text{--C(CH}_3\text{)(CH}_3\text{)]}-$	56	16,000
Polydimethylsiloxane	PDMS	$-\text{[Si(CH}_3\text{)(CH}_3\text{)--O]}-$	74	25,000
Poly(methyl methacrylate)	PMMA	$-\text{[CH}_2\text{--C(CO\{OCH}_3\text{)}(CH}_3\text{)]}-$	100	30,000
Polystyrene (atactic)	PS	$-\text{[CH}_2\text{--CH(C}_6\text{H}_5\text{)]}-$	104	31,000

Literature values for M_c from different sources can scatter in a range of about $\pm 15\%$. They may also depend moderately on the temperature [1, 29, 31]. In the chemical formulas of the monomers, main (or side)-chain valence bonds are indicated by *dashes*. Side groups other than hydrogen, oxygen, or chlorine atoms are specified in *parenthesis* (or *curly braces* in the case of secondary side groups) and refer to the preceding main (or side)-chain atom

entanglement molecular mass M_e . Historically, the shear relaxation modulus $G(t)$ of polymer melts was compared with that of permanently cross-linked networks. As schematically depicted in Fig. 5.16, three principally different situations can be distinguished: polymer melts with $M < M_e$ (“freely draining”), uncross-linked

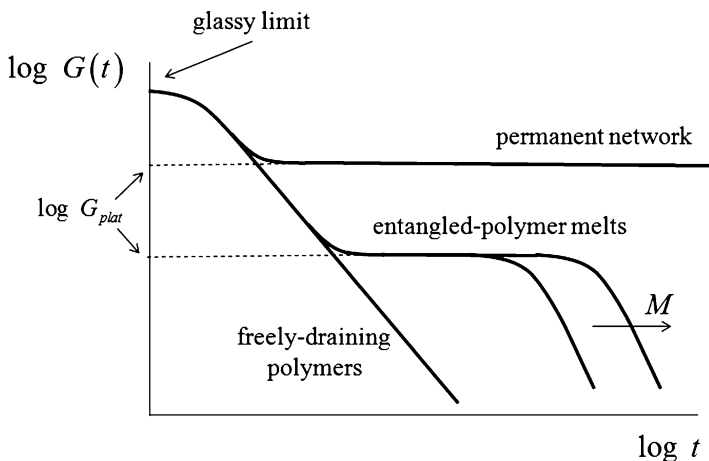


Fig. 5.16 Schematic (and somewhat idealized) representation of the shear relaxation modulus as a function of time in freely draining ($M < M_c$), entangled ($M > M_c$), and permanently cross-linked polymers. Starting from the limit of glassy behavior at short times and some initial decay common to all polymer systems, the shear relaxation modulus shows characteristic long-time features. The modulus of entangled and cross-linked polymers shows *rubber-elastic plateaus* with the modulus G_{plat} . The extension of the plateaus increases with the molecular mass and is infinite for permanent networks. The glassy limit arises at deformation times shorter than the shortest molecular reorientation time

polymer melts $M > M_c$ (“entangled”), and permanent networks. In the latter two cases, more or less extended plateaus arise after some initial decay of the shear relaxation modulus. The discussion on the dynamic background of these particular phenomena and limits will be resumed in Sects. 5.4.3.9 and 5.4.6.5.

For the moment, we are only interested in the so-called *plateau modulus* G_{plat} . According to Eq. (5.88), the plateau modulus of permanently cross-linked polymers is inversely proportional to the mesh molecular mass. The fact that above M_c a similar plateau arises for uncross-linked polymer melts suggests the notion of a *temporary network* which appears to exist up to the molecular-mass-dependent *terminal relaxation time*. At longer times, the shear relaxation modulus will drop further down. The plateau modulus G_{plat} (see Eq. 5.88) of such polymer melts is then interpreted in terms of the *entanglement molecular mass*

$$M_e \approx \rho RT / G_{\text{plat}} \quad (5.90)$$

where ρ is the mass density and $R = N_A k_B$ is the universal gas constant. This definition is thus specifically based on the shear plateau modulus dominating mechanical relaxation experiments in the time (or frequency) regime where the polymer liquid behaves like a permanently cross-linked polymer network.

The entanglement molecular mass M_e so to speak acts as the effective mesh molecular mass.⁶

In relation to the critical molecular mass, typical values for M_e lie in the range $M_e = (0.3 \cdots 1.0)M_c$.⁷ A compilation of data for different polymer species can be found in Ref. [33], for instance. Note however, that a variation of definitions of the entanglement molecular mass somewhat deviating from Eq. (5.90) are in use as discussed in Ref. [34].

In view of the model theories to be discussed in later sections, the term *entanglement* expresses what is thought to be responsible for the special character of long-chain dynamics, namely, long-living contacts with neighboring chains *relative to the relaxation times of chain modes*. In illustrative sketches, the so-called entanglements are often represented by enlacements sparsely occurring around the chain under consideration. More realistically, the entanglement effect should be understood as the *effective* result of all interchain interactions provided they persist on a time scale longer than chain relaxation takes. Especially in polymer melts, chains are so tightly packed that interchain contacts are ubiquitous along a chain as depicted in the cartoon in Fig. 5.17.

This view is corroborated by an interesting discussion in Ref. [35] on the polymer density. For example, the density of crystallites in polyethylene is 1 g/cm^3 at most, whereas the density in the melt is about 0.8 g/cm^3 [36]. That is, the specific volume in the molten state is only 25% larger than in crystallites. The mean chain distances are consequently increased by only 8%. The conclusion is that entanglements cannot be regarded as isolated chain contacts. The character of this phenomenon must rather be attributed to *unlocalized* chain interactions effectively acting as if there were temporary cross-links. The notion of an entanglement network with wide meshes has a largely illustrative character.

5.4.1.3 Basic Model Scenarios

The model scenarios for chain dynamics to be delineated in the subsequent sections are (1) the Rouse model of *freely draining polymers* in a viscous medium, (2) the renormalized Rouse formalism taking into account *interchain interactions*, (3) the harmonic radial potential theory for polymeric liquids confined in a *tube*, and (4) the classical tube/reptation model more descriptively mimicking *entanglement effects*.

The Rouse model was designed for relatively short chains not being subject to long-living interchain contacts. In the equation of motion, intermolecular

⁶ In terms of the tube/reptation model, Sect. 5.4.6, this regime refers to a time scale between the so-called entanglement time τ_e and the tube disengagement time (or terminal relaxation time) τ_d [7].

⁷ For a discussion, see, for example, Refs. [10, 32] or Ref. [1], Chapter 25 by L.J. Fetters, D.J. Lohse, R.H. Colby.

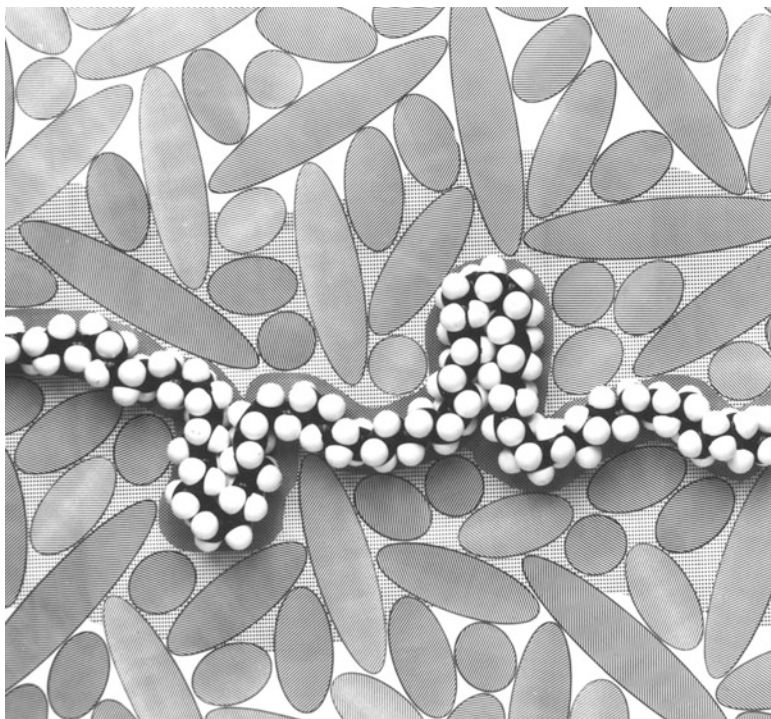


Fig. 5.17 Cartoon of a (polyethylene) model chain entangled by neighboring chains intersecting the drawing plane. The cross sections of the neighboring chains are represented by ellipses produced as the transverse sections of the drawing plane and cylinders enveloping the chains. The scattering inclination angles of those cylinders lead to different semiaxes of the ellipses. The shaded background area is to represent the fluctuation range of the polymer on the time scale of chain relaxation times. In the reptation model concept [7], this restricted space area is usually referred to as “tube” (Reproduced from Ref. [14] with kind permission of © Elsevier 1988)

interactions can then globally be taken into account by viscous drag and stochastic forces. In this sense, the Rouse model can be regarded as a single-chain model.

By contrast, in the presence of the entanglement effect, that is, above the critical molecular mass M_c , this approach is no longer adequate. We are then dealing with a multichain problem as illustrated in Fig. 5.18a. For mathematical reasons, the dynamics of the interacting chains mutually affecting each other cannot be treated directly in such a way, that the dynamics of each individual interaction partner comes out. Corresponding model theories therefore refer to a representative chain, while the influence of the neighboring chains is accounted for in a global manner in principle. This *tagged* chain selected from the chain ensemble can then be subjected to analytical treatments (see Fig. 5.18b).

Contrary to the Rouse case, it is no longer adequate to project the interchain contacts onto a constant parameter such as the viscosity of the surrounding medium. In the case of the reptation model, chains adjacent to the tagged chain are rather

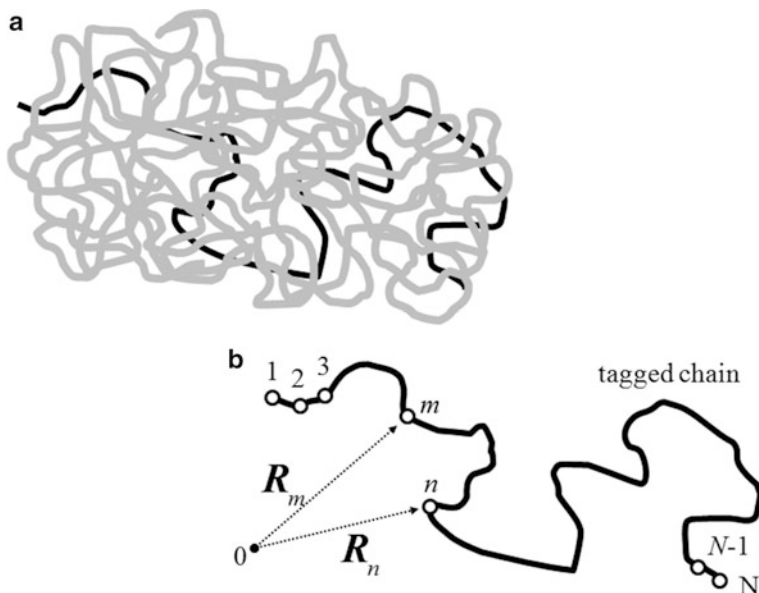


Fig. 5.18 Illustration of the multichain problem of entangled polymer fluids. For treatments, a *tagged chain* is thought to be selected out of the chain ensemble as marked in (a). The tagged chain (b) is then taken to be representative for all other chains as concerns dynamics. The entanglement effect is accounted for in an effective way such as the fictitious tube of the tube/reptation model or by the memory kernel in the renormalized Rouse model

thought to form a kind of effective *tube* confining the tagged chain. An illustration is shown in Fig. 5.19. By character, this results in a semiphenomenological theory. Another approach serving the same purpose is to add an appropriate *time-dependent* friction term in the equation of motion of the tagged chain. This latter strategy will be outlined below in the context of the renormalized Rouse formalism.

5.4.2 The Bead-and-Spring Model Chain

Typical model theories for polymer dynamics are commonly based on the concept of the *bead-and-spring model chain*. The polymer is subdivided into subchains as short as possible but long enough to warrant the Gaussian end-to-end statistics in Eq. (5.26) as an approach. This implies that excluded-volume effects are neglected. The subchains are called *Rouse segments* and tend to be slightly longer (typically 5–6 chemical segments) than the Kuhn length b defined in Sect. 5.2.2 in the frame of the freely jointed chain model.

As mentioned before, the definition of Kuhn segments does not necessarily stipulate Gaussian end-to-end statistics in contrast to Rouse subchains. The definition of Kuhn segments merely anticipates freely jointed nearest-neighbor links.

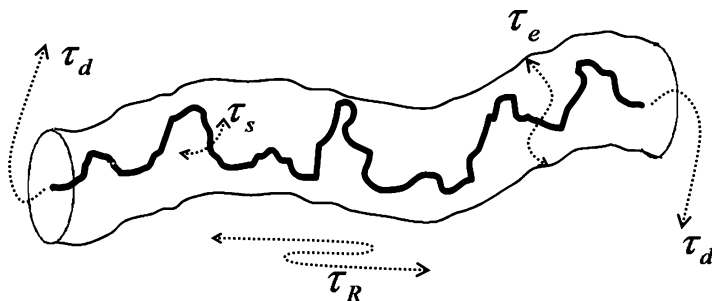


Fig. 5.19 Illustration of a polymer chain confined in a fictitious *tube* according to the tube/reptation model. Effectively, the tube represents the *shaded background area* already depicted in Fig. 5.17. It indicates the range of motional freedom in the matrix of “entangling” neighbor chains. The *dotted double-arrow lines* indicate the diverse types of dynamic processes on different time scales as defined in the frame of the Doi/Edwards tube/reptation model [7]. The characteristic time constants are as follows: τ_s , (Kuhn) segment relaxation time; τ_e , entanglement time; τ_R , (longest) Rouse relaxation time; and τ_d , tube disengagement time. The latter defines the lifetime of tube confinements and, hence, the longest time scale of chain fluctuations compatible with the existence of the tube constraint (A detailed discussion of the time constants will follow in Sect. 5.4.6)

However, it is possible to prove rigorously that fluctuations of Kuhn segments (with slightly non-Gaussian end-to-end statistics) in freely draining chains lead to exactly the same initial decay of the binary normal-mode correlation functions as predicted by the formalism based on Rouse subchains [37]. In this sense, the term *Kuhn segment* is less restrictive than *Rouse subchain* and is therefore preferable. The same symbol b will be employed for both segment definitions unless the context requires a distinction.

Each Rouse segment is modeled by a “bead” (where the mass is concentrated) and a massless “spring” (providing the entropy–elastic property). The freely jointed bead-and-spring chain formed in this way is illustrated in Fig. 5.5 (right-hand section) and in Fig. 5.20. The dynamics of such a model chain can be treated on the basis of the Langevin equation. For this purpose, expressions for the segmental friction coefficient and for the spring constant of entropy–elastic forces must be developed.

5.4.2.1 Segmental Friction Coefficient

The friction force acting on a sphere moving through a viscous medium is given by Stokes’ law given in Eq. (4.56). This relation can be generalized for applications to Kuhn segments. The segment is thought to be replaced by a spherical bead of *hydrodynamic radius* a_h being subject to the *same* friction properties as a segment would have in a phantom fluid consisting of unpolymerized segments. The friction force acting on a segment can thus be expressed as

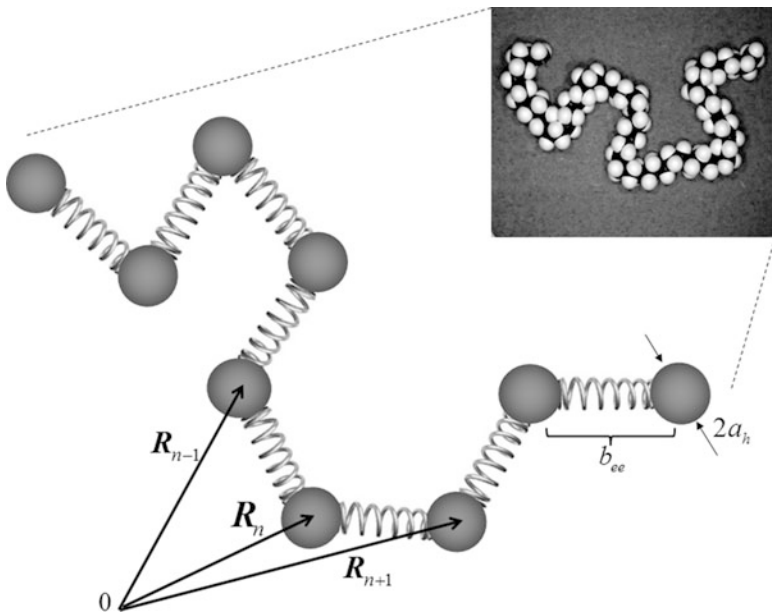


Fig. 5.20 Schematic representation of a bead-and-spring model chain (*bottom*) as a replacement scheme for valence-angle chains (*model picture at the top*). The Rouse subchain length is defined by $b = \sqrt{\langle b_{ee}^2 \rangle}$. Although it tends to be a bit longer, it may be identified with the Kuhn length in formal treatments in view of the argument provided in Ref. [37]. The hydrodynamic radius of a “bead” is designated as a_h

$$\mathbf{F}_{\eta,n} = -\zeta \frac{\partial \mathbf{R}_n}{\partial t} = -6\pi\eta_{\text{micr}}a_h \frac{\partial \mathbf{R}_n}{\partial t} \quad (5.91)$$

where the *segmental friction coefficient* is defined by

$$\zeta = 6\pi\eta_{\text{micr}}a_h \quad (5.92)$$

The subscript n formally indicates the number of the segment in representations such as in Fig. 5.20.

Here we have replaced the (macroscopic) viscosity η one usually measures in rheological experiments by a *microscopic* variant η_{micr} relevant on atomistic or molecular length scales. In the case of polymers, the difference can be dramatic both with respect to the quantitative values and to the dependences on experimental parameters. Since η_{micr} as well as a_h are effective quantities hard to predict on first principles, no attempt will be made to analyze ζ any further.

5.4.2.2 Entropy Spring Constant

One of the most distinct consequences stipulated by the statistical character of flexible polymer chains is entropy elasticity. Since the bead-and-spring chain model

represents a freely jointed chain, any elasticity must be of a purely entropic nature by definition. The conformational entropy contribution of a chain with Gaussian end-to-end statistics was already derived in Eq. (5.70) with the aid of Boltzmann's entropy equation. Assuming the same sort of statistics for Rouse segments, this expression can be rewritten as

$$S_{\text{conf}}(b_{\text{ee}}) = \text{const} - k_{\text{B}} \frac{3b_{\text{ee}}^2}{2b^2} \quad (5.93)$$

where b_{ee} is the end-to-end distance of the Rouse segment and $b = \sqrt{\langle b_{\text{ee}}^2 \rangle}$ is the root-mean-square end-to-end distance. Obviously, Eq. (5.93) suggests that the conformational entropy will be *reduced* upon stretching the Rouse segment because the number of possible chain conformations will be diminished.

There is a second contribution to entropy, S_{space} , which also depends on the end-to-end separation. It has to do with the variety of chain-end positions in space relative to the other chain end [38]. In contrast to the conformational contribution S_{conf} , this type of entropy *increases* with the end-to-end distance. The reason is that the number of spatial configurations scales with the surface area of a sphere of radius b_{ee} , so that the configuration number is proportional to this area: $\Omega \propto 4\pi b_{\text{ee}}^2$. Using Boltzmann's law again provides the expression

$$S_{\text{space}}(b_{\text{ee}}) = \text{const} + k_{\text{B}} \ln b_{\text{ee}}^2 \quad (5.94)$$

for this spatial contribution to the entropy of a Rouse segment. Together with Eq. (5.93), the total entropy related to end-to-end separations thus amounts to

$$S_{\text{tot}}(b_{\text{ee}}) = S_{\text{conf}}(b_{\text{ee}}) + S_{\text{space}}(b_{\text{ee}}) = \text{const} - k_{\text{B}} \frac{3b_{\text{ee}}^2}{2b^2} + 2k_{\text{B}} \ln b_{\text{ee}} \quad (5.95)$$

The counteracting tendency of the two contributions is manifested by the opposite signs of the last two terms on the right-hand side.

Reversible stretching of Rouse segments changes the thermodynamic potentials according to the first law of thermodynamics:

$$\delta U = \delta W + \delta Q \quad (5.96)$$

δU is the variation of the internal energy upon conveying the work δW and/or the heat δQ to or from the Rouse segment. As a freely jointed subchain, the internal energy can be taken as constant with this process, that is, $\delta U \approx 0$. The work needed to stretch a Rouse segment a small distance δb_{ee} is then

$$\delta W = -\mathbf{F}_r \cdot \delta \mathbf{b}_{\text{ee}} = F_r \delta b_{\text{ee}} \quad (5.97)$$

where the minus sign indicates that the retractive force F_r is directed opposite to the vector $\delta \mathbf{b}_{ee}$. Since stretching is assumed to be performed reversibly at the fixed temperature T , the heat abduction will be $\delta Q = T\delta S_{\text{tot}}$. Combining the expressions for δU , δW , and δQ with Eq. (5.96) gives

$$\begin{aligned}\delta U &= \delta W + \delta Q \\ &= F_r \delta b_{ee} + T\delta S_{\text{tot}} \\ &\approx 0\end{aligned}\tag{5.98}$$

Based on (5.95), the magnitude of the entropy–elastic retraction force is thus obtained as

$$\begin{aligned}F_r &\approx -T \frac{\partial S_{\text{tot}}}{\partial b_{ee}} \\ &= \frac{k_B T}{b} \left(3 \frac{b_{ee}}{b} - 2 \frac{b}{b_{ee}} \right)\end{aligned}\tag{5.99}$$

Obviously, $F_r = F_r(b_{ee})$ is a nonlinear function of the end-to-end distance of the Rouse segment. A plot is shown in Fig. 5.21. In the limit $b_{ee} \gg b$, this relationship is very well approached by the linear function

$$F_r \approx \frac{3k_B T}{b^2} b_{ee} = K b_{ee}\tag{5.100}$$

We have thus arrived at the known Hooke’s law in its version for entropy elasticity. The *entropy–elastic spring constant of Rouse segments* is accordingly defined by

$$K = \frac{3k_B T}{b^2}\tag{5.101}$$

In the limit under consideration, the entropy–elastic force is dominated by the conformational contribution S_{conf} as demonstrated in Fig. 5.21.

5.4.2.3 Stochastic Force

The stochastic force was introduced in Sect. 2.4.2.1 for a Brownian particle. In the present context, this scenario would correspond to a macromolecule in solution. This raises the question how this concept can be applied to a melt where there is no solvent. Fortunately, the situation is not that different as expected at first sight. The reason is that the intermolecular interactions take place on a segment-length scale. In this respect, a macromolecule can be considered to be dissolved in the “Rouse

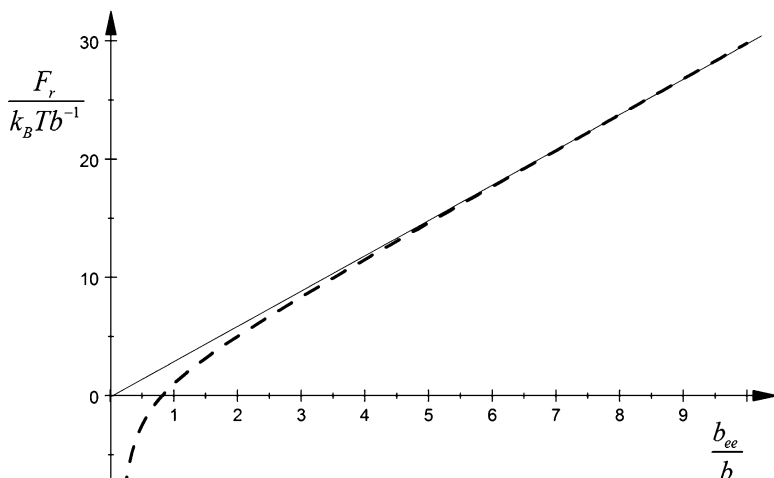


Fig. 5.21 Entropy-elastic force F_r in units $k_B T b^{-1}$ as a function of the end-to-end distance b_{ee} of a Kuhn segment in units of b . The *dashed curve* represents Eq. (5.99). The *straight line* corresponds to Hooke's law, Eq. (5.100)

segment fluid" of adjacent macromolecules. The stochastic force results from random impacts of neighboring segments. As long as we restrict ourselves to melts of flexible nonelectrolyte polymers, where all intermolecular interactions are short-range, the Brownian-particle concept works therefore remarkably well.

The properties of the stochastic force $\mathbf{f}_n$ acting on a Rouse segment numbered by the subscript n can be expressed by its first two moments, that is, the ensemble average and the autocorrelation function concerning two times t' and t'' . According to Eqs. (2.147) and (2.148), the following relations will be relevant:

$$\langle \mathbf{f}_n \rangle = 0 \quad \text{and} \quad \langle \mathbf{f}_n(t') \cdot \mathbf{f}_n(t'') \rangle = 6\zeta k_B T \delta(t' - t'') \quad (5.102)$$

where the segmental friction coefficient ζ is given by Eq. (5.92) and $\delta(t' - t'')$ is Dirac's delta function.

5.4.3 Rouse Model (Freely Draining Polymer Chains)

The *Rouse model* for freely draining polymers may be considered as a landmark of theoretical polymer science. It refers to Kuhn segment chains⁸ in a viscous medium without any topological constraint. This concept was originally established in Refs. [4, 5] and has emerged as an obligatory part of textbooks on chain dynamics such as

⁸ Recall that we are using the term *Kuhn segment* synonymously to the term *Rouse subchain* frequently quoted in this context. For a discussion and justification, see Sect. 5.4.2.

Refs. [7, 9], for example. It is a paradigm of polymer-chain dynamics par excellence. As the most elementary model in the present context, it is taken as the standard starting formalism for more sophisticated theories of polymer dynamics. Concomitantly, it can be regarded as a particularly successful formalism reproducing experimental findings in melts or concentrated solutions of polymers below the critical molecular mass.

5.4.3.1 Equation of Motion

Let us start with the bead-and-spring model outlined in Sect. 5.4.2. The model chain to be considered in the following is to consist of N_K beads and $N_K - 1$ entropy springs. Excluded-volume effects and hydrodynamic (i.e., flow-related) interactions among segments are not taken into account. The differences of neighboring bead position vectors are given by the end-to-end vectors such as $\mathbf{b}_{ee} = \mathbf{R}_{n+1} - \mathbf{R}_n$ of the Kuhn segments (see Fig. 5.20). The equation of motion of a bead can then be established on the basis of the Langevin equation formulated in Eq. (2.157). The entropy–elastic force given in Eq. (5.100) is the only force of an intra-molecular nature to be considered here. As suggested by Fig. 5.20, the sum of the forces acting on the Kuhn segment labeled by the number n is then

$$\begin{aligned} K(\mathbf{R}_{n-1} - \mathbf{R}_n) + K(\mathbf{R}_{n+1} - \mathbf{R}_n) - \zeta \frac{\partial \mathbf{R}_n}{\partial t} + \mathbf{f}_n = \\ K(\mathbf{R}_{n-1} + \mathbf{R}_{n+1} - 2\mathbf{R}_n) - \zeta \frac{\partial \mathbf{R}_n}{\partial t} + \mathbf{f}_n = 0 \end{aligned} \quad (5.103)$$

The segmental spring constant K and the segmental friction coefficient ζ are given in Eqs. (5.101) and (5.92), respectively. The first two terms on the left side represent the entropy–elastic forces acting on bead number n from both sides as a consequence of the elongations $(\mathbf{R}_{n-1} - \mathbf{R}_n)$ and $(\mathbf{R}_{n+1} - \mathbf{R}_n)$ of the adjacent entropy springs. The remaining terms refer to the segmental friction force, $-\zeta \partial \mathbf{R}_n / \partial t$, and the stochastic force, $\mathbf{f}_n$, acting on the bead.

On a length scale much longer than the Kuhn length b , the subscript n can be treated as a continuous variable⁹ in the range $0 \leq n \leq N_K$. From Eq. (5.103), we thus obtain the *bead-and-spring variant of the Langevin equation* for freely draining polymers

$$\underbrace{K \frac{\partial^2 \mathbf{R}(t, n)}{\partial n^2}}_{\text{elastic force}} - \underbrace{\zeta \frac{\partial \mathbf{R}(t, n)}{\partial t}}_{\text{friction}} + \underbrace{\mathbf{f}(t, n)}_{\text{stochastic force}} = 0 \quad (5.104)$$

⁹The rules for the transformation from discrete to continuous variables are for example summarized in Tab. 2.1 of Ref. [7] in convenient form.

The segment position vector $\mathbf{R}(t, n)$ is now a function of two continuous variables t and n instead of the discrete quantities used in Eq. (5.103). Note the change in the nomenclature we have employed here: When speaking of discrete segments, we use *subscripts* for the segment number such as with $\mathbf{R}_n(t)$. Referring to n as a continuous variable, we prefer the *functional* notation $\mathbf{R}(t, n)$.

The second derivative in Eq. (5.104) results from the following argument: The term $(\mathbf{R}_{n-1} + \mathbf{R}_{n+1} - 2\mathbf{R}_n)$ can be rewritten as double difference quotient

$$\begin{aligned} (\mathbf{R}_{n-1} + \mathbf{R}_{n+1} - 2\mathbf{R}_n) &= [(\mathbf{R}_{n+1} - \mathbf{R}_n) - (\mathbf{R}_n - \mathbf{R}_{n-1})] \\ &= \frac{\left[\frac{\Delta \mathbf{R}}{\Delta n} \Big|_n - \frac{\Delta \mathbf{R}}{\Delta n} \Big|_{n-1} \right]}{\Delta n} \rightarrow \frac{\partial^2 \mathbf{R}}{\partial n^2} \end{aligned} \quad (5.105)$$

which approaches the second derivative in the continuum limit. The formally introduced difference of the segment numbers is $\Delta n = 1 \ll N_K$.

Equation (5.104) is a most fundamental equation of motion in polymer science. Anticipating some reference to later sections, we will encounter extended variants of this relation in the frame of the renormalized Rouse model (Sect. 5.4.4), the harmonic radial potential theory (Sect. 5.4.5), and the tube/reptation concept (Sect. 5.4.6). The following polymer-dynamics scenarios of interest here will be treated on this basis:

$$\begin{aligned} K \frac{\partial^2 \mathbf{R}(t, n)}{\partial n^2} - \zeta \frac{\partial \mathbf{R}(t, n)}{\partial t} + \mathbf{f}(t, n) &= 0 \quad (\rightarrow \text{freely draining chains}) \\ K \frac{\partial^2 \mathbf{R}(t, n)}{\partial n^2} - \zeta \frac{\partial \mathbf{R}(t, n)}{\partial t} + \mathbf{f}(t, n) + (\text{memory term}) &= 0 \quad (\rightarrow \text{entangled chains}) \\ K \frac{\partial^2 \mathbf{R}(t, n)}{\partial n^2} - \zeta \frac{\partial \mathbf{R}(t, n)}{\partial t} + \mathbf{f}(t, n) + (\text{potential term}) &= 0 \quad (\rightarrow \text{confined chains}) \end{aligned} \quad (5.106)$$

The vectorial relation in Eq. (5.104) represents a set of N_K coupled linear differential equations with constant coefficients for the N_K Kuhn segments of a chain. To be more precise, Eq. (5.104) even represents $3N_K$ differential equations if the three Cartesian components of the vectors are considered separately. The chain ends are specified by the Neumann boundary conditions

$$\frac{\partial \mathbf{R}}{\partial n} \Big|_{n=0, N_K} = 0 \quad (5.107)$$

in the sense that no segment position can exist outside the chain.

5.4.3.2 Normal-Coordinate Transformation

The task is now to solve the set of differential equations expressed by Eq. (5.104) for different segment numbers n . We note that these equations are not independent of each other owing to the second derivative $\partial^2 \mathbf{R}(t, n) / \partial n^2$. A remedy for this problem is provided by a well-known concept of the theory of lattice dynamics (see, e.g., Ref. [39]): The system of differential equations can be decoupled (i.e., solved independently) by introducing *normal coordinates* defined in vectorial form by

$$\mathbf{X}_p(t) = \frac{1}{N_K} \int_0^{N_K} \cos\left(\frac{\pi p n}{N_K}\right) \mathbf{R}(t, n) dn \quad (5.108)$$

with the Cartesian components

$$X_{p,\alpha}(t) = \frac{1}{N_K} \int_0^{N_K} \cos\left(\frac{\pi p n}{N_K}\right) R_\alpha(t, n) dn \quad (\alpha = x, y, z) \quad (5.109)$$

The normal-coordinate number (or *mode number* as it will be called later) can take the values $p = 0, 1, \dots, (N_K - 1)$ where $N_K \gg 1$. The normal-coordinate vector for $p = 0$ coincides with the position vector of the center of mass of the polymer chain,

$$\mathbf{X}_0(t) = \mathbf{R}_{\text{cm}}(t) \quad (5.110)$$

as suggested by Eq. (5.35). The zeroth normal-coordinate vector therefore describes center-of-mass motions of the whole macromolecule. The respective transformations inverse to Eqs. (5.108) and (5.109) read

$$\mathbf{R}(t, n) = \mathbf{X}_0(t) + 2 \sum_{p=1}^{N_K-1} \mathbf{X}_p(t) \cos\left(\frac{\pi p n}{N_K}\right) \quad (5.111)$$

and

$$R_\alpha(t, n) = X_{0,\alpha}(t) + 2 \sum_{p=1}^{N_K-1} X_{p,\alpha}(t) \cos\left(\frac{\pi p n}{N_K}\right) \quad (\alpha = x, y, z) \quad (5.112)$$

The conjugate character of the two sets $\mathbf{X}_p(t)$ and $\mathbf{R}(t, n)$ can readily be demonstrated by substituting Eq. (5.111) into Eq. (5.108). Obviously, the normal-coordinate number p is conjugate to the Kuhn segment number n .

An important property of normal coordinates is their *orthogonality*. That is, there is no correlation neither between different components of normal-coordinate vectors nor for different normal-coordinate numbers. For a given time t , this rule can be expressed by

$$\begin{aligned}\langle X_{p,\alpha} X_{q,\beta} \rangle &= \frac{1}{N_K^2} \int_0^{N_K} dn \int_0^{N_K} dn' \left\langle \cos\left(\frac{\pi p n}{N_K}\right) \cos\left(\frac{\pi q n'}{N_K}\right) R_\alpha(t, n) R_\beta(t, n') \right\rangle \\ &= \delta_{pq} \delta_{\alpha\beta} \langle X_{p,\alpha}^2 \rangle\end{aligned}\quad (5.113)$$

where δ_{pq} and $\delta_{\alpha\beta}$ are Kronecker symbols for potentially different normal-coordinate numbers $p, q = 0, 1, \dots, (N_K - 1)$ and potentially different subscripts $\alpha, \beta = x, y, z$, respectively. This property will be exploited in the following treatments of chain dynamics at various occasions.

Equation (5.111) reveals the physical nature of the normal-coordinate transformation. Essentially, it is a cosine Fourier analysis of the bead-and-spring chain conformations. Not unlike string vibrations, random lateral displacements of the segments are described as a linear superposition of spatial harmonics of wavelengths $\pi p/N_K$, that is, integer multiples of π/N_K . The amplitudes are determined by the normal coordinates. A schematic illustration of this sort of superposition is shown in Fig. 5.22. In this context, the reader should however be reminded that there is no inertial term effective in the equation of motion. In this sense, chain dynamics is not like that of periodically oscillating strings. There is no periodic time dependence. One rather deals with *relaxation modes*, that is, exponential decays of the time-correlation functions of the normal coordinates, as will be outlined in the following.

Multiplying the equation of motion given in Eq. (5.104) on both sides by $N_K^{-1} \cos(\pi p n/N_K)$ and integrating all terms over the variable n , that is, $\int_0^{N_K} \dots dn$, yields the desired set of decoupled differential equations for the N_K normal-coordinate vectors. Two subsequent integrations by parts and the boundary conditions in Eq. (5.107) lead to

$$\frac{\pi^2 p^2}{N_K^2} K X_p(t) + \zeta \frac{\partial}{\partial t} X_p(t) - F_p(t) = 0 \quad (p = 0, 1, \dots, N_K - 1) \quad (5.114)$$

where the functions $X_p(t)$ are defined in Eq. (5.108) and

$$F_p(t) = \frac{1}{N_K} \int_0^{N_K} f(t, n) \cos\left(\frac{\pi p n}{N_K}\right) dn \quad (5.115)$$

is basically the cosine Fourier transform of the stochastic force.

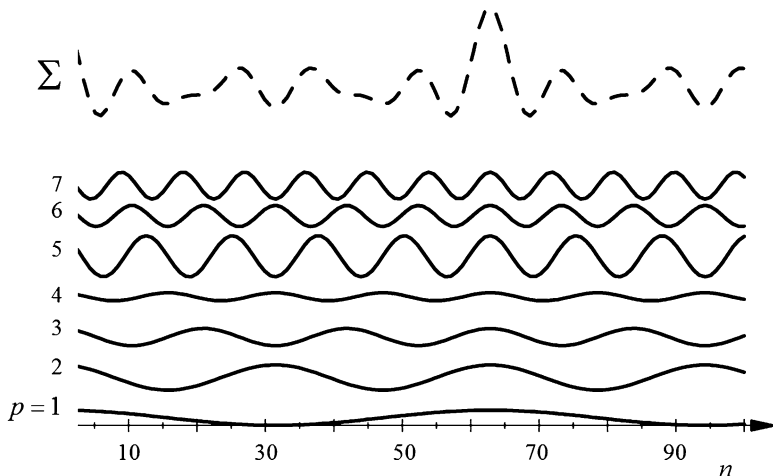


Fig. 5.22 Schematic representation of the linear superposition of a normal-coordinate component for $p = 1 \dots 7$ of arbitrary amplitudes according to Eq. (5.112). The *dashed curve* refers to the component $R_x(t, n)$ of the vector $\mathbf{R}(t, n)$ describing a potential chain conformation in the sense of a “snapshot” at a given time t

5.4.3.3 Correlation Function of Normal Coordinates

All we know about the force $\mathbf{f}(t, n)$ is that it is a *stochastic* function of time. The Fourier transform $\mathbf{F}_p(t)$ in the normal-coordinate space will therefore be a stochastic function of time as well. The question is then how Eq. (5.114) can be solved without any knowledge of the analytical details of this function. The trick is to form autocorrelation functions of the normal-coordinate vectors:

$$\begin{aligned} c_p(t) &= \langle \mathbf{X}_p(t) \cdot \mathbf{X}_p(0) \rangle \quad (p = 1, \dots, N_K - 1) \\ c_0(t) &= \langle \mathbf{R}_{\text{cm}}(t) \cdot \mathbf{R}_{\text{cm}}(0) \rangle \quad (p = 0) \end{aligned} \quad (5.116)$$

The correlation functions of the normal-coordinate components are analogously

$$\begin{aligned} c_{p,\alpha}(t) &= \langle X_{p,\alpha}(t) X_{p,\alpha}(0) \rangle \quad (p = 1, \dots, N_K - 1; \alpha = x, y, z) \\ c_{0,\alpha}(t) &= \langle R_{\text{cm},\alpha}(t) R_{\text{cm},\alpha}(0) \rangle \quad (p = 0; \alpha = x, y, z) \end{aligned} \quad (5.117)$$

The angle brackets indicate ensemble averages as usual. $c_0(t)$ is the autocorrelation function of the center-of-mass position vector.

Correspondingly reformulating Eq. (5.114) by multiplying all terms with $\mathbf{X}_p(0)$ and by averaging over a chain ensemble leads to a new set of differential equations referring now to these normal-coordinate autocorrelation functions:

$$\frac{\pi^2 p^2}{N_K^2} K c_p(t) + \zeta \frac{\partial}{\partial t} c_p(t) - \langle \mathbf{F}_p(t) \cdot \mathbf{X}_p(0) \rangle = 0 \quad (5.118)$$

Since $\mathbf{F}_p(t)$ is a random function of time, there will be no correlation to $\mathbf{X}_p(0)$, and the term $\langle \mathbf{F}_p(t) \cdot \mathbf{X}_p(0) \rangle$ vanishes. We thus obtain a decoupled set of linear differential equations with constant coefficients,

$$\frac{\pi^2 p^2}{N_K} K c_p(t) + N_K \zeta \frac{\partial}{\partial t} c_p(t) = 0 \quad (p = 1, \dots, N_K - 1) \quad (5.119)$$

where $N_K \zeta$ is the friction coefficient of the whole chain. In this way, the unknown function $\mathbf{F}_p(t)$ has been eliminated. In terms of the correlation functions of the components, Eq. (5.117), this set of differential equations reads

$$\frac{\pi^2 p^2}{N_K} K c_{p,\alpha}(t) + N_K \zeta \frac{\partial}{\partial t} c_{p,\alpha}(t) = 0 \quad (p = 1, \dots, N_K - 1; \quad \alpha = x, y, z) \quad (5.120)$$

The respective solutions of Eqs. (5.119) and (5.120),

$$c_p(t) = c_p(0) \exp \left\{ -\frac{t}{\tau_p} \right\} \quad (5.121)$$

and

$$c_{p,\alpha}(t) = c_{p,\alpha}(0) \exp \left\{ -\frac{t}{\tau_p} \right\} \quad (5.122)$$

are called *Rouse normal modes* or *Rouse relaxation modes*, where the mode number varies in the range $p = 1, 2, \dots, N_K - 1$. The time constant τ_p is the *Rouse relaxation time* associated to the p th normal coordinate. Inserting Eq. (5.121) into Eq. (5.119) leads to

$$\tau_p = \frac{\zeta N_K^2}{\pi^2 p^2 K} = \frac{\zeta N_K^2 b^2}{3\pi^2 k_B T p^2} \quad (p = 1, 2, \dots, N_K - 1) \quad (5.123)$$

where we have made use of Eq. (5.101) for the segmental spring constants.

The shortest Rouse relaxation time arises for the highest harmonic of the normal-modes, $p = N_K - 1$, and is referred to as the *segment relaxation time*:

$$\tau_{N_K-1} \equiv \tau_s = \frac{\zeta N_K^2}{\pi^2 K (N_K - 1)^2} \quad (5.124)$$

In the limit $N_K \gg 1$, this expression reduces to

$$\tau_s \approx \frac{\zeta}{\pi^2 K} = \frac{\zeta b^2}{3\pi^2 k_B T} \quad (5.125)$$

The longest Rouse relaxation time refers to mode number $p = 1$. It is often called plainly *the* Rouse relaxation time:

$$\tau_1 \equiv \tau_R = \frac{\zeta N_K^2}{\pi^2 K} = \frac{\zeta N_K^2 b^2}{3\pi^2 k_B T} = N_K^2 \tau_s \quad (5.126)$$

The actual time dependence the dynamics of a Kuhn segment chain is subject to is the result of the superposition of all Rouse modes.

5.4.3.4 Initial Condition

For the complete determination of the solutions given in Eqs. (5.121) and (5.122), the initial conditions, $c_p(0) = \langle X_p^2 \rangle$ and $c_{p,\alpha}(0) = \langle X_{p,\alpha}^2 \rangle$, are required. In thermal equilibrium, the normal modes are distributed according to the statistical weight¹⁰ $\exp\{-A_H^{\text{elast}}(\mathbf{X}_p)/k_B T\}$, where $A_H^{\text{elast}}(\mathbf{X}_p)$ is the elastic Helmholtz free energy for normal mode $\mathbf{X}_p$. This thermodynamic potential is formally given as the sum of the elastic energies of all entropy springs in a chain according to

$$A_H^{\text{elast}} = \frac{1}{2} K \sum_{n=1}^{N_K-1} (\mathbf{R}_{n+1} - \mathbf{R}_n)^2 = \frac{3k_B T}{2b^2} \sum_{n=1}^{N_K-1} (\mathbf{R}_{n+1} - \mathbf{R}_n)^2 \quad (5.127)$$

where the entropy spring constant has been substituted by Eq. (5.101). The segment position vectors can be replaced by the normal-coordinate expression given in Eq. (5.111), so that

$$A_H^{\text{elast}} = \frac{3k_B T}{2b^2} \sum_{n=1}^{N_K-1} \left[2 \sum_{p=1}^{N_K-1} \mathbf{X}_p \left(\cos \frac{\pi p(n+1)}{N_K} - \cos \frac{\pi p n}{N_K} \right) \right]^2 \quad (5.128)$$

Employing the known relation

$$\cos \frac{\pi p(n+1)}{N_K} - \cos \frac{\pi p n}{N_K} = -2 \sin \left\{ \frac{\pi p}{N_K} \left(n + \frac{1}{2} \right) \right\} \sin \left\{ \frac{\pi p}{2N_K} \right\} \quad (5.129)$$

¹⁰The reader may wonder why we do not use the ordinary Boltzmann factor defined by $\exp\{-U(\mathbf{X}_p)/k_B T\}$, where U is the potential energy of the state under consideration. The reason is that, in the present case, we are dealing with *entropy elasticity*. That is, the states are degenerate with respect to all conformations of the Rouse segments for a given normal mode. Let us call the degeneracy factor $\Omega(\mathbf{X}_p)$. The statistical weight for a certain normal mode is therefore $\Omega(\mathbf{X}_p) \exp\{-U(\mathbf{X}_p)/k_B T\}$. According to Boltzmann's law, $S = k_B \ln \Omega$, the degeneracy factor can be expressed as $\Omega = \exp\{S/k_B\}$, so that the statistical weight adopts the form $\Omega \exp\{-U/k_B T\} = \exp\{-(U - TS)/k_B T\} = \exp\{-A_H^{\text{elast}}/k_B T\}$ with the Helmholtz free energy $A_H^{\text{elast}} = U - TS$.

gives us

$$A_H^{\text{elast}} = \frac{12k_B T}{b^2} \sum_{n=1}^{N_K-1} \left[\sum_{p=1}^{N_K-1} X_p \sin \left\{ \frac{\pi p}{N_K} \left(n + \frac{1}{2} \right) \right\} \sin \left\{ \frac{\pi p}{2N_K} \right\} \right]^2 \quad (5.130)$$

The square of the inner sum on the right-hand side of Eq. (5.130) leads to cross terms for different normal-mode numbers p . In the continuum limit, that is, $N_K \gg 1$, the outer sum over the segment number n can be replaced by an integral,

$$\sum_{n=1}^{N_K-1} \dots \approx \int_0^{N_K-1/2} \dots dn \quad (5.131)$$

so that any explicit dependence on n is eliminated. In this limit, the cross terms for different p values vanish as a consequence of the orthogonality of normal coordinates (see Eq. 5.113). This reduces the expression for the entropy-elastic Helmholtz free energy to

$$A_H^{\text{elast}} = \frac{12k_B T}{b^2} \sum_{p=1}^{N_K-1} X_p^2 \sin^2 \left\{ \frac{\pi p}{2N_K} \right\} \quad (5.132)$$

The mean-square normal-coordinate vector of number p in the range $1, 2, \dots, N_K - 1$ can thus be calculated straightforwardly as

$$c_p(0) = \langle X_p^2 \rangle = \frac{\int_{-\infty}^{\infty} X_p^2 \exp \left\{ -\frac{A_H^{\text{elast}}}{k_B T} \right\} dX_p}{\int_{-\infty}^{\infty} \exp \left\{ -\frac{A_H^{\text{elast}}}{k_B T} \right\} dX_p} = \frac{b^2}{8N \sin^2 \frac{\pi p}{2N_K}} \overset{N_K \gg \pi p/2}{\approx} \frac{N_K b^2}{2\pi^2 p^2} \quad (5.133)$$

This is the initial condition for the correlation function of the normal-coordinate vector X_p . Since the components of normal coordinates are stochastically independent of each other (see Eq. 5.113 again), we may moreover write $\langle X_p^2 \rangle = \langle X_{p,x}^2 + X_{p,y}^2 + X_{p,z}^2 \rangle = \langle X_{p,x}^2 \rangle + \langle X_{p,y}^2 \rangle + \langle X_{p,z}^2 \rangle$ and $\langle X_{p,x}^2 \rangle = \langle X_{p,y}^2 \rangle = \langle X_{p,z}^2 \rangle = c_{p,\alpha}(0)$. The initial conditions for the correlation function of the normal-coordinate components can thus be specified by the expression

$$c_{p,\alpha}(0) \overset{N_K \gg \pi p/2}{\approx} \frac{N_K b^2}{6\pi^2 p^2} \quad (\alpha = x, y, z) \quad (5.134)$$

5.4.3.5 Complete Set of the Formulas for Rouse Mode Solutions

In later sections, we will often refer to the Rouse formalism developed above. For the sake of convenience of the reader, let us summarize the Rouse-mode solutions in all parameter details as they will be needed in applications. The vector correlation functions are

$$\begin{aligned}
 c_0(t) &= \langle \mathbf{R}_{\text{cm}}(t) \cdot \mathbf{R}_{\text{cm}}(0) \rangle & (p = 0) \\
 c_p(t) &\equiv \langle \mathbf{X}_p(t) \cdot \mathbf{X}_p(0) \rangle \\
 &= c_p(0) \exp \left\{ -\frac{t}{\tau_p} \right\} \\
 &= \frac{N_K b^2}{2\pi^2 p^2} \exp \left\{ -\frac{3\pi^2 k_B T p^2 t}{\zeta N_K^2 b^2} \right\} & (p = 1, 2, \dots, N_K - 1)
 \end{aligned} \tag{5.135}$$

Expressed in components, the relations read:

$$\begin{aligned}
 c_{0,\alpha}(t) &= \langle \mathbf{R}_{\text{cm},\alpha}(t) \cdot \mathbf{R}_{\text{cm},\alpha}(0) \rangle & (p = 0; \quad \alpha = x, y, z) \\
 c_{p,\alpha}(t) &\equiv \langle X_{p,\alpha}(t) X_{p,\alpha}(0) \rangle \\
 &= c_{p,\alpha}(0) \exp \left\{ -\frac{t}{\tau_p} \right\} \\
 &= \frac{N_K b^2}{6\pi^2 p^2} \exp \left\{ -\frac{3\pi^2 k_B T p^2 t}{\zeta N_K^2 b^2} \right\} & (p = 1, 2, \dots, N_K - 1; \quad \alpha = x, y, z)
 \end{aligned} \tag{5.136}$$

The characteristic time constants are the *segmental relaxation time* ($p = N_K - 1 \approx N_K$),

$$\tau_s = \frac{b^2 \zeta}{3\pi^2 k_B T} \tag{5.137}$$

the *Rouse relaxation time of the p th normal mode in general*,

$$\tau_p = \frac{N_K^2}{p^2} \tau_s = \frac{\tau_R}{p^2} \tag{5.138}$$

and the (*longest*) *Rouse relaxation time* ($p = 1$),

$$\tau_R = N_K^2 \tau_s = p^2 \tau_p \tag{5.139}$$

The latter relation can be rewritten as

$$\tau_R = \frac{\zeta b^2}{3\pi^2 k_B T M_K^2} M^2 \tag{5.140}$$

where M is the molecular mass of the whole chain, and M_K refers to a Kuhn segment. We state that the Rouse relaxation time is subject to a characteristic *square* dependence on the molecular mass.

The expressions given in Eqs. (5.135) and (5.136) have been derived for the limits for long chains and long times, that is, $N_K \gg 1$ and $t \gg \tau_s = \zeta b^2 / (3\pi^2 k_B T)$, respectively. On the other hand, as concerns the chain length, the polymers should not be too long since beyond the critical molecular mass M_c , entanglement effects arise so that the Rouse model will no longer be adequate. To be quantitative, the melt value of M_c corresponds to typically $N_K = 40 \dots 50$ Kuhn segments (see Table 5.2), which suggests a range of validity of roughly $10 < N_K < 50$. Practically, the condition $N_K \gg 1$ is however rather uncritical as it was demonstrated in Ref. [37]. As mentioned before, it was also shown in that reference that the essential features of the Rouse model are valid even if the segments deviate to some degree from Gaussian end-to-end statistics. Likewise, the time limit $t \gg \tau_s$ is not too restrictive. The crossover to *local dynamics* on the time scale $t < \tau_s$ to be discussed in Sect. 5.4.7 is rather gradual as can be confirmed with the aid of computer simulations [40]. In this sense, the application range of the Rouse model is fortunately not as limited as it might appear at first sight in view of the diverse restrictions anticipated.

The relaxation-mode character of the solutions given in Eq. (5.135) is obvious: Chain dynamics is determined by a superposition of exponential functions decaying with the relaxation times defined in Eq. (5.123). Since there is no temporal periodicity, we speak of *relaxation* modes in contrast to the *vibration* modes one would expect in the case of strings. The superposition of the relaxation modes can be elucidated by expressing the chain end-to-end vector by the back-transformation formula in Eq. (5.111):

$$\mathbf{r}_{ee}(t) = \mathbf{R}(t, N_K) - \mathbf{R}(t, 0) = 2 \sum_{p=1}^{N_K-1} \mathbf{X}_p(t) [\cos(\pi p) - 1] \quad (5.141)$$

On this basis, it follows that the time autocorrelation function of the end-to-end vector is composed of a *sum* of the Rouse modes in Eq. (5.135):

$$\langle \mathbf{r}_{ee}(t) \cdot \mathbf{r}_{ee}(0) \rangle = 16 \sum_{p: \text{ odd}} c_p(t) = \frac{8N_K b^2}{\pi^2} \sum_{p: \text{ odd}} \frac{1}{p^2} \exp\left\{-\frac{t}{\tau_p}\right\} \quad (5.142)$$

In subsequent sections, we will translate the above results for the Rouse model of freely draining polymers to expressions for a number of observables directly accessible in experiments. The measuring techniques to be considered refer to translational diffusion, NMR relaxation, dynamic mechanical relaxation, and neutron scattering.

5.4.3.6 Mean-Squared Segment Displacement

Using the inverse normal-coordinate transformation in Eq. (5.111), the mean-square displacement (msd) of Kuhn segment n in a time interval t can be expressed as

$$\begin{aligned} & \left\langle [\mathbf{R}(t, n) - \mathbf{R}(0, n)]^2 \right\rangle \\ &= \underbrace{\left\langle [\mathbf{X}_0(t) - \mathbf{X}_0(0)]^2 \right\rangle}_{\text{msd of the center-of-mass}} + \underbrace{\left\langle \left(2 \sum_{p=1}^{N_K-1} [\mathbf{X}_p(t) - \mathbf{X}_p(0)] \cos\left(\frac{\pi p n}{N_K}\right) \right)^2 \right\rangle}_{\text{msd of segment } n \text{ relative to center-of-mass}} \end{aligned} \quad (5.143)$$

Since the vectorial normal coordinate for $p = 0$ is identical to the center-of-mass position vector, $\mathbf{X}_0(t) = \mathbf{R}_{\text{cm}}(t)$, the first term on the right-hand side of Eq. (5.143) can be replaced by

$$\left\langle [\mathbf{X}_0(t) - \mathbf{X}_0(0)]^2 \right\rangle = \left\langle [\mathbf{R}_{\text{cm}}(t) - \mathbf{R}_{\text{cm}}(0)]^2 \right\rangle = 6D_{\text{cm}}t \quad (5.144)$$

where D_{cm} is the *center-of-mass diffusion coefficient* of the whole chain. This parameter is related to the friction coefficient $N_K\zeta$ by

$$D_{\text{cm}} = \frac{k_B T}{N_K \zeta} \quad (5.145)$$

in accordance with the Einstein relation in Eq. (2.197). Expressing the number of Kuhn segments per chain by the molecular mass of the polymer and that of a Kuhn segment, M and M_K , respectively, suggests an *inverse* proportionality between D_{cm} and M :

$$D_{\text{cm}} = \frac{k_B T M_K}{\zeta} \frac{1}{M} \quad (5.146)$$

The second term on the right-hand side of Eq. (5.143) can be replaced by $8 \sum_{p=1}^{N_K-1} \left[\left\langle \mathbf{X}_p^2 \right\rangle - \left\langle \mathbf{X}_p(t) \cdot \mathbf{X}_p(0) \right\rangle \right] \cos^2(\pi p n / N_K)$ because different normal coordinates are uncorrelated to each other as stated in Eq. (5.113). That is, the ensemble average of all cross terms vanishes. Additionally averaging the result over all segments of a chain with the aid of the relation $N_K^{-1} \int_0^{N_K} \cos^2(\pi p n / N_K) dn = \frac{1}{2}$ leads to

$$\begin{aligned}
\langle r^2 \rangle &\equiv \frac{1}{N_K} \int_0^{N_K} \langle [\mathbf{R}(t, n) - \mathbf{R}(0, n)]^2 \rangle dn \\
&= 6D_{\text{cm}}t + 4 \sum_{p=1}^{N_K-1} [c_p(0) - c_p(t)] \\
&= 6D_{\text{cm}}t + \frac{2N_K b^2}{\pi^2} \sum_{p=1}^{N_K-1} \left[\frac{1}{p^2} \left(1 - \exp \left\{ -\frac{tp^2}{\tau_R} \right\} \right) \right] \quad (5.147)
\end{aligned}$$

where we have substituted the Rouse-mode solutions given in Eq. (5.135).

In the limit $t \gg \tau_R$, the expression in the last line of Eq. (5.147) will be dominated by the first term on the right-hand side. The exponential function in the second term can be neglected relative to 1. That is, the sum can be approximated by

$$\sum_{p=1}^{N_K-1} p^{-2} \approx \sum_{p=1}^{\infty} p^{-2} = \frac{\pi^2}{6} \quad (5.148)$$

which is independent of time and therefore much smaller than $6D_{\text{cm}}t$ in the long-time limit.

At short times, the limiting time constant is the segmental relaxation time τ_s . In the limit, $\tau_s \ll t \ll \tau_R$, the sum in Eq. (5.147) will be governed by large mode numbers p . In this case, the sum can be approached by an integral according to

$$\begin{aligned}
\sum_{p=1}^{N_K-1} \left[\frac{1}{p^2} \left(1 - \exp \left\{ -\frac{tp^2}{\tau_R} \right\} \right) \right] &\approx \int_0^{\infty} \left[\frac{dp}{p^2} \left(1 - \exp \left\{ -\frac{tp^2}{\tau_R} \right\} \right) \right] \\
&= \left(\frac{\pi t}{\tau_R} \right)^{1/2} \quad (5.149)
\end{aligned}$$

The detailed expressions for the limits of the mean-square segment displacement following from Eqs. (5.144), (5.148) and (5.149) can thus be combined to

$$\langle r^2 \rangle = \begin{cases} \frac{2}{\pi^{3/2}} b^2 \left(\frac{t}{\tau_s} \right)^{1/2} & \text{for } \tau_s \ll t \ll \tau_R = N_K^2 \tau_s \\ \frac{2}{\pi^2} \frac{b^2}{N_K} \frac{t}{\tau_s} & \text{for } t \gg \tau_R = N_K^2 \tau_s \end{cases} \quad (5.150)$$

(compare Table 5.3). In compact form, the two limits can roughly be combined for $t \gg \tau_s$ as

$$\langle r^2 \rangle \approx \frac{2}{\pi^2} \frac{b^2}{N_K} \frac{t}{\tau_s} + \frac{2}{\pi^{3/2}} b^2 \left(\frac{t}{\tau_s} \right)^{1/2} \quad (5.151)$$

Table 5.3 Diverse limits of the mean-square segment displacement $\langle r^2 \rangle$ (in the Euclidean space), the (intra)segment spin–lattice relaxation rate T_1^{-1} , the transverse relaxation rate T_2^{-1} , and the mechanical moduli G' , G'' , G as predicted by the *Rouse model* for freely draining polymers

Limit	$\tau_s \ll (t; 1/\omega) \ll \tau_R$		$(t; 1/\omega) \gg \tau_R$	
$\langle r^2 \rangle$	$\frac{2}{\pi^{3/2}} b^2 \left(\frac{t}{\tau_s} \right)^{1/2}$	Eq. (5.150)	$\frac{2}{\pi^2} \frac{b^2}{N_K} \frac{t}{\tau_s}$	Eq. (5.150)
T_1^{-1}	$-\tilde{C} \tau_s \ln(\omega \tau_s)$	Eq. (5.177)	$2\tilde{C} \tau_s \ln(N_K)$	Eq. (5.177)
T_2^{-1}			$2\tilde{C} \tau_s \ln(N_K)$	
G'	$0.54 \frac{\rho N_A k_B T}{M} \sqrt{\omega \tau_R}$	Eq. (5.197)	$\frac{\pi^4}{360} G_0 \omega^2 \tau_R^2$	Eq. (5.198)
G''	$0.54 \frac{\rho N_A k_B T}{M} \sqrt{\omega \tau_R}$	Eq. (5.197)	$\frac{\pi^2}{6} G_0 \omega \tau_R$	Eq. (5.198)
G	$\frac{\pi^{1/2}}{2^{3/2}} G_0 \left(\frac{\tau_R}{t} \right)^{1/2}$	Eq. (5.196)	$G_0 \exp\{-2t/\tau_R\}$	Eq. (5.198)

The experimental parameters are molecular mass ($M = N_K M_K$), time (t), and angular frequency (ω)

In a somewhat more distinct way, the crossover between the two limits in Eq. (5.150) can also be approximated by

$$\langle r^2 \rangle \approx \frac{2}{\pi^2} \frac{b^2}{N_K} \frac{t}{\tau_s} + \frac{2}{\pi^{3/2}} b^2 \left(\frac{t}{\tau_s} \right)^{1/2} \frac{1}{1 + \frac{6}{\pi^{3/2} N_K} \left(\frac{t}{\tau_s} \right)^{1/2}} \quad (5.152)$$

Of course, a further limitation of the validity of the Rouse theory is that the molecular mass of the polymer, M , must be larger than that of a Kuhn segment, M_K . In this respect, the range of validity of Eqs. (5.147), (5.151), and (5.152) is $M_K < M < M_c$.

The plot in Fig. 5.23 shows theoretical data based on Eq. (5.147) verifying the limits specified in Eq. (5.150). Experimentally, the characteristic square-root time dependence expected for $\tau_s \ll t \ll \tau_R$, that is, the *subdiffusive* displacement behavior already mentioned in Sect. 2.5.2, can be demonstrated by quasi-elastic neutron scattering which probes the relatively short time scale stipulated by the Rouse relaxation times of polymers below the critical molecular mass. A discussion will follow in Sect. 5.4.3.8. On the other hand, the limit $t \gg \tau_R$ can conveniently be examined with the aid of field-gradient NMR diffusometry.

The above limits for the mean-square displacement apply to polymers *below* the critical molecular mass. In the opposite case, that is, for entangled polymers, Rouse behavior is predicted as well but only under very restricted conditions as will be outlined in Sects. 5.4.4 and 5.4.6. Instead of the critical molecular mass M_c , the term *entanglement molecular mass* M_e has been discussed in Sect. 5.4.1.2 as a criterion in this respect.

5.4.3.7 Spin-Lattice Relaxation

The spin–lattice relaxation time T_1 is further measurable for which the Rouse model predicts indicative features that can readily be examined in experiments [41–43].

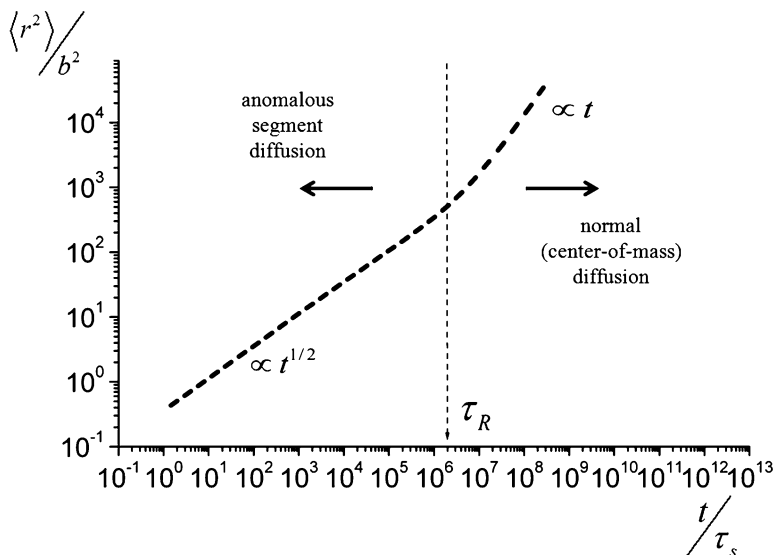


Fig. 5.23 Theoretical time dependence of the mean-square segment displacement for the Rouse model of freely draining polymers as predicted by Eq. (5.147) [40]

This in particular refers to the dependence on the angular resonance frequency $\omega = \gamma B_0$ given by the gyromagnetic ratio γ and the external magnetic flux density B_0 . As derived in Sects. 3.1.5.7 and 3.1.5.9, the spin-lattice relaxation rate is given by

$$\frac{1}{T_1} = C[I_1(\omega) + 4I_2(2\omega)] \quad (5.153)$$

According to Eqs. (3.139) and (3.148), this relation is commonly valid both for an ensemble of dipolar-coupled homonuclear, segment-internal spin pairs with spins $\frac{1}{2}$ (e. g. protons), and quadrupolar-coupled spins 1 (e. g., deuterons). C is a constant specific for the type of the coupling. In the case of dipolar coupling, it implies the internuclear distance which is assumed to be fixed. The reduced spectral densities $I_m(\omega)$ of the fluctuations of spin couplings are defined by

$$I_m(\omega) = 2 \int_0^\infty G_m(t) \cos(\omega t) dt \quad (5.154)$$

as the Fourier transform of the normalized correlation function $G_m(t)$ of the spherical harmonics of second degree into which the spatial part of dipolar interactions can be decomposed:

$$G_m(t) = 4\pi(-1)^m \langle Y_{2,m}(t) Y_{2,-m}(0) \rangle \quad (m = 1, 2) \quad (5.155)$$

The factor of 4 in the brackets in Eq. (5.153) accounts for the different prefactors with which the spherical harmonics are weighted in the Hamiltonians of the spin interactions (see, e. g., Eq. 3.127 for the dipolar case).

In Eqs. (5.153), (5.154), and (5.155), different orders m of the spherical harmonics relevant for spin–lattice relaxation are distinguished and specified by subscripts. As argued in Sects. 3.1.5.6 and 3.1.7.1, there is normally no need for this distinction since the same normalized correlation function $\bar{G}(t)$ results for both $m = 1$ and $m = 2$. To demonstrate this for the present case as well, we will nevertheless carry out separate calculations for both orders. For the sake of simplicity, we will restrict ourselves to the explicit treatment of the dipolar-coupling case. The result will however be applicable to quadrupolar coupling as well.

Spherical harmonics, Eq. (1.8), are normally expressed as functions of spherical polar coordinates of the internuclear vectors ξ connecting coupled nuclear dipoles in pairs. In the present application, the representation in Cartesian coordinates is however more favorable since we are seeking relations of these functions with the orientation of Kuhn segments. The objective is to express Eq. (5.155) in terms of correlation functions of the segment orientation vectors.

In terms of the Cartesian components ξ_x, ξ_y, ξ_z and the magnitude ξ of the internuclear vector ξ , the relevant spherical harmonics of second order can be decomposed according to

$$\begin{aligned} Y_{2,\pm 1} &= \mp \sqrt{\frac{15}{8\pi}} \frac{(\xi_x \pm i\xi_y)\xi_z}{\xi^2} = \mp \sqrt{\frac{15}{8\pi}} (u_x u_z \pm i u_y u_z) \\ Y_{2,\pm 2} &= \sqrt{\frac{15}{32\pi}} \frac{(\xi_x \pm i\xi_y)^2}{\xi^2} = \sqrt{\frac{15}{32\pi}} (u_x^2 \pm 2i u_x u_y - u_y^2) \end{aligned} \quad (5.156)$$

where $u_x = \xi_x/\xi, u_y = \xi_y/\xi, u_z = \xi_z/\xi$ are the Cartesian components of the unit vector $\mathbf{u}$ along the internuclear vector ξ (see, e. g., Ref. [44]). Since molecular fluctuations of dipolar coupling are subject to stationary statistics, the correlation functions $\bar{G}_m(t)$ are even. The imaginary part therefore vanishes. Combining Eqs. (5.155) and (5.156) thus gives for the correlation functions for the respective orders $m = 1$ and $m = 2$:

$$\begin{aligned} \bar{G}_1(t) &= -4\pi \langle Y_{2,1}(t, n) Y_{2,-1}(0, n) \rangle \\ &= \frac{15}{2} [\langle u_x(t, n) u_x(0, n) u_z(t, n) u_z(0, n) \rangle + \langle u_y(t, n) u_y(0, n) u_z(t, n) u_z(0, n) \rangle] \\ \bar{G}_2(t) &= 4\pi \langle Y_{2,2}(t, n) Y_{2,-2}(0, n) \rangle \\ &= \frac{15}{8} \left[\langle u_x^2(t, n) u_x^2(0, n) \rangle + \langle u_y^2(t, n) u_y^2(0, n) \rangle - 2 \langle u_x^2(t, n) u_y^2(0, n) \rangle \right. \\ &\quad \left. - 2 \langle u_y^2(t, n) u_x(0, n) u_y(0, n) \rangle + 4 \langle u_x(t, n) u_y(t, n) u_x(0, n) u_y(0, n) \rangle \right] \end{aligned} \quad (5.157)$$

where n is the number variable of the Kuhn segment under consideration. As usual, the angle brackets indicate the ensemble average over all segments. Note that both correlation functions are composed of terms of the common format

$$\langle u_\alpha(t, n) u_\beta(0, n) u_\gamma(t, n) u_\delta(0, n) \rangle \quad (\alpha, \beta, \gamma, \delta = x, y, z) \quad (5.158)$$

The problem is now to evaluate expressions of this type in more detail.

The Rouse model of chain dynamics refers to the time limit $t \gg \tau_s$ corresponding to the coarse-grained length scale beyond the Kuhn length. Segment-internal motions taking place on a shorter length or time scale are not implicated. The Hamiltonians of spin interactions are therefore averaged in part when the time scale relevant for the Rouse model begins. At the time $t \approx \tau_s$, the correlation functions have already decayed to some residual value. This initial decay is not of interest in the current context. A discussion will follow later in Sect. 5.4.7. At present, we will rather focus on the attenuation of the correlation functions beyond the time scale of local motions where Rouse chain modes dominate. The initial values $G_1(0)$ and $G_2(0)$ thus refer to the corresponding residual correlations remaining *after* a delay τ_s . Whenever a time t will be mentioned in the frame of the current treatment, it will from now on be understood to refer to the time limit $t > \tau_s$.

In order to account for these effective starting conditions, we introduce the mean end-to-end vector of the Kuhn segment at the number variable n averaged over a period τ_s around the instant of time t :

$$\bar{\mathbf{b}}_{ee}(t > \tau_s, n) \equiv \langle \mathbf{b}_{ee}(t, n) \rangle_{\tau_s} \quad (5.159)$$

The function $\mathbf{b}_{ee}(t, n)$ reflects the instantaneous *orientation* of the Kuhn segment at the number variable n at time t . The *segment orientation vector* $\mathbf{b}_{ee}$ defined in this way fluctuates only on a time scale $t > \tau_s$. In the following, the Cartesian components of $\mathbf{b}_{ee}$ will be denoted by $\bar{b}_\alpha$ with $\alpha = x, y, z$. Furthermore, the magnitude of $\mathbf{b}_{ee}$ will be identified with the root-mean-square length of a Kuhn segment, that is, $|\mathbf{b}_{ee}| = b$.

Analogously, the internuclear vector $\boldsymbol{\xi}(t, n)$ of a dipole pair in the segment at the number variable n at time t must be averaged over the period τ_s as well:

$$\bar{\boldsymbol{\xi}}(t > \tau_s, n) \equiv \langle \boldsymbol{\xi}(t, n) \rangle_{\tau_s} \quad (5.160)$$

This mean internuclear vector determines the decay of the residual correlation of spin interactions for times $t > \tau_s$. When speaking of the internuclear vector in the following, we therefore mean the average quantity $\bar{\boldsymbol{\xi}}$ throughout.

The result of the averaging process is that both vectors, $\bar{\mathbf{b}}_{ee}(t > \tau_s, n)$ and $\bar{\boldsymbol{\xi}}(t > \tau_s, n)$, effective on a time scale $t > \tau_s$ are *parallel* to each other. The unit vector common to them can be defined as

$$\mathbf{u}(t > \tau_s, n) = \frac{\bar{\mathbf{b}}_{ee}}{b} = \frac{\bar{\boldsymbol{\xi}}}{\xi} \quad (5.161)$$

Substituting the components of the unit vector in the expression given in Eq. (5.158) by those specified in Eq. (5.161) gives

$$\langle u_\alpha(t, n) u_\beta(0, n) u_\gamma(t, n) u_\delta(0, n) \rangle = \frac{1}{b^4} \langle \bar{b}_\alpha(t, n) \bar{b}_\beta(0, n) \bar{b}_\gamma(t, n) \bar{b}_\delta(0, n) \rangle \quad (5.162)$$

where the subscripts correspond to $\alpha, \beta, \gamma, \delta = x, y, z$.

The segment orientation vector $\bar{\mathbf{b}}_{\text{ec}}(t, n)$ can be interpreted as the derivative of the segment position vector $\mathbf{R}(t, n)$ with respect to the (continuous) segment number variable n . In this reading, the components of the segment orientation vector can be reformulated as

$$\bar{b}_\alpha(t, n) = \frac{\partial}{\partial n} R_\alpha(t, n) = -\frac{2\pi}{N_K} \sum_{p=1}^{N_K-1} p X_{p,\alpha}(t) \sin \frac{\pi p n}{N_K} \quad (\alpha = x, y, z) \quad (5.163)$$

where we have exploited the inverse normal-coordinate transformation given in Eq. (5.111). Combining this with Eq. (5.162) gives

$$\begin{aligned} \langle \bar{b}_\alpha(t, n) \bar{b}_\beta(0, n) \bar{b}_\gamma(t, n) \bar{b}_\delta(0, n) \rangle &= \left(\frac{2\pi}{N_K} \right)^4 \\ &\times \sum_{p_1, p_2, p_3, p_4}^{N_K-1} p_1 p_2 p_3 p_4 \sin \frac{\pi p_1 n}{N_K} \sin \frac{\pi p_2 n}{N_K} \sin \frac{\pi p_3 n}{N_K} \sin \frac{\pi p_4 n}{N_K} \\ &\times \langle X_{p_1,\alpha}(t) X_{p_2,\beta}(0) X_{p_3,\gamma}(t) X_{p_4,\delta}(0) \rangle \end{aligned} \quad (5.164)$$

The right-hand side of this equation can be treated further by making use of the orthogonality property of normal coordinates given in Eq. (5.113). Cross terms with respect both to the mode numbers and the Cartesian components are uncorrelated and vanish therefore. Furthermore, we can make use of the fact that the x, y, z components have identical ensemble averages. Taking this into account converts Eq. (5.164) to

$$\langle \bar{b}_\alpha(t, n) \bar{b}_\beta(0, n) \bar{b}_\gamma(t, n) \bar{b}_\delta(0, n) \rangle = \left(\frac{2\pi}{N_K} \right)^4 \left\{ \sum_p^{N_K-1} p^2 \langle X_{p,\alpha}(t) X_{p,\alpha}(0) \rangle \sin^2 \frac{\pi p n}{N_K} \right\}^2 \quad (5.165)$$

and, after substituting the normal-coordinate terms on the right-hand side by Eq. (5.163), to

$$\begin{aligned} \langle \bar{b}_\alpha(t, n) \bar{b}_\beta(0, n) \bar{b}_\gamma(t, n) \bar{b}_\delta(0, n) \rangle &= \langle \bar{b}_\alpha(t, n) \bar{b}_\beta(0, n) \rangle^2 \\ &= \frac{1}{9} \langle \bar{\mathbf{b}}_{\text{ec}}(t, n) \cdot \bar{\mathbf{b}}_{\text{ec}}(0, n) \rangle^2 \end{aligned} \quad (5.166)$$

In the isotropic case assumed here, the components for $\alpha = x, y, z$ contribute *equivalently*. Equation (5.162) can thus be reformulated as

$$\langle u_\alpha(t, n) u_\beta(0) u_\gamma(t, n) u_\delta(0, n) \rangle = \frac{1}{9b^4} \langle \bar{\mathbf{b}}_{ee}(t, n) \cdot \bar{\mathbf{b}}_{ee}(0, n) \rangle^2 \quad (5.167)$$

The correlation functions in Eq. (5.157) of the *spherical harmonics* for $m = 1, 2$ can thus commonly be expressed as squares of correlation functions of the *segment orientation vectors*:

$$\mathcal{G}_m(t) \propto \langle \bar{\mathbf{b}}_{ee}(t, n) \cdot \bar{\mathbf{b}}_{ee}(0, n) \rangle^2 \quad (5.168)$$

On this basis, the spin–lattice relaxation rate of polymers, Eq. (5.153), combined with Eq. (5.154) can be traced back to a Kuhn segment-specific function according to

$$\begin{aligned} \frac{1}{T_1(\omega, n)} \propto & \int_0^\infty \langle \bar{\mathbf{b}}_{ee}(t, n) \cdot \bar{\mathbf{b}}_{ee}(0, n) \rangle^2 \cos(\omega t) dt + \\ & 4 \int_0^\infty \langle \bar{\mathbf{b}}_{ee}(t, n) \cdot \bar{\mathbf{b}}_{ee}(0, n) \rangle^2 \cos(2\omega t) dt \end{aligned} \quad (5.169)$$

This is the spin–lattice relaxation rate of the Kuhn segment at the number variable n . It is relevant for a length scale much longer than the Kuhn length b and stipulates a fluctuation time scale much longer than the segmental relaxation time τ_s .

The spin–lattice relaxation rate in Eq. (5.169) is still a function of the segment number variable n . In order to eliminate this dependence, we replace the corresponding terms by averages over all segment numbers. Actually, such averages correspond to the experimental expectation and are therefore reasonable: Short-distance heterogeneities of the local spin–lattice relaxation properties in homonuclear systems tend to be leveled by immaterial spin diffusion, that is, flip-flop transitions of dipolar-coupled spins mediated by spin-operator terms such as $\mathcal{O}_1^{(0)}$ and $\mathcal{O}_2^{(0)}$ in Eq. (3.97) (see also the discussion in Sect. 3.2.2.5). What will actually be measured in undiluted proton systems is the *average* spin–lattice relaxation rate.

For the averaging purpose, let us return to Eqs. (5.165) and (5.166) which can commonly be formulated as

$$\langle \bar{\mathbf{b}}_{ee}(t, n) \cdot \bar{\mathbf{b}}_{ee}(0, n) \rangle^2 = 9 \left(\frac{2\pi}{N_K} \right)^4 \left\{ \sum_p^{N_K-1} p^2 \langle X_{p,\alpha}(t) X_{p,\alpha}(0) \rangle \sin^2 \frac{\pi p n}{N_K} \right\}^2 \quad (5.170)$$

Replacing the term depending on the segment-number variable n by its average, that is, the normalized integral over this variable, gives

$$\begin{aligned}
\langle \bar{\mathbf{b}}_{ee}(t) \cdot \bar{\mathbf{b}}_{ee}(0) \rangle^2 &= 9 \left(\frac{2\pi}{N_K} \right)^4 \left\{ \sum_{p=1}^{N_K-1} p^2 \langle X_{p,\alpha}(t) X_{p,\alpha}(0) \rangle \frac{1}{N_K} \int_0^{N_K} \sin^2 \frac{\pi p n}{N_K} dn \right\}^2 \\
&= 4 \left(\frac{\pi}{N_K} \right)^4 \left\{ \sum_{p=1}^{N_K-1} p^2 \langle \mathbf{X}_p(t) \cdot \mathbf{X}_p(0) \rangle \right\}^2
\end{aligned} \tag{5.171}$$

so that Eq. (5.169) takes the effective form

$$\frac{1}{T_1(\omega)} \propto \int_0^\infty \langle \bar{\mathbf{b}}_{ee}(t) \cdot \bar{\mathbf{b}}_{ee}(0) \rangle^2 \cos(\omega t) dt + 4 \int_0^\infty \langle \bar{\mathbf{b}}_{ee}(t) \cdot \bar{\mathbf{b}}_{ee}(0) \rangle^2 \cos(2\omega t) dt \tag{5.172}$$

which is now independent of the variable n .

As concerns the derivation of Eq. (5.172), we have so far not made any reference to the Rouse or other models for chain dynamics. The only polymer-specific basis was the assumption of a Kuhn segment chain and the use of the inverse transformation to normal coordinates according to Eq. (5.111). These are quite general steps giving ample scope for further interpretations in terms of different scenarios of polymer dynamics. In this sense, Eq. (5.169) represents a crucial result for all models predicting chain modes as will be discussed in later sections.

Let us now specify Eq. (5.172) for the Rouse model of freely draining polymers. Inserting the Rouse-mode solutions $\langle \mathbf{X}_p(t) \cdot \mathbf{X}_p(0) \rangle = c_p(t)$ given in Eq. (5.135) into Eq. (5.171) and the result into Eq. (5.172) gives

$$\begin{aligned}
\frac{1}{T_1(\omega)} &\propto \int_0^\infty \langle \bar{\mathbf{b}}_{ee}(t) \cdot \bar{\mathbf{b}}_{ee}(0) \rangle^2 \cos(\omega t) dt \\
&= \frac{b^4}{N_K^2} \int_0^\infty \left(\sum_{p=1}^{N_K-1} \exp \left\{ -\frac{p^2 t}{\tau_R} \right\} \right)^2 \cos(\omega t) dt
\end{aligned} \tag{5.173}$$

For the sake of simplicity, the spectral density term for twice the angular frequency has been omitted in this expression. Relative to the accuracy that can be achieved in typical experiments, the error due to this approximation is minor.

As an approach for long-enough polymer chains, that is, large numbers of Kuhn segments, $N_K \gg 1$, and for short times, $t \ll \tau_R$, the sum in Eq. (5.173) can be replaced by an integral:

$$\sum_{p=1}^{N_K-1} \exp \left\{ -\frac{p^2 t}{\tau_R} \right\} \approx \int_0^\infty \exp \left\{ -\frac{p^2 t}{\tau_R} \right\} dp = \pi^{1/2} 2^{-1} \tau_R^{1/2} t^{-1/2} \tag{5.174}$$

The cosine Fourier transform in Eq. (5.173) can furthermore be restricted to the range of normal-mode relaxation times, that is, $\tau_s \leq t \leq \tau_R$. Combining Eqs. (5.173) and (5.174) thus leads to the approximate relation

$$\begin{aligned} \frac{1}{T_1(\omega)} &\propto \frac{\pi b^4 \tau_s}{4} \int_{\tau_s}^{\tau_R} t^{-1} \cos(\omega t) dt \\ &= \frac{\pi b^4 \tau_s}{4} \int_{\omega \tau_s}^{\omega \tau_R} \xi^{-1} \cos(\xi) d\xi \overset{\omega \tau_R=1}{\approx} -\frac{\pi b^4 \tau_s}{4} \ln(\omega \tau_s) \end{aligned} \quad (5.175)$$

valid in the angular-frequency interval $\tau_R^{-1} < \omega < \tau_s^{-1}$.

Below this scale, no further normal-mode contribution arises, so that a low-frequency plateau $T_1^{-1}(\omega < \tau_R^{-1}) = \text{const}$ is expected. Equating the angular frequency in the last approximation of Eq. (5.175) with the maximum value for the relevant angular-frequency range, that is, $\omega = \tau_R^{-1} = N_K^{-2} \tau_s^{-1}$, gives the plateau relaxation rate

$$\frac{1}{T_1(\omega = \tau_R^{-1})} \propto -\frac{\pi b^4 \tau_s}{4} \ln\left(\frac{\tau_s}{\tau_R}\right) = \frac{\pi b^4 \tau_s}{2} \ln(N_K) \quad (5.176)$$

Taking both limits together thus suggests the *intrasegmental (proton or deuteron) spin–lattice relaxation rates for Rouse dynamics*

$$\frac{1}{T_1} = \begin{cases} -\tilde{C} \tau_s \ln(\omega \tau_s) & \text{for } \tau_R^{-1} < \omega < \tau_s^{-1} \\ 2\tilde{C} \tau_s \ln(N_K) & \text{for } \omega < \tau_R^{-1} \end{cases} \quad (5.177)$$

where $\tilde{C}$ is a constant. Figure 5.24 shows a plot of experimental data in comparison with the spin–lattice relaxation dispersion curves evaluated from Eq. (5.177). In the first limit, $\tau_R^{-1} < \omega < \tau_s^{-1}$, the spin–lattice relaxation rate obeys a characteristic logarithmic frequency dependence, while the frequency-independent plateau arises for $\omega < \tau_R^{-1}$ as predicted. Note that the chain length matters only in the latter limit. In Table 5.3, the above expressions are compared with results for other methods in the same limits.

As concerns frequency dependences of dipolar-coupled systems, transverse relaxation is of minor interest as already mentioned in Sect. 3.1.4.4. It may however be noteworthy that the transverse relaxation time approaches the spin–lattice relaxation time in the low-frequency limit: $T_2(\omega \ll \tau_R^{-1}) = T_1(\omega \ll \tau_R^{-1})$. Since T_1 and T_2 are measured with independent experimental protocols, this equality can be a criterion for the accuracy of low-frequency experiments and for having reached this limit indeed (for an example, see Ref. [45]).

The limits to which the expressions in Eq. (5.177) refer have been defined for freely draining polymers complying to the scale of molecular masses $M_K < M < M_c$,

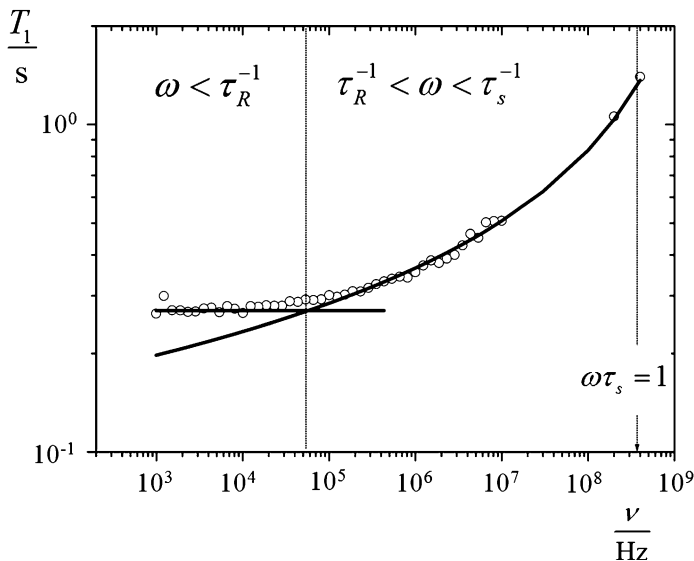


Fig. 5.24 Frequency dependence of the proton spin–lattice relaxation measured in polyethyleneoxide melts ($M_w = 1665 < M_c$; $T = 355$ K) [45]. The *solid lines* have been calculated for the Rouse limits given in Eq. (5.177) for freely draining polymer chains. The segmental fluctuation time was fitted to the data as $\tau_s = 4.7 \times 10^{-11}$ s. The position $2\pi\nu\tau_s \equiv \omega\tau_s = 1$, that is, the upper validity limit of the theory on the frequency scale, is indicated by an *arrow*

that is, between the values for a Kuhn segment and the critical molecular mass. Rouse behavior is predicted for entangled polymers as well, but in a reduced time range as will be outlined in Sects. 5.4.5 and 5.4.6. The point will be that the freely draining feature is retained even under topological constraints of chain dynamics provided that the root-mean-square segment displacements remain short enough relative to the length scale of constraints.

5.4.3.8 Quasi-Elastic Neutron Scattering

Let us now examine how the Rouse model reveals itself in neutron scattering experiments in their incoherent and coherent variants, the principles of which have been detailed in Sect. 3.6.

(a) Incoherent Neutron Scattering

The function of interest evaluated in this sort of scattering experiments is the *incoherent dynamic structure factor* which probes *translational self-diffusion* of the scattering centers. In polymer studies, the incoherent feature of the scattering process is due to protons, that is, nuclei of light hydrogen, normally ubiquitous in such materials [46, 47] (see Table 3.1). Assuming homonuclear and homogeneously distributed scattering centers in the target, the incoherent dynamic structure factor in Eq. (3.454) is given by

$$\mathcal{G}_{\text{inc}}(\mathbf{q}, t) = \left\langle e^{-i\mathbf{q}\cdot\mathbf{R}(0)} e^{i\mathbf{q}\cdot\mathbf{R}(t)} \right\rangle \stackrel{\text{Gauss}}{=} \exp\left\{-\frac{1}{6}q^2\langle r^2 \rangle\right\} \quad (5.178)$$

$\mathbf{q}$ is the scattering vector. The displacement vector of a representative scattering center in a time interval t ,

$$\mathbf{r}(t) = \mathbf{R}(t) - \mathbf{R}(0) \quad (5.179)$$

is defined by the positions of the scattering center $\mathbf{R}(0)$ and $\mathbf{R}(t)$ at times 0 and t , respectively. For comparisons with predictions of model treatments, one usually identifies the displacement vector $\mathbf{r}(t)$ with that of the polymer segments on which the scattering centers are located. The displacements probed in the experiments thus refer to chemical segments in principle. However, in the time limit beyond the segment relaxation time, they can also be equated with those of Kuhn segments.

The last expression in Eq. (5.178) is based on a Gaussian probability density function for the displacements of the scattering centers. Even though one cannot expect in general that segment diffusion as far as predicted by the Rouse model obeys a normal-diffusion propagator, the Gaussian approximation is anticipated following the common practice in the literature. Judged from successful descriptions of experimental data, it appears that the second moment of the propagator, that is, the mean-square displacement, is fortunately not very sensitive to the exact analytical form of the propagator (compare the discussions in Sects. 5.4.6 and 5.4.8).

According to Eq. (5.151), that is, in the limits $t > \tau_s$ and $M_K < M < M_c$, the mean-square segment displacement is predicted by the Rouse model to obey the approximate relation

$$\langle r^2 \rangle \approx \frac{2}{\pi^2} \frac{b^2}{N_K} \frac{t}{\tau_s} + \frac{2}{\pi^{3/2}} b^2 \left(\frac{t}{\tau_s} \right)^{1/2} = 6D_{\text{cm}}t + \frac{2}{\pi^{3/2}} b^2 \left(\frac{t}{\tau_s} \right)^{1/2} \quad (5.180)$$

where τ_s is the segment relaxation time (Eq. 5.137) and τ_R is the Rouse relaxation time (Eq. 5.139). Further parameters are the center-of-mass diffusion coefficient D_{cm} (Eq. 5.145), the Kuhn length b , and the number of Kuhn segments per chain N_K . Inserting Eq. (5.180) into Eq. (5.178) leads to the incoherent-scattering function for the Rouse model of freely draining polymers:

$$\mathcal{G}_{\text{inc}}(\mathbf{q}, t) = \exp\left\{-q^2 \frac{b^2}{3\pi^{3/2}} \left(\frac{t}{\tau_s} \right)^{1/2}\right\} \exp\{-q^2 D_{\text{cm}}t\} \quad (5.181)$$

The characteristic *square-root* time dependence of the mean-square segment displacement of freely draining polymers in the limit $\tau_s < t < \tau_R$ is also predicted for the reduced time scale $\tau_s < t < \tau_e$ for entangled polymers, where τ_e is the entanglement time mentioned before. Details will be discussed below in Sects. 5.4.5 and

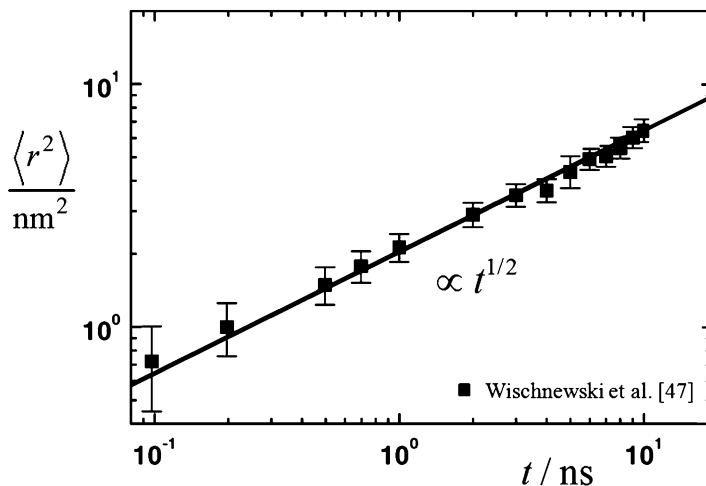


Fig. 5.25 Verification of the characteristic square-root time dependence of the mean-square segment displacement predicted by the Rouse model for polymer melts with molecular masses $M_K < M < M_c$ in the limit $\tau_s < t < \tau_R$. Above the critical molecular mass, that is, for $M > M_c$, the applicability range is $\tau_s < t < \tau_e$, where τ_e is the so-called entanglement time. The data have been evaluated in Ref. [47] from incoherent neutron scattering. For $t > \tau_e$, entanglement effects become perceptible which are beyond the scope of the Rouse model

5.4.6. Actually, this Rouse-specific law was successfully verified in Ref. [47] under such conditions after evaluating $G_{\text{inc}}(\mathbf{q}, t)$ from experimental data. Corresponding results are shown in Fig. 5.25.

The incoherent dynamic structure factor, Eq. (5.181), can also be probed by field-gradient NMR diffusometry. However, the experimentally accessible time scale is much longer as discussed in Sect. 3.10. Therefore, the *linear* time dependence for ordinary diffusion predicted for $t \gg \tau_R$ will normally dominate experimental data obtained on this basis.

(b) Coherent Neutron Scattering

As the counterpart to the incoherent variant, coherent neutron scattering refers to the dynamic structure factor for *pairs* of scattering centers. This function characterizes diffusive displacements of the pair partners *relative to each other*. This in particular provides information on *correlated* motions of segments. Experimental access to this scattering phenomenon in polymers is typically based on deuterated systems due to the favorable coherent-scattering cross-section of deuterons (see Table 3.1) [46, 48].

The pair analogue to Eq. (5.179) is

$$\mathbf{r}_{j,l}(t) = \mathbf{R}_j(t) - \mathbf{R}_l(0) \quad (5.182)$$

where the subscripts j and l indicate a pair of scattering centers. Again anticipating a Gaussian distribution function, the coherent-scattering function defined in Eq. (3.446) is derived as

$$G_{\text{coh}}(\mathbf{q}, t) = \frac{1}{N_t} \sum_{j,l=1}^{N_t} \left\langle e^{-i\mathbf{q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{q} \cdot \mathbf{R}_l(t)} \right\rangle$$

$$\stackrel{\text{Gauss}}{=} \frac{1}{N_t} \sum_{j,l=1}^{N_t} \exp \left\{ -\frac{1}{6} q^2 \langle r_{j,l}^2 \rangle \right\} \quad (5.183)$$

The relative displacement $\mathbf{r}_{j,l}$ of a pair can be expressed in terms of normal coordinates with the aid of the inverse transformation relation given in Eq. (5.111). Inserting the Rouse solutions for the normal coordinates leads to mean-square *pair* displacement

$$\begin{aligned} \langle r_{j,l}^2 \rangle &= \langle [\mathbf{R}_j(t) - \mathbf{R}_l(0)]^2 \rangle \\ &= 6D_{\text{cm}}t + |j - l|b^2 \\ &\quad + 4 \frac{N_K b^2}{\pi^2} \sum_{p=1}^{N_K-1} \frac{1}{p^2} \cos\left(\frac{\pi j}{N_K}\right) \cos\left(\frac{\pi l}{N_K}\right) \left(1 - \exp\left\{-\frac{p^2 t}{\tau_R}\right\}\right) \end{aligned} \quad (5.184)$$

in analogy to Eqs. (5.143) and (5.147) predicted for *self*-diffusion. The constant term $|j - l|b^2$ represents the mean-square distance between segments (i.e., scattering centers) j and l . Combining Eqs. (5.183) and (5.184) gives the Rouse version of the coherent *dynamic* structure factor,

$$\begin{aligned} G_{\text{coh}}(q, t) &= \frac{1}{N_t} \sum_{j,l=1}^{N_t} \exp \left\{ -\frac{1}{6} q^2 \langle r_{j,l}^2 \rangle \right\} \\ &= \frac{1}{N_t} \sum_{j,l=1}^{N_t} \exp \left\{ \begin{aligned} &-q^2 D_{\text{cm}}t - \frac{1}{6} |j - l| q^2 b^2 \\ &- \frac{2N_K b^2}{3\pi^2} \sum_{p=1}^{N_K-1} \frac{1}{p^2} \cos\left(\frac{\pi j}{N_K}\right) \cos\left(\frac{\pi l}{N_K}\right) \left(1 - \exp\left\{-\frac{p^2 t}{\tau_R}\right\}\right) \end{aligned} \right\} \end{aligned} \quad (5.185)$$

Setting $t = 0$ provides the *static* structure factor $G_{\text{coh}}(\mathbf{q}, 0)$. A comparison of this formalism with typical experimental data is represented by Fig. 5.26.

5.4.3.9 Dynamic Mechanical Relaxation

The constitutive relation between shear stress and shear rate, Eq. (3.493),

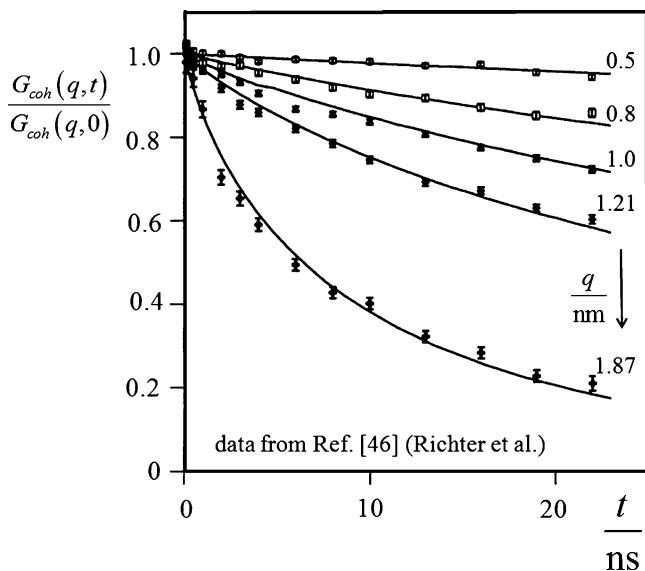


Fig. 5.26 Coherent dynamic structure factor $G_{\text{coh}}(q, t)$ relative to the static structure factor $G_{\text{coh}}(q, 0)$ as a function of time in a polymer melt. The *solid lines* represent the Rouse theory for different scattering wave numbers q (see Eq. 5.185) [46]

$$\sigma_{\text{shear}}(t) = \int_{-\infty}^t G(t-t') \dot{\gamma}(t') dt' \quad (5.186)$$

can be expressed in terms of the Rouse normal-mode correlation functions $c_p(t) \equiv \langle \mathbf{X}_p(t) \cdot \mathbf{X}_p(0) \rangle$ given in Eq. (5.135) [7, 17]. The crucial point is that the shear relaxation modulus $G(t-t')$ in this relation acts as a *linear response function* which is based on the microscopic fluctuations in the system at equilibrium (see Sect. 1.2). In the frame of the Rouse model for freely draining polymers, these fluctuations are described by the superposition of normal modes as detailed above. Instead of an exhaustive analysis of Eq. (5.186) in terms of the Rouse model, let us restrict ourselves to a more heuristic argument.

Chain dynamics can be described by a set of independent normal coordinates as defined in Eq. (5.108). Each of the normal coordinates represents a damped elastic element and therefore contributes to the shear modulus of the sample. Apart from a proportionality factor, the normalized correlation function of the normal coordinates given in Eq. (5.136),

$$\frac{\langle X_{p,\alpha}(t) X_{p,\alpha}(0) \rangle}{\langle X_{p,\alpha}^2 \rangle} = \exp\left\{-\frac{t}{\tau_p}\right\} \quad (\alpha = x, y, z) \quad (5.187)$$

can be interpreted as probability that the normal-mode component α with the mode number p and the relaxation time τ_p persists unchanged after a time t . Shearing the sample affects two Cartesian components, whereas the third one remains unaffected. In the example shown in Fig. 3.45, the “passive” element is the x component. The probability that both “active” components, that is, the y and z component in the present example, survive a period t in unaltered form is then given by the product

$$P = \frac{\langle X_{p,y}(t)X_{p,y}(0) \rangle}{\langle X_{p,y}^2 \rangle} \frac{\langle X_{p,z}(t)X_{p,z}(0) \rangle}{\langle X_{p,z}^2 \rangle} = \exp\left\{-\frac{2t}{\tau_p}\right\} \quad (5.188)$$

Here we have exploited the fact that different components of normal coordinates are stochastically independent as manifested by Eq. (5.113). As a consequence, the above exponential function decays *twice* as fast as suggested by the correlation function of the normal coordinates.

In the limit $t \rightarrow 0$ when relaxation and flow are not yet effective, the probability P takes the value 1 and the relaxation modulus approaches the static shear modulus of a network already treated in Sect. 5.3. The molecular mass of the mesh chains in Eq. (5.88) needs merely to be replaced by that of the total polymer, M :

$$G(t \rightarrow 0) = G_0 = \frac{\rho N_A k_B T}{M} \quad (5.189)$$

where ρ is the mass density. Multiplying this expression with the probability given in Eq. (5.188) results in the decaying contribution of the normal mode to the total relaxation modulus for arbitrary times:

$$G_p(t) = \frac{\rho N_A k_B T}{M} \exp\left\{-\frac{2t}{\tau_p}\right\} \quad (5.190)$$

where the mode relaxation times obey $\tau_p = p^{-2}\tau_R$.

The independence of the normal modes implicates that the elastic elements which they effectively represent are so to speak arranged in a parallel circuit in complete analogy to a parallel connection of springs. That is, the total *Rouse relaxation modulus* of the sample is just the sum of Eq. (5.190) over all mode numbers p :

$$G(t) = \sum_{p=1}^{N_K-1} G_p(t) = G_0 \sum_{p=1}^{N_K-1} \exp\left\{-\frac{2p^2 t}{\tau_R}\right\} \quad (5.191)$$

We note that the relaxation modulus of the system finally takes its maximum value for $t \rightarrow 0$,

$$G(t \rightarrow 0) = G_0(N_K - 1) \overset{N_K \gg 1}{\approx} \frac{\rho N_A k_B T}{M_K} \quad (5.192)$$

where we have made use of Eq. (5.189) and where M_K is the molecular mass of a Kuhn segment. The remarkable result of this consideration is that in the absence of relaxation, that is, in the short-time limit, the shear modulus corresponds to a network with the Kuhn segments as meshes analogous to that considered in Sect. 5.3.

The usual measurands in dynamic relaxation experiments are the storage and the loss modulus as outlined in Sect. 3.8.4.1. Inserting the Rouse relaxation modulus in Eq. (5.191) into the relations given in Eq. (3.515) suggests

$$G'(\omega) = G_0 \sum_{p=1}^{N_K-1} \frac{\omega^2 \tau_p^2}{4 + \omega^2 \tau_p^2} \quad (5.193)$$

for the *storage modulus* and

$$G''(\omega) = G_0 \sum_{p=1}^{N_K-1} \frac{2\omega \tau_p}{2 + \omega^2 \tau_p^2} \quad (5.194)$$

for the *loss modulus*. The Rouse relaxation times are specified in Eqs. (5.137), (5.138), (5.139), and (5.140) as

$$\tau_p = \frac{1}{p^2} \frac{\zeta b^2}{3\pi^2 k_B M_K} \frac{M^2}{T} \quad (5.195)$$

Graphical representations of Eqs. (5.191), (5.193), and (5.194) are shown in Figs. 5.27 and 5.28.

In the limit $t \ll \tau_R = p^2 \tau_p$ and $N_K \gg 1$, the sum in Eq. (5.191) can be approached by an integral leading to the square-root law

$$G(t \ll \tau_R) \approx G_0 \int_0^\infty \exp\left\{-\frac{2tp^2}{\tau_R}\right\} dp = \frac{\pi^{1/2}}{2^{3/2}} G_0 \left(\frac{\tau_R}{t}\right)^{1/2} \quad (5.196)$$

On the angular-frequency scale conjugate to $t \ll \tau_R$, the storage and loss moduli commonly approach the expression

$$G'(\omega \tau_R \gg 1) = G''(\omega \tau_R \gg 1) \approx 0.54 \frac{\rho N_A k_B T}{M} \sqrt{\omega \tau_R} \quad (5.197)$$

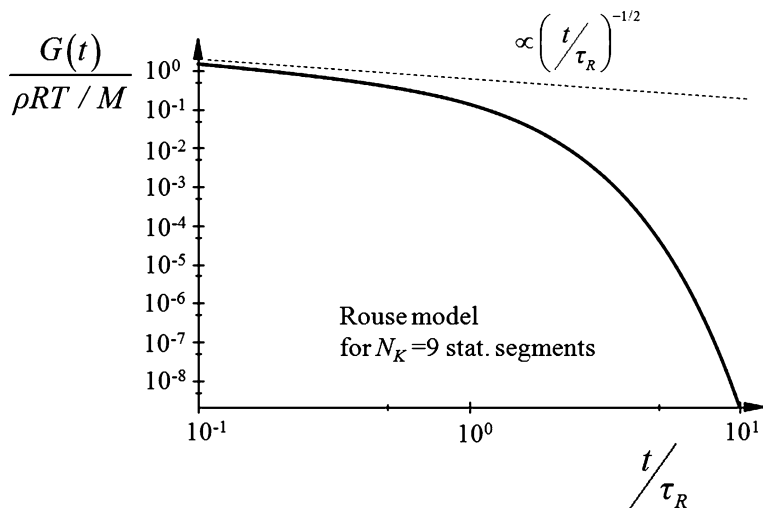


Fig. 5.27 Mechanical relaxation modulus as a function of time calculated according to the Rouse model for $N_K = 9$ Kuhn segments (see Eq. 5.191)

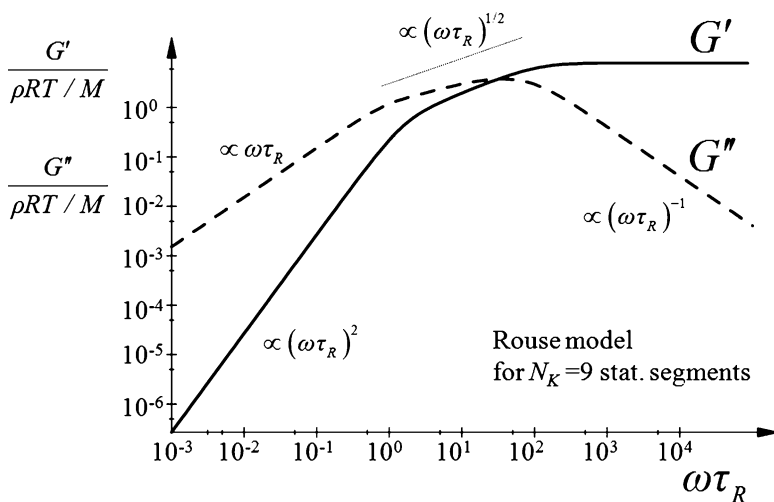


Fig. 5.28 Dynamic shear moduli G' and G'' as functions of $\omega\tau_R$ calculated for $N_K = 9$ statistical segments according to the Rouse model (see Eqs. 5.193 and 5.194)

The so-called *terminal zone*, that is, the low-frequency ($\omega\tau_R \ll 1$) and long-time ($t \gg \tau_R$) limits relative to the Rouse relaxation rates and times, respectively, is of particular interest. The limiting expressions for the diverse moduli are

$$\begin{aligned}
G(t \gg \tau_R) &\approx G_0 \exp\left\{-\frac{2t}{\tau_R}\right\} \\
G'(\omega\tau_R \ll 1) &\approx \frac{1}{4}G_0\omega^2\tau_R^2 \sum_{p=1}^{N_K-1} \frac{1}{p^4} \overset{N_K \rightarrow \infty}{\approx} \frac{\pi^4}{360} G_0\omega^2\tau_R^2 \propto \omega^2 \\
G''(\omega\tau_R \ll 1) &\approx G_0\omega\tau_R \sum_{p=1}^{N_K-1} \frac{1}{p^2} \overset{N_K \rightarrow \infty}{\approx} \frac{\pi^2}{6} G_0\omega\tau_R \propto \omega
\end{aligned} \tag{5.198}$$

A comparison with results for other measurands in the same limits can be found in Table 5.3.

Note that the limiting laws in Eqs. (5.196), (5.197), and (5.198) have been derived for “infinitely” long chains, that is, for the limit $N_K \gg 1$. As a consequence, the curves in the respective graphs in Figs. 5.27 and 5.28 calculated for only $N_K = 9$ segments approach the limiting power laws only in correspondingly restricted ranges.

In Eq. (3.530), the low-frequency limit $\omega\tau_R \ll 1$ of the loss modulus was specified as

$$G''(\omega\tau_R \ll 1) = \omega\eta_0 \tag{5.199}$$

where the parameter η_0 is the zero-shear viscosity and τ_R is the longest Rouse relaxation time. On the other hand, Eq. (5.194) suggests

$$G''(\omega\tau_R \ll 1) = G_0\omega \sum_{p=1}^{N_K-1} \tau_p \tag{5.200}$$

By comparison of these expressions and inserting Eq. (5.195), we find

$$\eta_0 = G_0 \sum_{p=1}^{N_K-1} \tau_p = \frac{\rho N_A \zeta b^2}{3\pi^2} \frac{M}{M_K^2} \sum_{p=1}^{N_K-1} p^{-2} \overset{N_K \rightarrow \infty}{\approx} \frac{\rho N_A \zeta b^2}{18} \frac{M}{M_K^2} \tag{5.201}$$

where the sum can be approached by the known relation $\sum_{p=1}^{\infty} p^{-2} = \pi^2/6$. The Rouse model predicts a *linear* increase of the zero-shear viscosity with the molecular mass, $\eta_0 \propto M$. This corresponds to experimental findings for $M < M_c$ (corrected for chain-end effects according to Refs. [29] or [32], for instance) as already mentioned in Sect. 5.4.1.1 and as depicted in Fig. 5.15.

Furthermore, Eq. (5.195) can be regrouped as

$$\zeta b^2 = \frac{3\pi^2 k_B T p^2 M_K^2 \tau_p}{M^2} \tag{5.202}$$

Inserting this into Eq. (5.201) gives a relation between the zero-shear viscosity as a function of the Rouse relaxation times,

$$\eta_0 = \frac{\pi^2}{6} \frac{\rho N_A k_B T p^2}{M} \tau_p \quad (5.203)$$

or vice versa,

$$\tau_p = \frac{6\eta_0 M}{\pi^2 \rho N_A k_B T p^2} \quad \text{and} \quad \tau_R \equiv \tau_1 = \frac{6\eta_0 M}{\pi^2 \rho N_A k_B T} \quad (5.204)$$

In principle, the Rouse relaxation times can be determined on this basis by measuring the zero-shear viscosity for known density and molecular mass $M < M_c$ of the material.

5.4.3.10 Discussion of the Applicability of the Rouse Model

The Rouse model is expected to apply to unconstrained polymer liquids. Neither entanglement nor spatial confinement effects should restrict chain dynamics. Crucial conditions are that the coarse-grain limits $t \gg \tau_s$ and $N_K \gg 1$ apply. As concerns molecular masses above the critical value, $M > M_c$ (see Table 5.2), the relevant time scale ranges up to the entanglement time $t \approx \tau_e$. From the theoretical point of view, restrictions of this sort are predicted by the tube/reptation model (Sect. 5.4.6) and the renormalized Rouse formalism (Sect. 5.4.4), for instance. The typical NMR relaxometry data set shown in Fig. 5.24 and the neutron scattering results plotted in Fig. 5.25 demonstrate how well the predictions of the model theory coincide with experimental findings in the application span.

For the sake of completeness, it should be mentioned at this point that experimental diffusion and relaxation data of short polymers especially below the critical molecular mass M_c can have been subjected to *chain-end free-volume* effects. This phenomenon in particular causes an additional dependence on the molecular mass apart from that predicted by the Rouse model for the center of mass diffusion coefficient (Eq. 5.146) and for the Rouse relaxation time (Eq. 5.140). An empirical description of the consequences of chain-end effects can be based on the *William/Landell/Ferry (WLF) equation*. For details see, for example, Refs. [29, 32].¹¹

Another problem is dynamics within Kuhn segments, that is, on a length scale shorter than b and on a time scale below τ_s , where the coarse-grain picture does no longer apply. This is the regime of so-called *local dynamics* which is not accounted for in the frame of the Rouse model. A discussion will follow in Sect. 5.4.7.

¹¹ The enhanced mobility intrinsic to chain ends causes a locally reduced density which in turn gives rise to an inhomogeneous distribution of the magnetic susceptibility. The consequence is a strong broadening of NMR resonance lines as described in Ref. [48].

Anticipating a result that will be presented later in Fig. 5.38, really strong deviations between the analytical (coarse grain) result for the spin–lattice relaxation time, Eq. (5.177), and experimental data, that is, the true behavior, can be stated at frequencies corresponding to the short-time limit $t < \tau_s$.

In polymer solutions, the critical molecular mass is increased according to the empirical relation given in Eq. (5.89). This extends the realm of freely draining chain dynamics to molecular masses far above the melt value of the critical molecular mass. On the other hand, *hydrodynamic backflow* interactions between more or less remote sections of polymer random coil will come into play in dilute solutions. To account for this phenomenon, the formalism can be supplemented by corresponding interaction terms in the equations of motion. A typical example for such an extended treatment is the *Zimm model* [50]. The interested reader is referred to Refs. [7, 9], for instance. The strategy to add appropriate terms to the equations of motion to account for more complicated dynamic scenarios was already mentioned in the context of Eq. (5.106).

The two basic conditions of the Rouse formalism are on the one hand $M \ll M_c$, that is, $N_K \ll N_{K,c}$ in terms of Kuhn segment numbers, and $N_K \gg 1$ on the other. At least in polymer melts, these restrictions can hardly be fulfilled at the same time and certainly not in a wide range. As mentioned before, the consequences for practical applications are minor: Apart from a numerical scaling factor, the dynamic features remain unaffected by the moderate violations of these conditions [37].

A criticism of a more intriguing nature is the following: In Ref. [51], it is shown that a treatment of rheological properties solely based on *intramolecular* elastic forces conflicts with basic laws of physics. *Intermolecular* contributions to entropy elasticity may not be ignored. Zero-shear viscosity should rather be the result of chain-pair correlations and interactions even in the unentangled case for which the Rouse model is thought to be representative. From this point of view, the accordance of the Rouse single-chain formalism with rheological data must be considered to be a coincidental one. The computer simulations reported in Refs. [52, 53] support this conclusion.

5.4.4 The Renormalized Rouse Formalism (Entangled Polymer Chains)

The term “entanglement” paraphrases long-time interactions of the chain with the surrounding polymers as they become relevant above the critical molecular mass M_c . The time scale is understood relative to chain-mode relaxation times. In contrast to freely draining chain dynamics where interchain contacts can be assumed to be much shorter than the shortest relaxation time, we are now dealing with more persistent constraints which cannot simply be implied in an effective parameter such as the friction coefficient.

The idea of the *renormalized Rouse formalism* [54] is to account for entanglement interactions by supplementing the equation of motion by a memory term, that

is, *time-dependent* friction. This is a formal approach that cannot be expected to explain exhaustively all entanglement phenomena on the whole time scale that might be of interest. The range of applicability is rather limited to the proper Rouse regime $\tau_s < t < \tau_R$ by definition. On the other hand, the appealing advantage is that the ansatz is entirely analytical so that the features and limits of the solutions can directly be related to the modifications made in the equation of motion. If corroborated experimentally, the relations established in this way can be a key for our understanding of dynamic entanglement effects.

Paying tribute to the strategy adumbrated already in Eq. (5.106), the bead-and-spring equation of motion of Kuhn segment n , Eq. (5.104), is extended by a time-dependent friction term according to

$$\underbrace{K \frac{\partial^2 \mathbf{R}(t, n)}{\partial n^2}}_{\text{elastic force}} - \underbrace{\zeta \frac{\partial \mathbf{R}(t, n)}{\partial t} - \zeta \int_0^t \Gamma(t - \tau) \frac{\partial \mathbf{R}(t, n)}{\partial t} d\tau}_{\text{friction}} + \underbrace{\mathbf{f}(t, n)}_{\text{stochastic force}} = 0 \quad (5.205)$$

As before, inertial forces, hydrodynamic interactions, and excluded-volume effects are neglected. Equation (5.205) is often referred to as *generalized Langevin equation*. The friction term $-\zeta \partial \mathbf{R}(t, n) / \partial t$ with the segmental friction constant ζ is now supplemented by an integral term with the time-dependent memory kernel $\Gamma(t - \tau)$. This so-called *memory function* reflects the fact that the friction coefficient effective for fast motions, that is, short-time fluctuations, is larger than for slow displacements of segments. Qualitatively, it is therefore a function decaying with increasing time delay $t - \tau$. This may be associated with the notion that entanglement constraints are more and more released in the course of time by microstructural relaxation of the interchain interactions.

Strictly speaking, the memory function is a second-rank tensor. In matrix form, it is defined by elements $\{\cdots\}_{nm}$ essentially consisting of correlation functions between the *stochastic force* components acting on segment n at time 0 and on segment m at time t of a representative polymer chain.¹² The tensor property means that there is some orientation dependence of friction relative to the segment orientation. However, on the relatively short time scale, $\tau_s \ll t \ll \tau_R$, when entanglement effects are still weak, the memory matrix can be approached by a scalar independent of the momentary chain conformation. More detailed discussions can be found in Refs. [42, 43, 49, 54].

By definition, the memory function implies all information about intermolecular interactions causing entanglement effects. In the simplest case, that is, in the absence of correlated interchain interactions, the memory function can be represented by a delta function instantaneously decaying to zero. In this case, the Rouse solution comes out exactly as described in the previous sections. On the other hand, if entanglement (long-

¹² To be precise, the attribute *projected* should be added to all forces and dynamic quantities after subjecting the equation of motion to the *Mori/Zwanzig projector operator formalism* as needed in the frame of memory-function theories. An outline of this general way of treatment is given in Refs. [55] or [56], for instance.

time) interchain interactions exist, the problem is to find a physically plausible ansatz for the memory function. In principle, one could postulate a power law with an exponent as a parameter to be fitted to experimental data after having derived expressions for the observables of interest on this basis. Proceeding in this way would not however be very revealing. Fortunately, there is a less formal and less phenomenological approach.

The procedure can be sketched as follows: A Mori/Zwanzig projector operator treatment [55, 56] of the problem leads to an expression for the memory function depending on the mean-square segment displacement. As a short-time approach, this (unknown) function of time is replaced by the (known) Rouse power-law solution for the time dependence of the segment mean-square displacement (see Eq. 5.150). The renormalized equation of motion established in this way can then be solved in analogy to the treatment in previous sections. The steps of calculation are in principle equivalent. The treatment given in Ref. [43] is however too lengthy to be reproduced here. We therefore content ourselves with rendering some results for the mean-square segment displacement and the (intra-segment) spin–lattice relaxation time in Table 5.4.

A remarkable prediction is the crossover of the spin–lattice relaxation dispersion from a $\propto M^0 \omega^{1/5}$ law at *low* frequencies in limit (II)_{RR} to $\propto M^0 \omega^{1/2}$ at *high* frequencies in limit (I)_{RR}. The former limit corresponds to a *long* time scale and to *low* mode numbers, and the latter to a *short* time scale and *high* mode numbers. Figure 5.29 shows spin–lattice relaxation data of polyisobutylene melts as an example which evidently manifests this crossover. The reproduction of the power law exponents close to the prediction of the model treatment strongly supports the formalism. Nevertheless, the fact that the *crossover between the two limits* suggested by the theory has been observed in reality is much more important: It is an indication that the generalized Langevin equation given in Eq. (5.205) in principle contains the essential terms needed for the representation of entangled-chain dynamics on the time scale $\tau_s \ll t \ll \tau_R$.¹³

5.4.5 Harmonic Radial Tube Potential (Confined Polymer Chains)

Let us now turn to the third polymer scenario that can be treated with the aid of modifications of the bead-and-spring Langevin equation given in Eq. (5.104). As already suggested in the context of Eq. (5.106), a force term can be added to

¹³ On a time scale beyond limit (II)_{RR} (i.e. at still lower frequencies), a further power-law regime has been observed in polyethyleneoxide and polybutadiene melts [58]. The experimental finding is $T_1 \propto M^0 \omega^{0.4 \dots 0.5}$. The attempt to explain this power law by the influence of inter-chain dipolar interaction [49, 58] was ruled out since the same behavior was observed in melts of perdeuterated melts of the same species where intramolecular spin interactions dominate [59]. Thus, there is no explanation currently available for this distinct feature of spin–lattice relaxation dispersion in entangled polymer melts.

Table 5.4 Diverse limits of the mean-square segment displacement $\langle r^2 \rangle$ (in the Euclidean space) and the intrasegment spin–lattice relaxation time T_1 as predicted by the *renormalized Rouse model* [43]

Limit		$\langle r^2 \rangle$	T_1
(Rouse)	$\tau_s \ll (t; 1/\omega) \ll \tau_s/\psi \{*\}$	$\propto M^0 t^{1/2}$	$\propto -M^0 [\tau_s \ln(\omega \tau_s)]^{-1}$
(I) _{RR}	$\tau_s/(1.9\psi) \ll (t; 1/\omega) \ll (6\pi)^4 1.9\psi/\tau_s$	$\propto M^0 t^{1/4}$	$\propto M^0 \omega^{1/2}$
(II) _{RR}	$\frac{(6\pi)^4}{20} \psi \tau_s \ll (t; 1/\omega) \ll 2.14\psi \tau_s N_K^{2.5}$	$\propto M^0 t^{2/5}$	$\propto M^0 \omega^{1/5}$

The experimental parameters are molecular mass (M), time (t), and angular frequency (ω). The quantity ψ is the so-called entanglement parameter characterizing the strength of entanglement effects. The limit marked by an *asterisk* $\{*\}$ corresponds to the ordinary Rouse model (see Eqs. 5.150 and 5.177)

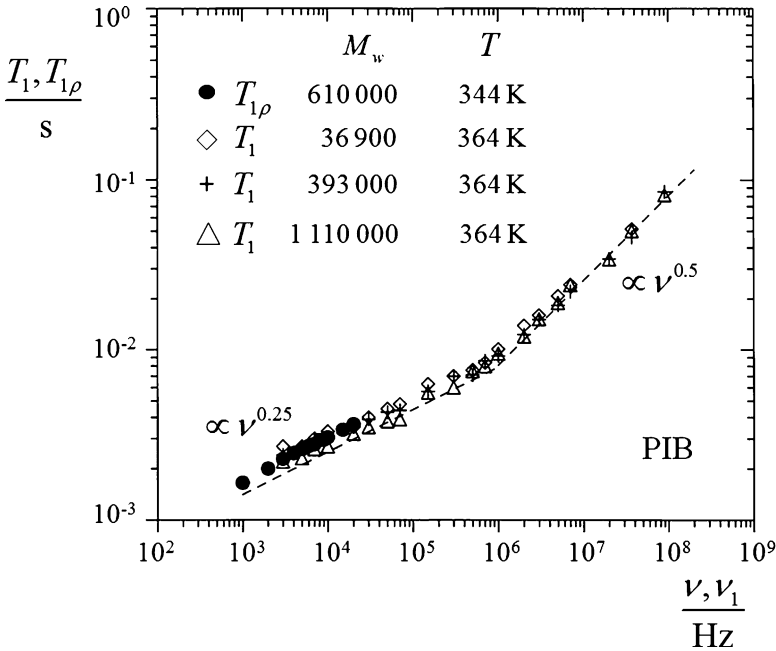
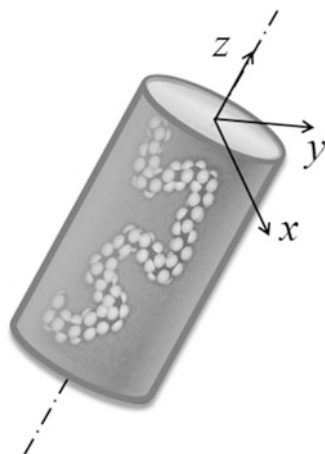


Fig. 5.29 Frequency dependences of the spin–lattice relaxation times in the laboratory (T_1) and rotating ($T_{1\rho}$) frames in polyisobutylene (PIB) melts above the critical molecular mass M_c . The *dashed lines* demonstrate power-law limits close to those predicted by the renormalized Rouse formalism (see Table 5.4). Methodological explanations of the techniques employed in the experiments can be found in Sect. 3.1.4. (Reproduced from Ref. [57] with kind permission of © ACS 1993)

the segment equation of motion for the treatment of the effect of *tube confinements* on polymer dynamics.

Consider polymer chains confined in a cylindrical tube as schematically illustrated in Fig. 5.30. The confining tube can be imagined as a pore in a solid matrix, for example. Figuratively, it could even mimic the *fictitious Doi/Edwards tube* anticipated in the frame of the tube/reptation model for entangled polymers to

Fig. 5.30 Reference frame and illustrative cartoon of a representative polymer chain confined in a cylindrical tube



be outlined in Sect. 5.4.6. To begin with, let us assume that the confining tube has a straight axis coinciding with the z direction of the reference frame. Later on, we will extend the formalism to randomly coiled tubes with Gaussian end-to-end statistics. As a consequence of the confinement, the polymers experience a potential exerting a reset force on the segments when approaching the tube walls. Before defining a corresponding distance law, let us first classify and discuss a variety of different tube-internal potential distributions.

5.4.5.1 Radial Distribution of the Tube Potential

Figure 5.31 shows a crude classification of prospective potential distributions in radial direction. *Sticky* tube walls, Fig. 5.31a, suggest that there is some tendency for adsorption of polymer segments at the tube walls. If adsorption is strong enough, even a sort of two-phase behavior due to adsorbed and free polymers is expected depending on the mutual affinity of the polymer species and the matrix material [60]. The conformation of adsorbed polymer chains will be deformed relative to bulk conditions as can be demonstrated with the aid of computer simulations.

The opposite tendency is expected for *hard* tube walls, Fig. 5.31b, where the potential well has a flat bottom but becomes infinite as soon as polymer segments begin to penetrate the walls. This is certainly an incisive idealization. In a sense, it is just this approach that is effectively anticipated in the original version of the tube/reptation model by Doi and Edwards [7] to facilitate the calculation of the configurational entropy of a confined polymer chain. We will get back to that concept in Sect. 5.4.6.

The third type of radial potential distribution of interest in the present context is characterized by *soft* tube walls. In this case, polymer segments will progressively be repelled when approaching the walls. The *soft* potential distribution best suited

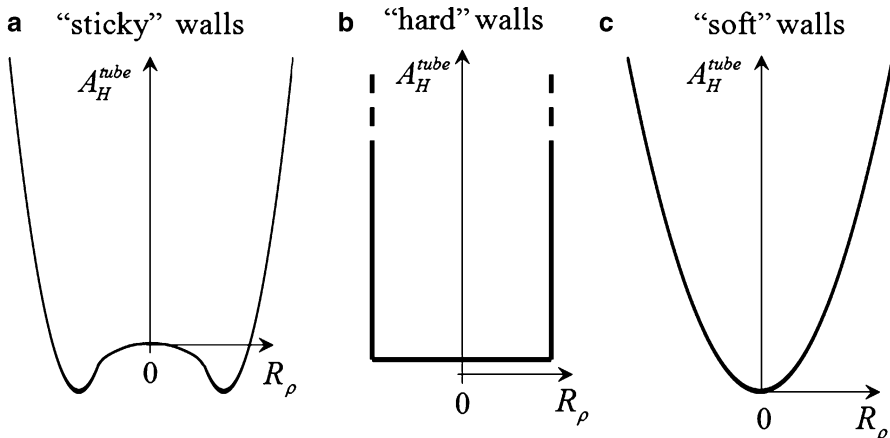


Fig. 5.31 Classification of radial potential distributions in a cylindrical tube. $R_\rho = \sqrt{R_x^2 + R_y^2}$ is the radial coordinate of a Kuhn segment. The origin is assumed on the tube axis. For the sake of generality, the potential is regarded to be of a thermodynamic nature in the form of the Helmholtz free energy A_H^{tube}

for analytical treatments turned out to be the parabolic (“harmonic”) radial function depicted in Fig. 5.31c. The assumption of a harmonic confinement potential is not unrealistic: Actually, a Hookean behavior for small displacements was recently detected in a single-molecule fluorescence experiment studying motions of tightly entangled F-actin filaments [61]. This ansatz may also be appropriate for polymers confined in pores as long as the walls are of a non- or only weakly adsorbing nature. From the theoretical point of view, the harmonic radial potential distribution is attractive since the theory based on it can be conducted in *closed* analytical form [40] (in contrast to the reptation model to be considered later).

5.4.5.2 Equation of Motion and Normal Modes

The position of Kuhn segment n of a confined polymer chain is described by the vector $\mathbf{R}(t, n)$, with the components $R_x(t, n)$, $R_y(t, n)$ and $R_z(t, n)$.¹⁴ The radial distance from the tube axis, $R_\rho(t, n) = \sqrt{R_x^2 + R_y^2}$, is determined by the transverse coordinates $R_x(t, n)$ and $R_y(t, n)$ measured from the tube axis (see Fig. 5.30). According to the conceptual relations in Eq. (5.106), the Rouse equation of motion in Eq. (5.104) must be supplemented by a force term reflecting the tube potential. The analytical form is assumed to be of the harmonic form sketched in Fig. 5.31c:

$$A_H^{\text{tube}}(R_\rho) = \frac{\sigma}{2} R_\rho^2, \quad (5.206)$$

¹⁴ Recall: The number n is on the one hand used as a *continuous* variable and as a *discrete* segment number on the other as suggested by the context.

The factor σ is a material constant. Instead of the ordinary potential energy, the Helmholtz free energy A_H^{tube} is quoted here as a thermodynamic potential. The reason is that the polymer conformation and consequently the configurational entropy must be expected to be modified as a function of the radial coordinate R_ρ .

In thermal equilibrium, the mean-square radius of the radial potential distribution in Eq. (5.206) can be calculated with the aid of Boltzmann factors according to

$$\langle R_\rho^2 \rangle = \frac{\int_0^\infty R_\rho^2 \exp\left\{-\frac{\sigma}{2k_B T} R_\rho^2\right\} 4\pi R_\rho dR_\rho}{\int_0^\infty \exp\left\{-\frac{\sigma}{2k_B T} R_\rho^2\right\} 4\pi R_\rho dR_\rho} = \frac{2k_B T}{\sigma} \quad (5.207)$$

Defining an *effective tube diameter* d_{eff} via the identities

$$\left(\frac{d_{\text{eff}}}{2}\right)^2 \equiv \langle R_\rho^2 \rangle = \frac{2k_B T}{\sigma} \quad \text{or} \quad d_{\text{eff}} \equiv 2\sqrt{\frac{2k_B T}{\sigma}} \quad (5.208)$$

leads to the relation $\sigma = 8k_B T/d_{\text{eff}}^2$. The definition of d_{eff} indicates that it can be regarded as the *root mean-square* diameter of the lateral space accessible for the confined polymer. Of course, this does not exclude temporally more extended conformations of the chain.

Combined with Eq. (5.208), the radial harmonic potential Eq. (5.206) reads

$$A_H^{\text{tube}}(R_x, R_y) = \frac{4k_B T}{d_{\text{eff}}^2} (R_x^2 + R_y^2) \quad (5.209)$$

In the continuum limit, that is, for a length scale much longer than the Kuhn length, the equation of motion for Kuhn segment n of a polymer confined in a radial harmonic potential can thus be established as

$$\underbrace{\frac{3k_B T}{b^2} \frac{\partial^2 \mathbf{R}(t, n)}{\partial n^2}}_{\text{entropy elastic force}} \underbrace{- \nabla_n A_H^{\text{tube}}(t, n)}_{\text{harmonic potential force}} \underbrace{- \zeta \frac{\partial \mathbf{R}(t, n)}{\partial t}}_{\text{friction}} \underbrace{+ \mathbf{f}(t, n)}_{\text{stochastic force}} = 0 \quad (5.210)$$

where

$$- \nabla_n A_H^{\text{tube}}(t, n) = - \frac{8k_B T}{d_{\text{eff}}^2} \mathbf{R}_\rho(t, n) \quad (5.211)$$

is the restoring force acting on the segment under consideration. $\mathbf{R}_\rho(t, n)$ is the two-dimensional radial-distance *vector* with the components R_x and R_y . As in the case of freely draining polymers, Eq. (5.107), the boundary conditions are again $\partial \mathbf{R} / \partial n|_{n=0, N_K} = 0$.

Multiplying Eq. (5.210) by $N_K^{-1} \cos(\pi pn/N_K)$ and integrating over the continuous segment-number variable n gives

$$\begin{aligned} & \frac{3k_B T}{N_K b^2} \int_0^{N_K} \frac{\partial^2 \mathbf{R}(t, n)}{\partial n^2} \cos\left(\frac{\pi pn}{N_K}\right) dn - \frac{8k_B T}{N_K d_{\text{eff}}^2} \int_0^{N_K} \mathbf{R}_\rho(t, n) \cos\left(\frac{\pi pn}{N_K}\right) dn \\ & - \frac{\zeta}{N_K} \int_0^{N_K} \frac{\partial \mathbf{R}(t, n)}{\partial t} \cos\left(\frac{\pi pn}{N_K}\right) dn + \frac{1}{N_K} \int_0^{N_K} \mathbf{f}(t, n) \cos\left(\frac{\pi pn}{N_K}\right) dn = 0 \end{aligned} \quad (5.212)$$

In analogy to the derivation of Eq. (5.114) for the Rouse model of freely draining polymers, we reformulate this equation with the aid of the normal-coordinate transformation

$$\begin{aligned} \mathbf{X}_p(t) &= \frac{1}{N_K} \int_0^{N_K} \cos\left(\frac{\pi pn}{N_K}\right) \mathbf{R}(t, n) dn \quad (p = 1, 2, \dots, N_K - 1) \\ X_{p,\alpha}(t) &= \frac{1}{N_K} \int_0^{N_K} \cos\left(\frac{\pi pn}{N_K}\right) R_\alpha(t, n) dn \quad (p = 1, 2, \dots, N_K - 1; \quad \alpha = x, y, z) \\ \mathbf{X}_0(t) &= \mathbf{R}_{\text{cm}}(t) \quad (p = 0) \end{aligned} \quad (5.213)$$

The vector $\mathbf{R}_{\text{cm}}$ specifies the position of the center of gravity according to Eq. (5.35). The result is the expression given in Eq. (5.114) plus a further term originating from the radial tube potential:

$$\frac{3k_B T \pi^2 p^2}{b^2 N_K^2} \mathbf{X}_p(t) + \frac{8k_B T}{d_{\text{eff}}^2} (X_{p,x} \mathbf{u}_x + X_{p,y} \mathbf{u}_y) + \zeta \frac{\partial}{\partial t} \mathbf{X}_p(t) - \mathbf{F}_p(t) = 0 \quad (5.214)$$

The stochastic function $\mathbf{F}_p(t)$ is defined by

$$\mathbf{F}_p(t) = \frac{1}{N_K} \int_0^{N_K} \mathbf{f}(t, n) \cos\left(\frac{\pi pn}{N_K}\right) dn \quad (5.215)$$

as before. The unit vectors along the x - and y - axes are denoted by $\mathbf{u}_x$ and $\mathbf{u}_y$, respectively. Equation (5.214) can be rewritten as

$$\frac{1}{\tau_p} \mathbf{X}_p(t) + \frac{1}{\tau_t} (X_{p,x} \mathbf{u}_x + X_{p,y} \mathbf{u}_y) + \frac{\partial}{\partial t} \mathbf{X}_p(t) - \frac{1}{\zeta} \mathbf{F}_p(t) = 0 \quad (5.216)$$

by making use of the *Rouse relaxation time of normal mode p* , Eq. (5.123),

$$\tau_p = \frac{N_K^2}{p^2} \tau_s \quad (5.217)$$

the *segmental relaxation time*, Eq. (5.125),

$$\tau_s = \frac{b^2 \zeta}{3\pi^2 k_B T} \quad (5.218)$$

and a new time constant called *tube time* directly reflecting the tube constraint,

$$\tau_t = \frac{3\pi^2 d_{\text{eff}}^2}{8b^2} \tau_s \quad (5.219)$$

Written in the more convenient component form, Eq. (5.216) can be expressed by

$$\begin{aligned} \frac{\partial}{\partial t} X_{p,x} &= - \left(\frac{1}{\tau_t} + \frac{1}{\tau_p} \right) X_{p,x} + \frac{1}{\zeta} F_{p,x} \\ \frac{\partial}{\partial t} X_{p,y} &= - \left(\frac{1}{\tau_t} + \frac{1}{\tau_p} \right) X_{p,y} + \frac{1}{\zeta} F_{p,y} \\ \frac{\partial}{\partial t} X_{p,z} &= - \frac{1}{\tau_p} X_{p,z} + \frac{1}{\zeta} F_{p,z} \end{aligned} \quad (5.220)$$

Multiplying these equations by $X_{p,\alpha}(0)$ and averaging over an ensemble lead to the set of differential equations of the normal-coordinate correlation functions

$$\frac{\partial}{\partial t} \langle X_{p,\alpha}(t) X_{p,\alpha}(0) \rangle = - \frac{1}{\tau_{p,\alpha}} \langle X_{p,\alpha}(t) X_{p,\alpha}(0) \rangle \quad (\alpha = x, y, z) \quad (5.221)$$

with the rate constants

$$\frac{1}{\tau_{p,\alpha}} = \begin{cases} \frac{1}{\tau_p} + \frac{1}{\tau_t} & \text{for } \alpha = x, y \\ \frac{1}{\tau_p} & \text{for } \alpha = z \end{cases} \quad (5.222)$$

In the derivation of Eq. (5.221), the orthogonality property of the normal coordinates, Eq. (5.113), has been exploited. Furthermore, the fact has been taken into account that there is no correlation between the stochastic force function $\mathbf{F}_p(t)$ and the normal coordinates.

The solutions of Eq. (5.221) are

$$\begin{aligned} \langle X_{p,\alpha}(t) X_{p,\alpha}(0) \rangle &= \langle X_{p,\alpha}^2 \rangle \exp \left\{ - \frac{t}{\tau_{p,\alpha}} \right\} \quad (p = 1, 2, \dots, N_K - 1) \\ \langle X_{0,\alpha}(t) X_{0,\alpha}(0) \rangle &= \langle R_{\text{cm},\alpha}(t) R_{\text{cm},\alpha}(0) \rangle \quad (p = 0) \end{aligned} \quad (5.223)$$

for the components $\alpha = x, y, z$. Analogous to the Rouse formalism for freely draining polymers, chain dynamics in tubes is composed of normal modes. The crucial difference is however the *anisotropy* in the sense that the three Cartesian components of the normal coordinates do not behave in the same way: As suggested

by Eq. (5.222), different time constants are valid for the x and y components on the one hand, and for the z component on the other.

The initial conditions, that is, the terms $\langle X_{p,\alpha}^2 \rangle$ in Eq. (5.223), are derived according to

$$\langle X_{p,\alpha}^2 \rangle = \frac{\int_{-\infty}^{\infty} X_{p,\alpha}^2 \exp\left\{-\frac{A_H^{\text{tot}}}{k_B T}\right\} dX_{p,\alpha}}{\int_{-\infty}^{\infty} \exp\left\{-\frac{A_H^{\text{tot}}}{k_B T}\right\} dX_{p,\alpha}} \quad (\alpha = x, y, z) \quad (5.224)$$

in analogy to the formalism in Sect. 5.4.3.4. In the present application, the elastic Helmholtz free energy A_H^{elast} must now be supplemented by the harmonic potential A_H^{tube} . The *total* Helmholtz free energy employed in Eq. (5.224) thus is

$$A_H^{\text{tot}} = A_H^{\text{elast}} + A_H^{\text{tube}} \quad (5.225)$$

Combining Eq. (5.127) for A_H^{elast} and Eq. (5.209) for A_H^{tube} gives

$$A_H^{\text{tot}} = \frac{3k_B T}{2b^2} \sum_{n=1}^{N_K-1} [\mathbf{R}_{n+1} - \mathbf{R}_n]^2 + \frac{4k_B T}{d_{\text{eff}}^2} \sum_{n=1}^{N_K} [R_{n,x}^2 + R_{n,y}^2] \quad (5.226)$$

The substitution of all spatial coordinates by the inverse normal-coordinate transformation in Eq. (5.111) leads to

$$\begin{aligned} A_H^{\text{tot}} = & \frac{12k_B T}{b^2} \sum_{n=1}^{N_K-1} \left[\sum_{p=1}^{N_K-1} X_p \sin\left\{\frac{\pi p}{N_K} \left(n + \frac{1}{2}\right)\right\} \sin\left\{\frac{\pi p}{2N_K}\right\} \right]^2 \\ & + \frac{4k_B T}{d_{\text{eff}}^2} \sum_{n=1}^{N_K} \sum_{\alpha=x,y} \left[X_{0,\alpha} + 2 \sum_{p=1}^{N_K-1} X_{p,\alpha} \cos\left\{\frac{\pi p n}{N_K}\right\} \right]^2 \end{aligned} \quad (5.227)$$

where we have again made use of the trigonometric relation given in Eq. (5.129).

In the continuum limit, the sum over the segment number can be replaced by an integral, $\sum_{n=1}^{N_K-1} \dots \approx \int_0^{N_K-1/2} \dots dn$, so that the explicit dependence on n is eliminated. As a consequence of the orthogonality property, Eq. (5.113), all cross terms for different normal-coordinate numbers and for different components vanish upon integration after squaring the sums in Eq. (5.227). In this way, the total Helmholtz free energy can be expressed as

$$\begin{aligned} A_H^{\text{tot}} = & \frac{k_B T}{2} \sum_{p=1}^{N_K-1} \sum_{\alpha=x,y} \left\{ \frac{24N_K}{b^2} \sin^2\left(\frac{\pi p}{2N_K}\right) + \frac{16N_K}{d_{\text{eff}}^2} \right\} X_{p,\alpha}^2 \\ & + \frac{k_B T}{2} \sum_{p=1}^{N_K-1} \frac{24N_K}{b^2} \sin^2\left(\frac{\pi p}{2N_K}\right) X_{p,z}^2 + \frac{4k_B T}{d_{\text{eff}}^2} (X_{0,x}^2 + X_{0,y}^2) \end{aligned} \quad (5.228)$$

The mean-square components of the normal coordinates are then obtained by inserting Eq. (5.228) into Eq. (5.224). The steps of this calculation can be summarized as follows: Starting from

$$\langle X_{p,x}^2 \rangle = \frac{\int_{-\infty}^{\infty} X_{p,x}^2 \exp\left\{-\frac{A_H^{\text{tot}}}{k_B T}\right\} dX_{p,x}}{\int_{-\infty}^{\infty} \exp\left\{-\frac{A_H^{\text{tot}}}{k_B T}\right\} dX_{p,x}} \quad (5.229)$$

we have

$$\langle X_{p,x}^2 \rangle = \frac{\int_{-\infty}^{\infty} X_{p,x}^2 \exp\left\{-\frac{1}{2} \underbrace{\left[\frac{24N_K}{b^2} \sin^2 \frac{\pi p}{2N_K} + \frac{16N_K}{d_{\text{eff}}^2}\right]}_{\equiv C^2} X_{p,x}^2\right\} dX_{p,x}}{\int_{-\infty}^{\infty} \exp\left\{-\frac{1}{2} \underbrace{\left[\frac{24N_K}{b^2} \sin^2 \frac{\pi p}{2N_K} + \frac{16N_K}{d_{\text{eff}}^2}\right]}_{\equiv C^2} X_{p,x}^2\right\} dX_{p,x}} \quad (5.230)$$

and an equivalent expression for the y component. With the definition

$$C^2 = \frac{12N_K}{b^2} \sin^2 \frac{\pi p}{2N_K} + \frac{8N_K}{d_{\text{eff}}^2} \quad (5.231)$$

this results in

$$\langle X_{p,x}^2 \rangle = \langle X_{p,y}^2 \rangle = \frac{1}{2C^2} = \frac{1}{\frac{24N_K}{b^2} \sin^2 \frac{\pi p}{2N_K} + \frac{16N_K}{d_{\text{eff}}^2}} \quad (5.232)$$

Likewise, the mean-square z component obeys

$$\langle X_{p,z}^2 \rangle = \frac{b^2}{24N_K \sin^2 \frac{\pi p}{2N_K}} \overset{N_K \gg \pi p/2}{\approx} \frac{b^2 N_K}{6\pi^2 p^2} \quad (5.233)$$

The mode number range is $p = 1, 2, \dots, N_K - 1$ as before. The mean-square expressions $\langle X_{p,x}^2 \rangle$, $\langle X_{p,y}^2 \rangle$, and $\langle X_{p,z}^2 \rangle$ are the initial values of the correlation functions of the normal-coordinate components. Note that the result Eq. (5.233) coincides with Eq. (5.133) derived for the Rouse model if a single component is considered instead of all three.

5.4.5.3 Mean-Square Segment Displacement

(a) Straight and “Infinitely” Long Tube

As a consequence of the confinement in a tube, translational segment displacements are expected to be strongly anisotropic. It will be necessary to discriminate between components along and transverse to the tube axis. Let us first consider diffusive segment displacements in a straight, “infinitely” long tube with an axis in z direction and generalize the result afterward to randomly-coiled tubes.

Analogous to the relation in Eq. (5.147) for freely draining polymers, the mean-square (msq) component of the segment displacement vector averaged over all segments of a chain can be set down as

$$\begin{aligned}
 \langle r_\alpha^2 \rangle_{\text{tube}} &\equiv \frac{1}{N_K} \int_0^{N_K} \langle [R_\alpha(t, n) - R_\alpha(0, n)]^2 \rangle dn \\
 &= \underbrace{\langle [X_{0,\alpha}(t) - X_{0,\alpha}(0)]^2 \rangle}_{\text{msq center-of-mass displacement}} \\
 &\quad + \underbrace{4 \sum_{p=1}^{N_K-1} \langle X_{p,\alpha}^2 \rangle \left(1 - \exp \left\{ -\frac{t}{\tau_{p,\alpha}} \right\} \right)}_{\text{msq displacements relative to the center-of-mass}} \quad (\alpha = x, y, z) \quad (5.234)
 \end{aligned}$$

where we have referred to Eq. (5.223). The subscript “tube” indicates that the displacements are measured relative to the tube coordinate system depicted in Fig. 5.30. Owing to the symmetry of the problem, the transverse components concerning the x and y directions are equivalent. The combined mean-square displacement *transverse* to the tube axis is consequently

$$\begin{aligned}
 \langle r_x^2 + r_y^2 \rangle_{\text{tube}} &= 2 \langle [X_{0,x}(t) - X_{0,x}(0)]^2 \rangle \\
 &\quad + 8 \sum_{p=1}^{N_K-1} \langle X_{p,x}^2(0) \rangle \left(1 - \exp \left\{ -\frac{t}{\tau_{p,x}} \right\} \right) \quad (5.235)
 \end{aligned}$$

In the limit $\tau_s \ll t \ll \tau_t$, that is, on a length scale much shorter than the effective tube diameter d_{eff} , there will be no perceptible influence of the tube constraint. A relation analogous to Eq. (5.150) for freely draining polymers is therefore expected for this time scale:

$$\langle r_x^2 + r_y^2 \rangle_{\text{tube}} \approx \frac{4}{3\pi^{3/2}} b^2 \left(\frac{t}{\tau_s} \right)^{1/2} = \left(\frac{2}{3\pi} \right)^{1/2} b d_{\text{eff}} \left(\frac{t}{\tau_t} \right)^{1/2} \quad \text{for } \tau_s \ll t \ll \tau_t \quad (5.236)$$

Note that this expression refers to only two dimensions instead of the three accounted for in Eq. (5.150). In the opposite limit, $t \gg \tau_t$, the tube constraint is effective and prevents mean-square displacements larger than compatible with the lateral tube dimension. In this limit, Eq. (5.235) takes the form

$$\begin{aligned} \langle r_x^2 + r_y^2 \rangle_{\text{tube}} &\approx 2 \langle [X_{0,x}(\infty) - X_{0,x}(0)]^2 \rangle + 8 \sum_{p=1}^{N_K-1} \langle X_{p,x}^2(0) \rangle \\ &= 4 \langle X_{0,x}^2(0) \rangle + 8 \sum_{p=1}^{N_K-1} \langle X_{p,x}^2(0) \rangle \quad \text{for } t \gg \tau_t \end{aligned} \quad (5.237)$$

In the evaluation of the first term on the right-hand side, we have exploited the fact that normal modes become uncorrelated after such long periods.

Inserting the results for the transverse components of the normal coordinates given in Eq. (5.230), approximating the sum by an integral, and considering the limit $N_K \gg \pi p/2$ lead to the time-independent relation

$$\begin{aligned} \langle r_x^2 + r_y^2 \rangle_{\text{tube}} &\approx \frac{d_{\text{eff}}^2}{4N_K} + 8 \int_1^{N_K-1} \frac{b^2 N_K d_{\text{eff}}^2}{6\pi^2 p^2 d_{\text{eff}}^2 + 16N_K^2 b^2} dp \\ &= \frac{d_{\text{eff}}^2}{4N} + \sqrt{\frac{2}{3}} \frac{d_{\text{eff}} b}{\pi} \left[\arctan \left(\sqrt{\frac{3}{8}} \pi \frac{d_{\text{eff}}}{b} \right) - \arctan \left(\sqrt{\frac{3}{8}} \pi \frac{d_{\text{eff}}}{N_K b} \right) \right] \\ &\approx \sqrt{\frac{2}{3}} \frac{d_{\text{eff}} b}{\pi} \arctan \left(\sqrt{\frac{3}{8}} \pi \frac{d_{\text{eff}}}{b} \right) \quad \text{for } t \gg \tau_t; \quad N_K \gg \frac{\pi p}{2} \end{aligned} \quad (5.238)$$

For effective tube diameters $d_{\text{eff}} \gg b$, the last line of Eq. (5.238) can be simplified as

$$\langle r_x^2 + r_y^2 \rangle_{\text{tube}} \approx \frac{1}{\sqrt{6}} d_{\text{eff}} b \quad \text{for } t \gg \tau_t; N_K \gg \pi p/2; d_{\text{eff}} \gg b \quad (5.239)$$

Finally, Eqs. (5.236) and (5.239) can be combined as the closed expression

$$\langle r_x^2 + r_y^2 \rangle_{\text{tube}} \approx \sqrt{\frac{2}{3\pi}} b d_{\text{eff}} \left(\frac{t}{\tau_t} \right)^{1/2} \frac{1}{1 + \frac{2}{\sqrt{\pi}} \left(\frac{t}{\tau_t} \right)^{1/2}} \quad \text{for } t \gg \tau_s; N_K \gg \frac{\pi p}{2}; d_{\text{eff}} \gg b \quad (5.240)$$

The third displacement component, that is, $\alpha = z$, is measured along the tube axis. Since there is no constraint in this direction, the result known from the Rouse model of freely draining polymers applies again. The only difference is a reduction of the mean-square displacement by a factor of 1/3, because we are referring now to a single component instead of all three. Based on Eq. (5.152), we thus obtain

$$\begin{aligned} \langle r_z^2 \rangle_{\text{tube}} &\approx \frac{2}{3\pi^2} \frac{b^2}{N_K} \frac{t}{\tau_s} + \frac{2}{3\pi^{3/2}} b^2 \left(\frac{t}{\tau_s} \right)^{1/2} \frac{1}{1 + \frac{6}{\pi^{3/2} N_K} \left(\frac{t}{\tau_s} \right)^{1/2}} \\ &\approx \begin{cases} \frac{2}{3\pi^{3/2}} b^2 \left(\frac{t}{\tau_s} \right)^{1/2} & \text{for } \tau_s \ll t \ll \tau_R = N_K^2 \tau_s \\ \frac{2}{3\pi^2} \frac{b^2}{N_K} \frac{t}{\tau_s} & \text{for } t \gg \tau_R = N_K^2 \tau_s \end{cases} \end{aligned} \quad (5.241)$$

The total, anisotropic mean-square displacement,

$$\langle \mathbf{r}^2 \rangle_{\text{tube}} = \langle r_x^2 \rangle_{\text{tube}} + \langle r_y^2 \rangle_{\text{tube}} + \langle r_z^2 \rangle_{\text{tube}} \quad (5.242)$$

in a straight tube of effective diameter d_{eff} can be formed by combining Eqs. (5.240) and (5.241).

(b) Randomly Coiled Tube

Let us now assume that the confining tube has a randomly coiled conformation. The quantity of interest is the mean-square segment displacement in the Euclidean space, $\langle r_z^2 \rangle_{\text{lab}}$, measured *relative to the laboratory frame*, while $\langle r_z^2 \rangle_{\text{tube}}$ in principle refers to tube coordinates (irrespective of the tube conformation). The transformation from tube to laboratory coordinates can readily be established by assuming that the tube conformation is subject to Gaussian statistics analogous to a freely jointed chain with a step length a . The end-to-end distance of any finite stretch of sufficient length $L_{\text{tube}} \gg a$ will then again be distributed according to a Gaussian function (see the discussion in Sect. 5.2.3.1). Under such conditions, the transformation relation reads

$$\langle r_z^2 \rangle_{\text{lab}} = a L_{\text{tube}} = a \sqrt{\langle r_z^2 \rangle_{\text{tube}}} \quad (5.243)$$

in close analogy to Eq. (5.32). Here, we have identified the length of the considered tube stretch with the root-mean-square displacement along the tube:

$$L_{\text{tube}} = \sqrt{\langle r_z^2 \rangle_{\text{tube}}}.$$

As a consequence, the time dependences of the mean-square displacement $\langle r_z^2 \rangle_{\text{tube}}$ given above in Eq. (5.241) must be rescaled by a square root operation. In Euclidean space, it takes correspondingly *longer* to reach a certain mean-square displacement than measured in curvilinear tube coordinates. By this transformation, Eq. (5.241) is converted for $\sqrt{\langle r_z^2 \rangle_{\text{tube}}} \gg a, b$ to the mean-square displacement relative to the laboratory frame

$$\begin{aligned}
\langle r_z^2 \rangle_{\text{lab}} &\approx \frac{2^{1/2}}{3^{1/2}\pi} \frac{ab}{N_K^{1/2}} \left(\frac{t}{\tau_s} \right)^{1/2} + \frac{2^{1/2}}{3^{1/2}\pi^{3/4}} ab \left(\frac{t}{\tau_s} \right)^{1/4} \left(\frac{1}{1 + \frac{6}{\pi^{3/2}N_K} \left(\frac{t}{\tau_s} \right)^{1/2}} \right)^{1/2} \\
&\approx \begin{cases} \frac{2^{1/2}}{3^{1/2}\pi^{3/4}} ab \left(\frac{t}{\tau_s} \right)^{1/4} & \text{for } \tau_s \ll t \ll \tau_R = N_K^2 \tau_s \\ \frac{2^{1/2}}{3^{1/2}\pi} \frac{ab}{N_K^{1/2}} \left(\frac{t}{\tau_s} \right)^{1/2} & \text{for } t \gg \tau_R = N_K^2 \tau_s \end{cases}
\end{aligned} \tag{5.244}$$

where b is the Kuhn length, and a is the step length of the tube.

This rescaling measure specifically refers to the mean-square displacements along the curvilinear z coordinate, whereas the (*independent*) transverse displacements characterized by Eq. (5.240) are not affected by the tube conformation. Thus, the total mean-square segment displacement in the laboratory frame can be composed as

$$\langle \mathbf{r}^2 \rangle_{\text{tot}} = \langle r_z^2 \rangle_{\text{lab}} + \langle r_x^2 + r_y^2 \rangle_{\text{tube}} \tag{5.245}$$

Let us now distinguish three time regimes: In the limit $\tau_s \ll t \ll \tau_t$, the total mean-square displacement $\langle \mathbf{r}^2 \rangle_{\text{tot}}$ will be dominated by the transverse contributions $\langle r_x^2 + r_y^2 \rangle_{\text{tube}}$ given in Eq. (5.236) without need to transform the expression to another reference frame. By contrast, the ranges $\tau_t \ll t \ll \tau_R$ and $t \gg \tau_R$ will be governed by $\langle r_z^2 \rangle_{\text{lab}}$. This latter contribution is based on longitudinal displacements according to the limits in Eq. (5.241) subject to the transformation mentioned before. In summary, the three regimes are predicted to scale with respect to time and number of Kuhn segments as

$$\langle \mathbf{r}^2 \rangle_{\text{tot}} \propto \begin{cases} N_K^0 t^{1/2} & \text{for } \tau_s \ll t \ll \tau_t \\ N_K^0 t^{1/4} & \text{for } \tau_t \ll t \ll \tau_R \\ N_K^{-1/2} t^{1/2} & \text{for } t \gg \tau_R \end{cases} \tag{5.246}$$

where the segment relaxation time τ_s and the tube time τ_t are defined in Eqs. (5.218) and (5.219), respectively, and the Rouse relaxation time is given by $\tau_R = N_K^2 \tau_s$.

The power laws in Eq. (5.246) reveal subdiffusive (i.e., anomalous) diffusion behavior in all cases. Recall that we have assumed an “infinitely” long tube here so that the polymer remains permanently under confinement. This is in contrast to the *disengagement* process to be discussed in Sect. 5.4.6 in the frame of the tube/reptation model.

Figure 5.32 shows a plot of the laboratory-frame mean-square segment displacement for various diameters of a tube with Gaussian conformation statistics. The crossover from the free Rouse model to the confined behavior is obvious. Likewise, the three limits given in Eq. (5.246) are evident. In Sect. 5.4.6, it will

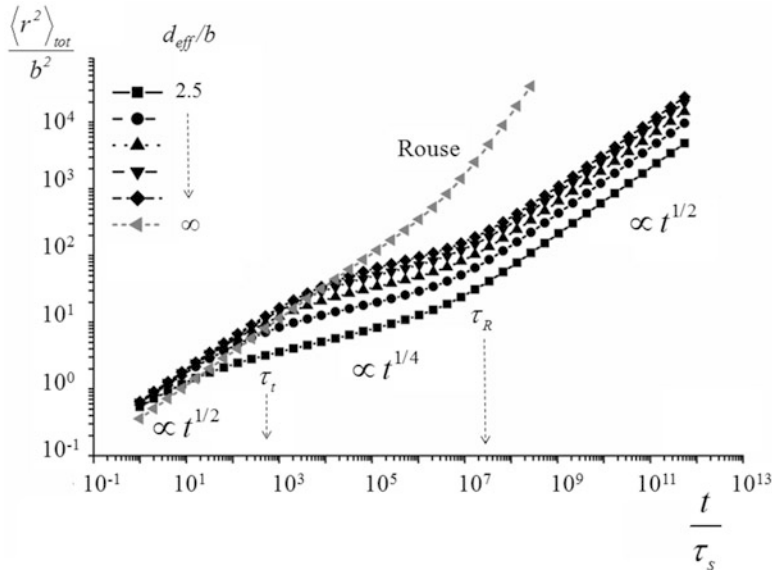


Fig. 5.32 Theoretical time dependence predicted by Eq. (5.245) combined with Eqs. (5.240) and (5.244) for the mean-square segment displacement of polymers confined in an “infinitely” long tube with Gaussian conformation statistics and a harmonic radial potential. In the calculation, the number of Kuhn segments was assumed to be $N_K = 1,600$. The limiting laws given in Eq. (5.246) are indicated. The time constants intersecting these limits, that is, the tube time τ_t and the Rouse relaxation time τ_R , are roughly marked. Data for freely draining polymer chains are plotted for comparison (“Rouse”). The mean-square segment displacement is scaled in units b^2 , the square of the Kuhn length. The time unit is the segmental relaxation time τ_s . Depending on the effective tube diameter d_{eff} , a crossover between freely draining and confined polymer dynamics reveals itself. The latter exhibits the same characteristics as the Doi/Edwards limits (I)_{DE}, (II)_{DE}, and (III)_{DE} as manifested by the indicated power laws (see Sect. 5.4.6). (Reproduced from Ref. [40] with kind permission of © AIP 2002)

be shown that these cases find their equivalents in the limits (I)_{DE}, (II)_{DE}, and (III)_{DE} introduced by Doi and Edwards in the frame of the tube/reptation model [7].

5.4.5.4 Spin-Lattice Relaxation

(a) Straight and “Infinitely” Long Tube

Let us resume the discussion in Sect. 5.4.3.7 about the spin-lattice relaxation rate T_1^{-1} . As a starting point, we refer to the general expression derived in Eq. (5.172) as

$$\frac{1}{T_1(\omega)} \propto \int_0^\infty \langle \bar{\mathbf{b}}_{ee}(t) \cdot \bar{\mathbf{b}}_{ee}(0) \rangle^2 \cos(\omega t) dt + 4 \int_0^\infty \langle \bar{\mathbf{b}}_{ee}(t) \cdot \bar{\mathbf{b}}_{ee}(0) \rangle^2 \cos(2\omega t) dt \quad (5.247)$$

The Kuhn segment vector $\bar{\mathbf{b}}_{ee}(t)$ is defined in Eq. (5.159).

Under tube confinement, the situation is a bit more complicated than it was in the case of the isotropic Rouse model. The first reason is that the component of the segment vector $\bar{\mathbf{b}}_{ee}$ along the tube axis must be distinguished from the transverse components. Fortunately, the analytical character of the correlation function remains practically the same so that only minor modifications are needed. This in particular refers to Eq. (5.166) which is no longer valid in this form since the isotropy condition is now lifted.

The anisotropy intrinsic to polymers confined in straight tubes does not only refer to segmental *reorientations relative to the tube axis*. In spin–lattice relaxation experiments, the *orientation of the tube axis relative to the external magnetic flux density* must be taken into account as well. All ensemble averages considered in the present context are therefore understood to imply a “powder average” referring to an equidistribution of tube orientations relative to the external field. In real experiments with dipolar-coupled proton systems, this averaging process will “automatically” take place on the relaxation time scale as a consequence of immaterial spin diffusion between all spin moieties in different tube environments not separated too far from each other (see Sect. 3.2.2.5).

In the analysis of the square of the temporal correlation function of the Kuhn segment vector [40],

$$\begin{aligned} \langle \bar{\mathbf{b}}_{ee}(t) \cdot \bar{\mathbf{b}}_{ee}(0) \rangle^2 &= 4 \langle \bar{b}_x(t) \bar{b}_x(0) \rangle^2 + 4 \langle \bar{b}_x(t) \bar{b}_x(0) \rangle \langle \bar{b}_z(t) \bar{b}_z(0) \rangle \\ &\quad + \langle \bar{b}_z(t) \bar{b}_z(0) \rangle^2 \end{aligned} \quad (5.248)$$

the (equivalent) x and y components must now be distinguished from the z component. As a consequence, the spin–lattice relaxation rate, Eq. (5.247), will depend on a *linear combination* of terms of the form

$$G_\alpha(t) G_\beta(t) = \langle \bar{b}_\alpha(t) \bar{b}_\alpha(0) \rangle \langle \bar{b}_\beta(t) \bar{b}_\beta(0) \rangle \quad (5.249)$$

where $\alpha, \beta = x, z$. The second transverse component, y , need not be considered individually since its contribution is equivalent to that of x . The anisotropy caused by the tube confinement is involved in numerical coefficients $C_{\alpha,\beta}$ with which the correlation functions Eq. (5.249) contribute to the linear combination. The spin–lattice relaxation rate can thus be expressed by

$$\frac{1}{T_1} \propto \sum_{\substack{\alpha=x, z \\ \beta=x, z}} C_{\alpha,\beta} \left\{ \int_0^\infty G_\alpha(t) G_\beta(t) \cos(\omega t) dt + 4 \int_0^\infty G_\alpha(t) G_\beta(t) \cos(2\omega t) dt \right\} \quad (5.250)$$

The next step is to calculate the autocorrelation functions of the components of the segment vector. According to Eq. (5.163), the α component of the segment vector at the segment-number variable n is given in terms of the α components of the normal coordinates by

$$\bar{b}_\alpha(t, n) = \frac{\partial}{\partial n} R_\alpha(t, n) = -\frac{2\pi}{N_K} \sum_{p=1}^{N_K-1} p X_{p,\alpha}(t) \sin \frac{\pi p n}{N_K} \quad (\alpha = x, y, z) \quad (5.251)$$

Forming the autocorrelation function and averaging over the number variable n lead to

$$\begin{aligned} G_\alpha(t) &= \langle \bar{b}_\alpha(t) \bar{b}_\alpha(0) \rangle \\ &= \frac{4\pi^2}{N_K^2} \sum_{p=1}^{N_K-1} p^2 \langle X_{p,\alpha}(t) X_{p,\alpha}(0) \rangle \frac{1}{N_K} \int_0^{N_K} \sin^2 \frac{\pi p n}{N_K} dn \\ &= \frac{2\pi^2}{N_K^2} \sum_{p=1}^{N_K-1} p^2 \langle X_{p,\alpha}(t) X_{p,\alpha}(0) \rangle \end{aligned} \quad (5.252)$$

and to an analogous expression for $G_\beta(t)$. The average over n accounts for the leveling effect due to spin diffusion by flip-flop transitions in homonuclear spin systems as already assumed in the case of the free Rouse model and discussed in Sect. 3.2.2.5. In the derivation of the result in Eq. (5.252), we have exploited the orthogonal properties in Eq. (5.113) of the normal coordinates again.

(b) Randomly Coiled Tube

So far, the treatment refers to straight confinement tubes where translations along the tube axis are not correlated with segment reorientations. Let us now turn to the more realistic scenario of randomly coiled tubes. In this case, segment displacements *along* the tube axis are intrinsically connected with reorientations in addition to those directly due to chain modes. That is, translational diffusion in the tube matters just in the sense of the *reptation* process suggested by de Gennes in Ref. [62]. We will get back to that particular picture in more detail in Sect. 5.4.6.

In order to take the tube conformation into account, we assume a Gaussian distribution of the end-to-end distance of any finite tube section (see the discussion in Sect. 5.2.3.1). In the limit $t \ll \tau_l$ relative to the tube time given in Eq. (5.219), segment displacements do not exceed the local vicinity of their initial position, so that the tube constraint is not yet effective. The Rouse formalism for segment reorientations by chain modes applies in the same way as before. With increasing time, reptation along the tube comes into play. As an *independent* reorientation mechanism, it is accounted for by an additional factor $P(l_p, t)$ being part of the orientation correlation functions. It is defined as the probability that a segment is still or again within a stretch of the tube where the axis is aligned practically in the same direction. Alluding to the wormlike chain model described in Sect. 5.2.4, the length of that stretch equals the *persistence length* l_p of the tube.

Assuming a Gaussian propagator for segment diffusion along the tube axis and introducing the curvilinear coordinate s along that axis yields the probability expression

$$P(l_p, t) = \frac{1}{\sqrt{2\pi\langle s^2 \rangle}} \int_{-l_p}^{l_p} \exp\left\{-\frac{s^2}{2\langle s^2 \rangle}\right\} dz \equiv \operatorname{erf}\left\{\frac{l_p}{\sqrt{2\langle s^2 \rangle}}\right\} \quad (5.253)$$

where the *error function* and its series expansion are given by [63]

$$\operatorname{erf}\{\kappa\} \equiv \frac{2}{\sqrt{\pi}} \int_0^\kappa \exp\{-\xi^2\} d\xi \approx \frac{2}{\sqrt{\pi}} \left(\kappa - \frac{1}{3}\kappa^3 + \frac{1}{10}\kappa^5 \mp \dots \right) \quad (5.254)$$

The mean-square curvilinear displacement *along the tube axis* was already derived in Eq. (5.241) as

$$\langle s^2 \rangle \equiv \langle r_z^2 \rangle_{\text{tube}} \approx \frac{2}{3\pi^2} \frac{b^2}{N_K} \frac{t}{\tau_s} + \frac{2}{3\pi^{3/2}} b^2 \left(\frac{t}{\tau_s} \right)^{1/2} \frac{1}{1 + \frac{6}{\pi^{3/2} N_K} \left(\frac{t}{\tau_s} \right)^{1/2}} \quad (5.255)$$

Here, we have identified the mean-square curvilinear displacement in a coiled tube with the mean-square displacement in a straight tube.

With the factor $P(l_p, t)$, the new segment orientation correlation functions accounting for reorientations both by normal modes and by the reptation mechanism along coiled tubes are of the form $G_\alpha(t)G_\beta(t)P(l_p, t)$. Instead of Eqs. (5.250) and (5.252), we are thus dealing with the following relations for spin–lattice relaxation in a coiled tube:

$$\begin{aligned} \frac{1}{T_1} \propto \sum_{\substack{\alpha=x,z \\ \beta=x,z}} C_{\alpha,\beta} \left\{ \int_0^\infty G_\alpha(t)G_\beta(t)P(l_p, t) \cos(\omega t) dt + 4 \int_0^\infty G_\alpha(t)G_\beta(t)P(l_p, t) \cos(2\omega t) dt \right\} \\ G_\alpha(t)G_\beta(t)P(l_p, t) \propto \sum_{p,q=1}^{N_K-1} p^2 q^2 \langle X_{p,\alpha}(t)X_{p,\alpha}(0) \rangle \langle X_{q,\beta}(t)X_{q,\beta}(0) \rangle \operatorname{erf}\left\{\frac{l_p}{\sqrt{2\langle s^2 \rangle}}\right\} \end{aligned} \quad (5.256)$$

where the mean-square curvilinear segment displacement $\langle s^2 \rangle$ is given by Eq. (5.255). The correlation functions of the normal coordinates are specified in Eq. (5.223). The initial values are detailed in Eq. (5.230). Taken all together, this formalism can conveniently be evaluated for graphical representations. The respective angular-frequency dependence of the spin–lattice relaxation time is plotted in Fig. 5.33 for different tube dimensions.

Let us now discuss the limiting cases to be expected on this basis. At relatively high angular frequencies, $\tau_l^{-1} \ll \omega \ll \tau_s^{-1}$, the features of the spin–lattice relaxation dispersion predicted by the free Rouse model, Eq. (5.177), dominate. The reason is that the tube constraint is not yet effective on the conjugate time scale

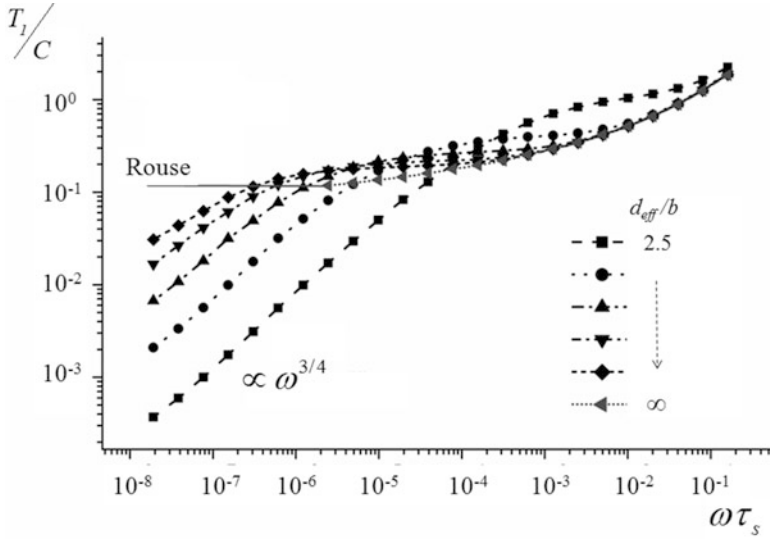


Fig. 5.33 Theoretical frequency dependence of the intrasegmental spin–lattice relaxation time T_1 of polymers confined in a randomly coiled tube with harmonic radial potential. The time unit C is a constant. The evaluations are based on Eq. (5.256) combined with the expressions specified in preceding equations. The angular-frequency axis is scaled in units of the inverse segmental relaxation time τ_s^{-1} . The number of Kuhn segments was assumed to be $N_K = 1,600$. Depending on the effective tube diameter d_{eff} , one observes a crossover from Rouse to confined polymer dynamics upon decreasing the frequency from high to low values. Likewise, the same transition is found if the tube is varied from wide to narrow diameters. Confined polymer dynamics exhibits the same characteristics as predicted by the original reptation model, namely, $T_1 \propto N_K^0 \omega^{3/4}$ [62]. The angular frequency separating the regimes of Rouse and confined dynamics is equal to the inverse tube time τ_t^{-1} . Note that the characteristics of these two limits correspond to the Doi/Edwards limits (I)_{DE} and (II)_{DE} (see Sect. 5.4.6). (Reproduced from Ref. [40] with kind permission of © AIP 2002)

$\tau_s \ll t \ll \tau_t$. Since the mean-square curvilinear segment displacement is small in this regime, $\langle s^2 \rangle \ll l_p^2$, the probability that a segment is still within the persistence range of the tube can be approximated by $P(l_p, t \ll \tau_t) \approx 1$. The orientation correlation functions in Eq. (5.256) are therefore governed by undisturbed Rouse normal modes. According to Eq. (5.219), the tube time is a function of the effective tube diameter, $\tau_t \propto d_{\text{eff}}^2$. The time or frequency ranges where Rouse dynamics dominates will therefore be the more extended the wider the confining tube is.

At lower angular frequencies, in the range $\tau_R^{-1} \ll \omega \ll \tau_t^{-1}$, the dispersion slope is dramatically changed by the tube confinement. In the conjugate limit $\tau_t \ll t \ll \tau_R$, the probability $P(l_p, t)$ starts to dominate the orientation correlation functions, while the transverse components of normal coordinates tend to be suppressed by the tube constraint. Equation (5.255) suggests

$$\langle s^2 \rangle \approx \frac{2}{3\pi^{3/2}} b^2 \left(\frac{t}{\tau_s} \right)^{1/2} \quad (5.257)$$

in this limit. Approximating the error function in Eqs. (5.253) and (5.254) in the lowest order gives

$$P(l_p, t) \propto t^{-1/4} \quad \text{for} \quad \tau_t \ll t \ll \tau_R \quad (5.258)$$

The spin–lattice relaxation rate, Eq. (5.256), is thus predicted to adopt the limiting expression

$$\begin{aligned} \frac{1}{T_1} \propto \sum_{\substack{\alpha=x,z \\ \beta=x,z}} C_{\alpha,\beta} \left\{ \int_0^\infty P(l_p, t) \cos(\omega t) dt + 4 \int_0^\infty P(l_p, t) \cos(2\omega t) dt \right\} \\ \propto N_K^0 \omega^{-3/4} \quad \text{for} \quad \tau_R^{-1} \ll \omega \ll \tau_t^{-1} \end{aligned} \quad (5.259)$$

as demonstrated in Fig. 5.33. This result coincides with the characteristic law $T_1 \propto N_K^0 \omega^{3/4}$ predicted by de Gennes in Ref. [62] in the frame of the original reptation model. As symbolized by the factor N_K^0 , there will be no dependence on the chain length. In other terms, the chain modes contributing in this case are subject to the limit $p \gg 1$.

For even lower frequencies, that is, the range $\omega \ll \tau_R^{-1}$ (not evaluated and plotted in Fig. 5.33), reptation will be dominated by *coherent* displacements of Kuhn segments on a curvilinear path along the curled tube axis. On the conjugated time scale, $t \gg \tau_R$, the polymer fluctuates in the tube back and forth as a whole. The *curvilinear* segment displacements are then subject to

$$\langle s^2 \rangle = \frac{2}{3\pi^2} \frac{b^2}{N_K} \frac{t}{\tau_s} \propto N_K^{-1} t \quad (5.260)$$

as suggested by Eq. (5.255). Inserting this limiting expression into Eq. (5.253), leads to the lowest-order approach

$$P(l_p, t) \propto N_K^{1/2} t^{-1/2} \quad \text{for} \quad t \gg \tau_R \quad (5.261)$$

In this case, the spin–lattice relaxation time accordingly complies with the low-frequency dispersion

$$T_1 \propto N_K^{-1/2} \omega^{1/2} \quad \text{for} \quad \omega \ll \tau_R^{-1} \quad (5.262)$$

5.4.5.5 Summary of the Predictions and Discussion

The limiting laws predicted on the basis of the harmonic radial potential formalism for translational diffusion and spin–lattice relaxation are summarized in Table 5.5.

Table 5.5 Diverse limits of the mean-square segment displacement $\langle r^2 \rangle$ (in the Euclidean space) and the (intra-segment) spin-lattice relaxation time T_1 as predicted by the *radial harmonic potential formalism* (for a randomly coiled tube)

Limit	$\langle r^2 \rangle$		T_1	
$\tau_s \ll (t; 1/\omega) \ll \tau_t$	$\propto M^0 t^{1/2}$	Eq. (5.246)	$\propto M^0 [\tau_s \ln(\omega \tau_s)]^{-1}$	Eq. (5.177)
$\tau_t \ll (t; 1/\omega) \ll \tau_R$	$\propto M^0 t^{1/4}$	Eq. (5.246)	$\propto M^0 \omega^{3/4}$	Eq. (5.259)
$\tau_R \ll (t; 1/\omega)$	$\propto M^{-1/2} t^{1/2}$	Eq. (5.246)	$\propto M^{-1/2} \omega^{1/2}$	Eq. (5.262)

The experimental parameters are molecular mass ($M = N_K M_K$), time (t), and angular frequency (ω)

As concerns the dispersion of *spin-lattice relaxation* (typically acquired with the field-cycling NMR relaxometry technique) and the *incoherent dynamic structure factor* (as probed by field-gradient NMR diffusometry or incoherent neutron scattering), studies of polymers *confined in mesoscopic pores* of a solid matrix permitted the almost perfect verification of the crucial predictions delineated above. This will be demonstrated and discussed in more detail in the context of the so-called *corset effect* to be described in Sect. 5.4.8.

As will be outlined in the subsequent section, many features of the tube/reptation model for entangled polymer melts are already implied in the harmonic radial potential concept. It should however be noted that especially the laws for the time/frequency scale $\tau_t \ll (t; 1/\omega) \ll \tau_R$ are at variance with experimental findings in bulk melts of entangled polymers (see, e.g., Fig. 5.29 and Ref. [49]). This is in contrast to findings in the frame of the corset effect arising in *real*, that is, physically existing, tubes (to be distinguished from the fictitious ones assumed in the reptation model). Typical data will be shown in Fig. 5.41a, for example. In view of the restrictive assumptions inherent to the treatment of reptation, this discrepancy appears to be not unexpected.

5.4.6 The Tube/Reptation Model

5.4.6.1 Definitions and Terminology

The above discussion of the dynamics of a single chain under tube confinement already anticipated crucial elements of the *tube/reptation model* originally proposed by de Gennes [62] and Doi and Edwards [7]. This partly phenomenological concept may be regarded as the currently most popular attempt to account for entanglement effects in concentrated polymer liquids. The terminology and the specific parameters introduced in this context have become indispensable means of expression in modern polymer science. The basic idea is to represent the matrix, that is, the entangling chains surrounding a representative (“tagged”) chain by a *fictitious* tube referred to as *Doi/Edwards tube* [65]. Illustrations are depicted in Figs. 5.17 and 5.19.

Chain motions within this fictitious Doi/Edwards tube are subsumed as “reptation” dynamics, a coinage made up of “reptile” and “migration” to remind of the anisotropic character of segment displacements expected in a tube [62]. Apart from allowing for more than just one chain in the tube, the main new aspect relative to the harmonic radial potential theory is that the tube length will no longer be assumed to be “infinite.” It will rather be adapted to the contour length of the polymer as illustrated in Fig. 5.19. *Tube disengagement* will therefore matter as a further process characterizing polymer dynamics.

The second conceptual point discriminating the reptation concept from the radial harmonic potential model is that the Doi/Edwards tube is thought to be “made” of the surrounding neighbor chains rather than by a pore in a solid matrix. In this allegoric sense, it is a fictitious object instead of a real one. Somewhat modified meanings must therefore be assigned to the tube diameter and to the relaxation time conjugated to the tube diameter.

Let us now make a half-hearted assumption for the moment, namely, that the matrix chains are immobilized, while the tagged macromolecule is still mobile. The tagged chain cannot cross the contours of the matrix chains due to intermolecular *excluded-volume interactions* and *chain connectivity*. As a consequence, motions of the tagged chain will be restricted to a tubelike region around the initial conformation. Owing to the remaining translational degrees of freedom, the tagged chain tends to weave out of that tube in the course of time. Simultaneously, it will thread into a new tube of an entirely different conformation. The diameter of such a frozen-in tube would be equal to the nearest-neighbor distance of the macromolecules.

However, reality is different: In real polymer melts or concentrated solutions, the matrix is as mobile as the tagged chain itself. In the tube/reptation model, this is tentatively taken into account by postulating the fictitious Doi/Edwards tube which consequently must have a much wider effective diameter (see the shaded background area in Fig. 5.17). The Doi/Edwards tube can nevertheless be considered to be quasi-static, since it is formed by such an enormous number of neighboring chains [66].

Apart from the above definitions, a distinct terminology has been established for the tube/reptation concept. Let us first itemize the most important parameters in this context before discussing the specific predictions. The *entanglement time* τ_e is defined as the Rouse relaxation time of a chain section of N_e Kuhn segments. This section corresponds to the entanglement molecular mass M_e specified in Eq. (5.90). According to Eq. (5.123), the entanglement time scales as the square of the number of Kuhn segments. That is,

$$\tau_e = \tau_s N_e^2 = \tau_s \left(\frac{M_e}{M_K} \right)^2 \quad (5.263)$$

where $N_e = M_e/M_K$ and M_K is the molecular mass of a Kuhn segment. Note that there is strong analogy between τ_e and the tube time τ_t defined by Eq. (5.219) under a somewhat different aspect.

The essence of the reptation model is that segment motions become highly anisotropic for times $t \gg \tau_e$ just as we had assumed it for the limit $t \gg \tau_t$ of the radial harmonic potential model. Intermolecular (entanglement) forces effectively localize the macromolecule in a space region characterized by the *Doi/Edwards tube diameter*

$$a = bN_e^{1/2} \quad (5.264)$$

around the *contour line* or *primitive path* of the tube (see Fig. 5.19). Equation (5.264) is a consequence of the Gaussian end-to-end statistics assumed for chain sections consisting of N_e Kuhn segments of length b (see Eq. 5.32 and the discussion in Sect. 5.2.3.1). The entanglement time, Eq. (5.263), is thus related with the tube diameter according to

$$\tau_e = \tau_s N_e^2 = \frac{a^4}{b^4} \tau_s = \frac{\zeta}{3\pi^2 k_B T} \frac{a^4}{b^2} \quad (5.265)$$

where we have made use of Eq. (5.137) for the segmental relaxation time τ_s . The entanglement time is the time after which the topological tube constraints become perceptible.

The conformation of the primitive path is again assumed to be subject to Gaussian end-to-end statistics, of course. That is, the primitive path can be represented as a freelyjointed chain of $z = N_K/N_e$ segment strands of dimension a each, where N_K is the total number of Kuhn segments per polymer chain. The contour length of the Doi/Edwards tube can consequently be expressed as

$$L_t = za = \frac{N_K}{N_e} a = \frac{N_K}{\sqrt{N_e}} b = \frac{N_K b^2}{a} \quad (5.266)$$

Segments moving inside the Doi/Edwards tube are considered to move in a viscous medium as it is anticipated in the free Rouse model. However, as soon as a segment approaches the fictitious walls of the DE tube, entanglement forces become abruptly large. Since the confining potential can be represented by a flat well as illustrated in Fig. 5.31b, no radial potential distribution needs to be taken account apart from the tube wall effect. The chain-end segments are exempted from the tube restraint: They are not subject to entanglement forces and can therefore fluctuate isotropically. The consequence is that the chain can thread with the chain ends ahead into new tube conformations completely uncorrelated to the initial one.

5.4.6.2 The Doi/Edwards Limits for Spin-Lattice Relaxation and Mean-Square Segment Displacements

The Doi/Edwards theory is not a closed formalism in contrast to the harmonic radial potential theory. Different time limits are rather treated separately one by one and are then pieced together to form a complete picture of chain dynamics in the presence of a hard-wall fictitious tube. The two concepts have nevertheless much in common as will be delineated in the following.

The four dynamic processes that can be identified in this context have been introduced and illustrated in Fig. 5.19. The characteristic time constants are the segment relaxation time τ_s (Eq. 5.125), the entanglement time τ_e (Eq. 5.263), the Rouse relaxation time τ_R (Eq. 5.126), and finally the *disengagement time* τ_d . This latter time constant still needs to be specified.

The disengagement time quantifies how long it takes in the average until a chain is detached from its initial tube via reptational displacements along the contour line. Being disengaged from the original tube concurrently means that the chain has threaded into a new tube with an entirely uncorrelated conformation. The topologically one-dimensional diffusion along the contour line is characterized by the *curvilinear chain diffusion coefficient* D_1 given by the Einstein relation for normal diffusion (see Eq. 2.197):

$$D_1 = \frac{k_B T}{N_K \zeta} \propto M^{-1} \quad (5.267)$$

The denominator $N_K \zeta$ is the friction coefficient of the whole chain given as N_K times the segmental friction coefficient ζ . The curvilinear diffusion coefficient is consequently *proportional to the inverse molecular weight*.

In order to escape from the initial tube, a chain must diffuse a distance in the order of L_t along the contour line of the initial tube. That is, the root-mean-square curvilinear displacement must be equal to the contour length L_t given in Eq. (5.266). Since curvilinear displacements are of a topologically one-dimensional character, the corresponding diffusion time will be

$$\tau_d = \frac{L_t^2}{2D_1} = \frac{N_K^3 b^2 \zeta}{2N_e k_B T} = \frac{3\pi^2}{2} \frac{N_K^3}{N_e} \tau_s \propto M^3 \quad (5.268)$$

(compare Eq. 2.169). This *tube disengagement time* remarkably scales as the molecular mass *cubed*. It suggests itself that the *zero-shear viscosity* (see Eq. (3.529) and footnote 10 of Chap. 2) and the *terminal (i.e. longest) mechanical relaxation time* scale in the same way as the tube disengagement time as concerns the molecular mass dependence.

Let us now refer to the center of mass of the polymer. The mean-square displacement of this center of mass reached in a time τ_d must be equal to the mean-square end-to-end distance $\langle r_{ee}^2 \rangle = N_K b^2$. Expressed by the (isotropic)

Table 5.6 Diverse limits of the mean-square segment displacement $\langle r^2 \rangle$ (in the Euclidean space), that is, the second moment of the propagator, and the (intra)segment spin–lattice relaxation time T_1 as predicted by the limit-by-limit approach in the frame of the *tube/reptation model*

Limit		$\langle r^2 \rangle$		T_1	
(I) _{DE}	$\tau_s \ll (t; 1/\omega) \ll \tau_e$	$\propto M^0 t^{1/2}$	Eq. (5.150)	$\propto M^0 [\tau_s \ln(\omega \tau_s)]^{-1}$	Eq. (5.177)
(II) _{DE}	$\tau_e \ll (t; 1/\omega) \ll \tau_R$	$\propto M^0 t^{1/4}$	Eq. (5.271)	$\propto M^0 \omega^{3/4}$	Eq. (5.272)
(III) _{DE}	$\tau_R \ll (t; 1/\omega) \ll \tau_d$	$\propto M^{-1/2} t^{1/2}$	Eq. (5.273)	$\propto M^{-1/2} \omega^{1/2}$	Eq. (5.274)
(IV) _{DE}	$\tau_d \ll (t; 1/\omega)$	$\propto M^{-2} t^1$	Eq. (5.275)	$\propto M^{-(1.5 \dots 2)} \omega^0$	Ref. [67]

The experimental parameters are molecular mass ($M = N_K M_K$), time (t), and angular frequency (ω)

center-of-mass self-diffusion coefficient in the Euclidean space, D_{cm} , the mean-square displacement in τ_d reads

$$\langle r_{\text{cc}}^2 \rangle = N_K b^2 = 6D_{\text{cm}} \tau_d \quad (5.269)$$

Inserting Eq. (5.268) thus suggests

$$D_{\text{cm}} = \frac{N_K b^2}{6\tau_d} = \frac{N_e k_B T}{3\zeta} \frac{1}{N_K^2} = \frac{k_B T}{3\zeta} \frac{a^2}{b^2} \frac{1}{N_K^2} \propto M^{-2} \quad (5.270)$$

where we have made use of $a = bN_e^{1/2}$ (see Eq. 5.264). The center-of-mass diffusion coefficient for reptation is proportional to the *inverse square of the molecular mass*.

Based on the four time constants τ_s , τ_e , τ_R , τ_d , four dynamic limits can be defined. These cases are referred to as Doi/Edwards limits (I)_{DE} to (IV)_{DE}. Table 5.6 and Fig. 5.34 render the limiting laws for the mean-square segment displacement and the spin–lattice relaxation time commonly expected on this basis, while Fig. 5.19 schematically illustrates the chain processes dominating in the four limits.

Judged from Table 5.6 and Fig. 5.34, the impression may arise that all limits for the time and molecular weight dependences of the mean-square segment displacement are reflected in the same way by corresponding limits for the frequency and molecular weight dependences of the spin–lattice relaxation time. This conclusion may be elusive. It must be kept in mind that spin–lattice relaxation probes primarily *rotational* fluctuations in contrast to the *translational* fluctuations reflected by the mean-square displacement. This distinction has already been addressed in Sect. 1.1 and deserves critical consideration in the present context: The topological constraints restricting translational segment diffusion are not necessarily the same as those being responsible for limited rotational reorientations. Experimental tests comparing the two phenomena are therefore expected to be particularly revealing. We will get back to this problem in Sect. 5.4.8 where chain dynamics under mesoscopic pore confinements will be discussed.

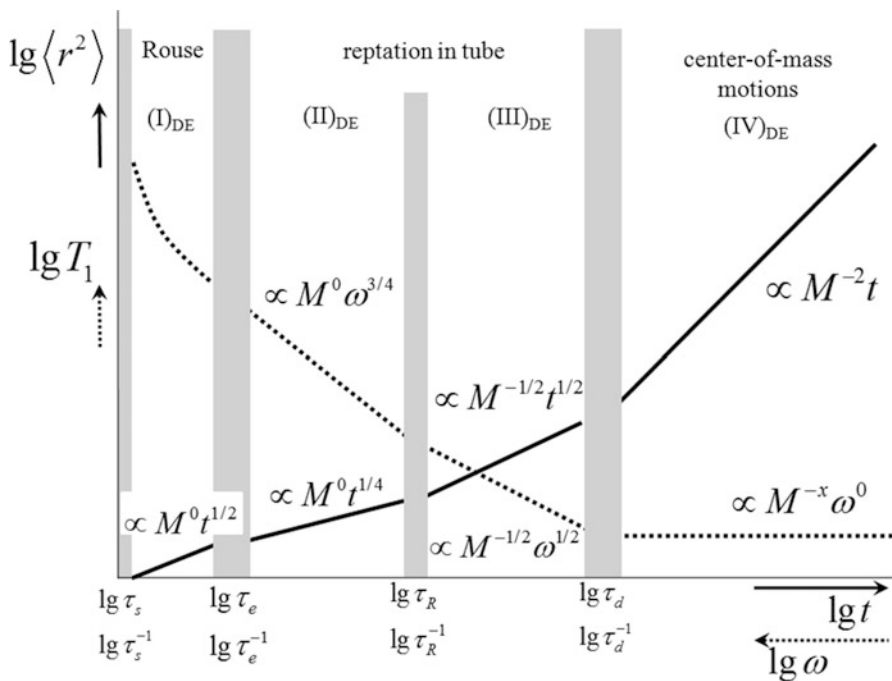


Fig. 5.34 Schematic representation of the time and angular-frequency power-law limits predicted both by the radial harmonic potential theory and by the tube/reptation concept for the mean-square segment displacement $\langle r^2 \rangle$ (solid lines) and the intrasegment spin-lattice relaxation time T_1 (dotted lines) (see Table 5.6). The characteristic time constants are τ_s (segment relaxation time), τ_e (entanglement time), τ_R (Rouse relaxation time), and τ_d (tube disengagement time). Note that the equivalence of the limits for $\langle r^2 \rangle$ as a function of (t, M) and T_1 as a function of (ω, M) anticipates that the tube constraint effects relevant for the two measurands are identical

In detail, *limit* (I)_{DE} is defined by the time (or reciprocal angular frequency) scale $\tau_s \ll (t; 1/\omega) \ll \tau_e$ and corresponds to the length scale $b \ll l \ll a$ of chain modes and of root-mean-square segment displacements. The parameters a and b are the Doi/Edwards tube diameter and the Kuhn length, respectively. In this limit, normal Rouse dynamics of chain sections slotting into the diameter of the DE tube is dominating. Entanglement interactions are not yet effective. Segment displacements are expected to be *isotropic* on the length scale relevant here. The segments of the tagged chain can be considered to be surrounded by an isotropic viscous medium just as assumed in the Rouse model for freely draining polymer chains.

On a longer time scale, in the *limit* (II)_{DE}, $\tau_e \ll (t; 1/\omega) \ll \tau_R$, the Doi/Edwards tube constraints become effective. Chain modes are consequently connected with a sort of “breathing” motions extending along the tube contour, the so-called *primitive path*. The distribution of relaxation times spreads up to the Rouse relaxation time τ_R . The tube constraint stipulates that segment motions are *anisotropic* on this time scale. Since segments distant enough from each other are fluctuating

independently of each other, the mean-square segment displacement remains independent of the molecular mass of the polymer up to $t \approx \tau_R$. The power laws for the time dependence of the mean-square segment displacement,

$$\langle r^2 \rangle \propto M^0 t^{1/4} \quad (5.271)$$

and the angular-frequency dependence of the (intrasegment) spin–lattice relaxation time,

$$T_1 \propto M^0 \omega^{3/4} \quad (5.272)$$

predicted under such conditions are particularly characteristic for the tube/reptation model. The derivation of Eqs. (5.271) and (5.272) is entirely analogous to the treatment in the frame of the harmonic radial potential theory leading to the formally equivalent expressions in Eqs. (5.246) and (5.259), respectively. The main difference is that the tube time τ_t is now replaced by the entanglement time τ_e .

Reptation in the narrow sense, that is, a topologically one-dimensional random walk of the whole chain along the contour line of the Doi/Edwards tube, becomes effective only beyond the Rouse time scale, namely, in *limit (III)_{DE}* defined by $\tau_R \ll (t; 1/\omega) \ll \tau_d$. In this regime, segments are subjected to *collective* fluctuations along the tube contour. The chain moves coherently as a whole with the diffusion coefficient D_1 given in Eq. (5.267). The mean-square segment displacement in curvilinear coordinates along the tube contour is then a linear function of time. Relative to Euclidean space, the mean-square displacement must be rescaled by a square-root operation due to the Gaussian tube conformation (see the argument in the context of Eq. (5.244)). The power laws for the mean-square displacement,

$$\langle r^2 \rangle \propto M^{-1/2} t^{1/2} \quad (5.273)$$

and for the spin–lattice relaxation time,

$$T_1 \propto M^{-1/2} \omega^{1/2} \quad (5.274)$$

in the limit $\tau_R \ll (t; 1/\omega) \ll \tau_d$ are again equivalent to results obtained in the frame of the radial harmonic potential model, namely, Eqs. (5.246) and (5.262), respectively.

Finally, $(t; 1/\omega) \gg \tau_d$ defines *limit (IV)_{DE}*. This is the regime of normal isotropic diffusion of the center of mass of the chain, when all correlations with the initial conformation are lost. The mean-square displacement then obeys the Einstein relation

$$\langle r^2 \rangle = 6D_{\text{cm}}t = 2 \frac{N_e k_B T}{\zeta} \frac{M_K^2}{M^2} t \quad (5.275)$$

On the other hand, the dispersion of the spin–lattice relaxation time becomes independent of the frequency in the form of a low-frequency plateau, as it is

expected for isotropic rotational tumbling of the spin-bearing object in the so-called extreme-narrowing limit, that is, $\omega\tau_d \ll 1$ in terms of the present scenario (compare the limit $\omega_0\tau_c \ll 1$ in the graph plotted in Fig. 3.19).

5.4.6.3 Incoherent Neutron Scattering and Spin-Echo Attenuation by Segment Diffusion in the Doi/Edwards Limits

In the previous section, we have dealt with a number of different limits for the mean-square segment displacement by translational diffusion. When considering experimental techniques probing such displacements, care must be taken whether the standard prerequisites for such applications are warranted for the tube/reptation model. Actually, the usual evaluation procedures such as those outlined in Sects. 3.2 and 3.6 are out of question for the particular diffusion scenario anticipated in the frame of the reptation model.

As mentioned several times before, incoherent (quasi-elastic) neutron scattering as well as field-gradient NMR diffusometry are commonly governed by the incoherent dynamic structure factor

$$\mathcal{G}_{\text{inc}}(\mathbf{q}, t) = \left\langle e^{-i\mathbf{q}\cdot\mathbf{R}(0)} e^{i\mathbf{q}\cdot\mathbf{R}(t)} \right\rangle \equiv \langle e^{i\mathbf{q}\cdot\mathbf{r}} \rangle = \langle e^{i\mathbf{q}\cdot\mathbf{r}_q} \rangle \quad (5.276)$$

$\mathbf{R}(0)$ and $\mathbf{R}(t)$ are the initial and final particle (i.e., spin or scattering center) positions, respectively. The particle displacement in the interval $0 \dots t$ is represented by $\mathbf{r}(t) = \mathbf{R}(t) - \mathbf{R}(0)$. The component along the vector $\mathbf{q}$ is designated by r_q . The respective definitions of $\mathbf{q}$ are given in Eq. (3.576). For the sake of clarity, let us repeat: $\mathcal{G}_{\text{inc}}(\mathbf{q}, t)$ is also termed *incoherent-scattering function* (in the case of quasi-elastic neutron scattering) and *echo attenuation function* (in the context of field-gradient NMR diffusometry).

As concerns NMR experiments, the short-gradient pulse limit will be considered for simplicity (see Sect. 3.2.2). The discussion of the Doi/Edwards limits can nevertheless be led on this basis without loss of generality.¹⁵ That is, the encoding-gradient intervals δ are assumed to be negligible relative to the diffusion time t . The diffusive attenuation of the spin-echo amplitude is then determined by Eq. (5.276) with $\mathbf{q} = \gamma\mathbf{g}\delta$, where γ is the gyromagnetic ratio of the resonant spins and $\mathbf{g}$ is the magnetic field gradient.

In principle, the evaluation of Eq. (5.276) for Doi/Edwards limit (I)_{DE}, that is, Rouse dynamics effective in the range $\tau_s \ll t \ll \tau_e$, has already been described in Sect. 5.4.3.8 as

$$\mathcal{G}_{\text{inc}}(\mathbf{q}, t) = \exp \left\{ -q^2 \frac{b^2}{3\pi^{3/2}} \left(\frac{t}{\tau_s} \right)^{1/2} \right\} \quad (5.277)$$

¹⁵ In case the short-gradient pulse limit is violated, the effective diffusion time must be rescaled as specified in Eq. (3.246) and in the context of Eqs. (3.252) and (3.253).

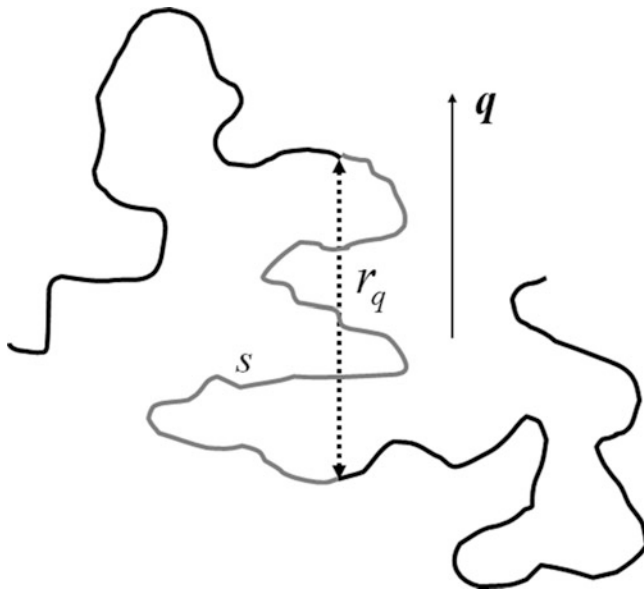


Fig. 5.35 Polymer segments confined in a tube are displaced along the randomly coiled contour of the tube schematically depicted by the *solid line*. The curvilinear displacement s reached in a given diffusion time t is represented by the gray section. The displacement component commonly effective for field-gradient NMR diffusometry and incoherent neutron scattering is the projection r_q on the vector $\mathbf{q}$. In the case of field-gradient NMR diffusometry, this vector is defined by $\mathbf{q} = \gamma\delta\mathbf{g}$, where γ is the gyromagnetic ratio of the nuclei, $\mathbf{g}$ is the magnetic-field gradient, and δ is the width of the encoding field gradient. For incoherent neutron scattering, $\mathbf{q}$ represents the scattering vector which is related to momentum transfer

(see Eq. 5.181). Likewise, the result for limit (IV)_{DE}, that is, ordinary (unrestricted and isotropic) center-of-mass diffusion of the polymer on the time scale $t \gg \tau_d$, is already known as

$$\mathcal{G}_{\text{inc}}(\mathbf{q}, t) = \exp\{-q^2 D_{\text{cm}} t\} \quad (5.278)$$

where the center-of-mass diffusion coefficient D_{cm} is given in Eq. (5.270) and where a Gaussian propagator is adequate.

Let us now turn to the proper reptation regime, that is the Doi/Edwards limits (II)_{DE}, $\tau_e \ll t \ll \tau_R$, and (III)_{DE}, $\tau_R \ll t \ll \tau_d$. As illustrated in Fig. 5.35, both techniques under consideration here probe the component of the polymer segment displacement r_q along the vector $\mathbf{q}$. That is, the real pathway along the tube contour, the curvilinear length s , is much longer than the distance r_q . The question is then, what propagator is relevant for the effective displacement r_q ? There are good reasons to suspect that the propagator will no longer be of a Gaussian nature. Let us demonstrate this by a treatment commonly referring to both limits (II)_{DE} and (III)_{DE} [68], while displacements by center-of-mass diffusion and displacements due to the Rouse motions are negligible.

Assuming a Gaussian probability density for the end-to-end vector of a given curvilinear path length $s(t)$ a segment migrates in a time t , the ensemble average represented by the angle brackets in Eq. (5.276) can be detailed into two steps according to

$$\begin{aligned}
 G_{\text{inc}}(\mathbf{q}, t) &= \langle e^{i\mathbf{q}r_q} \rangle_{(\text{II})_{\text{DE}} + (\text{III})_{\text{DE}}} \\
 &= \underbrace{\left\langle \int_{-\infty}^{\infty} \left(\frac{2\pi}{3} a|s| \right)^{-1/2} \exp \left\{ -\frac{3r_q^2}{2a|s|} \right\} \exp \{ i\mathbf{q}r_q \} dr_q \right\rangle}_{\text{average over all possible } r_q \text{ for a given } s} \\
 &\quad \underbrace{\hspace{10em}}_{\text{average over all possible } s \text{ in } t} \\
 &= \left\langle \exp \left\{ -\frac{1}{6} q^2 a |s(t)| \right\} \right\rangle
 \end{aligned} \tag{5.279}$$

As defined before, the parameter a is the step length of the primitive path and equals the tube diameter. The first average refers to all possible displacements r_q for a given curvilinear displacement s . The result needs then to be averaged over all possible curvilinear displacements s that can be reached in the diffusion time t . This can be done in the following way: The curvilinear segment displacements in the tube can be considered as a one-dimensional ordinary diffusion process, so that a Gaussian propagator is appropriate for this particular process. The resulting average of the above incoherent dynamic structure factor over all possible curvilinear distances s reached during the diffusion interval t thus turns out to be

$$\begin{aligned}
 G_{\text{inc}}(\mathbf{q}, t) &= \int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi \langle s^2(t) \rangle}} \exp \left\{ -\frac{s^2}{2 \langle s^2(t) \rangle} \right\} \exp \left\{ -\frac{1}{6} q^2 a |s| \right\} ds \\
 &= \exp \left\{ \frac{q^4 a^2 \langle s^2(t) \rangle}{72} \right\} \text{erfc} \left\{ \frac{q^2 a \sqrt{\langle s^2(t) \rangle}}{6\sqrt{2}} \right\}
 \end{aligned} \tag{5.280}$$

where the complementary error function is defined by $\text{erfc}\{z\} \equiv 2\pi^{-1/2} \int_z^{\infty} \exp\{-\xi^2\} d\xi$.

With Eq. (5.280), the problem is reduced to the specification of the mean-square curvilinear segment displacement $\langle s^2(t) \rangle$ in combined form for limits (II)_{DE} and (III)_{DE}. Inserting $\tau_s = b^2 \zeta / (3\pi^2 k_B T)$ (Eq. 5.137) for the segmental relaxation time and $D_1 = k_B T / (N_K \zeta)$ (Eq. 5.267) for the topologically one-dimensional chain diffusion coefficient into the full expression given in Eq. (5.241), provides the desired mean-square curvilinear segment displacement on the time scale of interest, $\tau_e \ll t \ll \tau_d$:

$$\langle s^2(t) \rangle \approx 2D_1 t + \frac{2b\sqrt{N_K D_1 t}}{\sqrt{3\pi} + 18 \frac{1}{b} \sqrt{\frac{D_1 t}{N_K}}} \tag{5.281}$$

In Ref. [68], an alternative relation was derived for a time scale $\tau_e \ll t < \approx \tau_d$ extended to somewhat longer times so that the tube disengagement time τ_d is more closely approached:

$$\langle s^2(t) \rangle = \frac{2D_1 t}{1 + \frac{12a^2 D_1 t}{N_K^2 b^4}} + \frac{2b\sqrt{N_K D_1 t}}{\sqrt{3\pi} + 18\frac{1}{b}\sqrt{\frac{D_1 t}{N_K}}} \quad (5.282)$$

So far, we have neglected segment displacements *lateral* to the tube axis. A modified formalism taking this degree of translational freedom into account was established in Ref. [69]. The incoherent dynamic structure factor in Eq. (5.280) modified correspondingly is

$$\begin{aligned} G_{\text{inc}}(\mathbf{q}, t) = & \exp\left\{\frac{q^4 a^2 \langle s^2(t) \rangle}{72}\right\} \text{erfc}\left\{\frac{q^2 a \langle s^2(t) \rangle}{6\sqrt{2}}\right\} \\ & \times \exp\left\{-\frac{1}{6}q^2 \frac{2\langle s^2(t) \rangle}{1 + 2\langle s^2(t) \rangle \left(\frac{2}{a}\right)^2}\right\} \end{aligned} \quad (5.283)$$

where the last factor on the right-hand side accounts for lateral displacements and where either Eq. (5.281) or Eq. (5.283) can be inserted for the mean-square *curvilinear* segment displacement $\langle s^2(t) \rangle$.

At this point, a general remark may be adequate: Translational segment diffusion is often discussed in terms of the second moment of the propagator. In cases where the propagator is a Gaussian function, this certainly implies all relevant features since all higher moments can be derived from the second moment. However, in the frame of the reptation model, the propagator is *non-Gaussian* as we have seen above. The second moment therefore contains only part of the information of the full propagator. Even if the specific limits for the second moment (see Table 5.6) should have been verified in experiments, the model may nevertheless fail to account for the complete propagator.

5.4.6.4 Coherent Dynamic Structure Factor

The coherent counterpart to the incoherent dynamic structure factor,

$$G_{\text{coh}}(\mathbf{q}, t) = \frac{1}{N_t} \sum_{j,l=1}^{N_t} \left\langle e^{-i\mathbf{q} \cdot \mathbf{R}_j(0)} e^{i\mathbf{q} \cdot \mathbf{R}_l(t)} \right\rangle \quad (5.284)$$

can be measured with the aid of *coherent quasi-elastic neutron scattering* as outlined in Sect. 3.6.4.1. $\mathbf{R}_j(0)$ is the position of scattering center j at time 0 and $\mathbf{R}_l(t)$ is the position of scattering center l at time t . The total number of scattering centers in the target is denoted by N_t . The coherent dynamic structure factor thus

relates the fluctuating positions of scattering centers relative to each other in pair form. Coherent neutron scattering is particularly effective with deuterons as scattering centers (see Table 3.1). Experiments are therefore carried out with preferably perdeuterated polymers. In case it is of interest that the partners of the pairs belong to the same molecule so that the dynamic structure factor will be of an *intra-molecular* nature, one can dilute deuterated molecules in their undeuterated counterparts. As argued in Ref. [70], the intermolecular contribution in undiluted polymers will however be weak so that dilution may be unnecessary.

The scattering centers can essentially be identified with segments so that experimental results can directly be compared with model calculations. Typical studies of this sort have been reported in Refs. [70, 71]. The pronounced variation of chain dynamics occurring in the *transition regime* of molecular masses between the limits of freely draining and of entangled polymer dynamics reveals itself on this basis. More specifically, the tube/reptation model has been examined with respect to consistency with Monte Carlo simulations of the coherent dynamic structure factor in Ref. [72].

5.4.6.5 Dynamic Mechanical Relaxation

To a great deal, the attractiveness of the tube/reptation model is its ability to provide a plausible explanation of *viscoelasticity* of entangled polymers. This is the realm of mechanical relaxation. In contrast to NMR relaxation and quasi-elastic neutron scattering, mechanical relaxation techniques are particularly suited for studies of *slow* processes such as the tube disengagement mechanism at high molecular masses. Viscoelastic behavior reveals itself by the *rubber-elastic plateau* of the shear relaxation modulus as schematically illustrated in Fig. 5.36a, b for the time and angular-frequency dependences.

Four regimes of molecular dynamics can be distinguished in this context. (a) In the glassy limit ($t; \omega^{-1} \ll \tau_s$, the shortest local molecular reorientation processes are slower than the deformation rates, so that the system cannot respond in this way to the distortions for thermodynamic reasons. τ_s is the segmental relaxation time given in Eq. (5.137). (b) The Doi/Edwards limit (I)_{DE}, $\tau_s \ll (t; \omega^{-1}) \ll \tau_e$, is characterized by features of Rouse dynamics. τ_e is the entanglement time given in Eq. (5.265). (c) The *rubber-elastic zone* in the range $\tau_e \ll (t; \omega^{-1}) \ll \tau_d$ implies the Doi/Edwards limits (II)_{DE} and (III)_{DE}. τ_d is the disengagement time defined in Eq. (5.268). This is the time/frequency scale on which entanglement interactions persist. The polymer chains are still confined in their original tubes at least in part. As long as this applies, shear stress is prevented from being relaxed completely as revealed by the *rubber-elastic plateau*. Since disengagement from the original tube is the decisive process for stress relaxation, the Doi/Edwards limits (II)_{DE} and (III)_{DE} do not manifest themselves as distinct relaxation features. (d) The time scale of final stress relaxation is the *terminal zone* ($t; \omega^{-1} \gg \tau_d$), which coincides with the Doi/Edwards limit (IV)_{DE}. Let us now examine the regimes relevant for the reptation model in more detail.

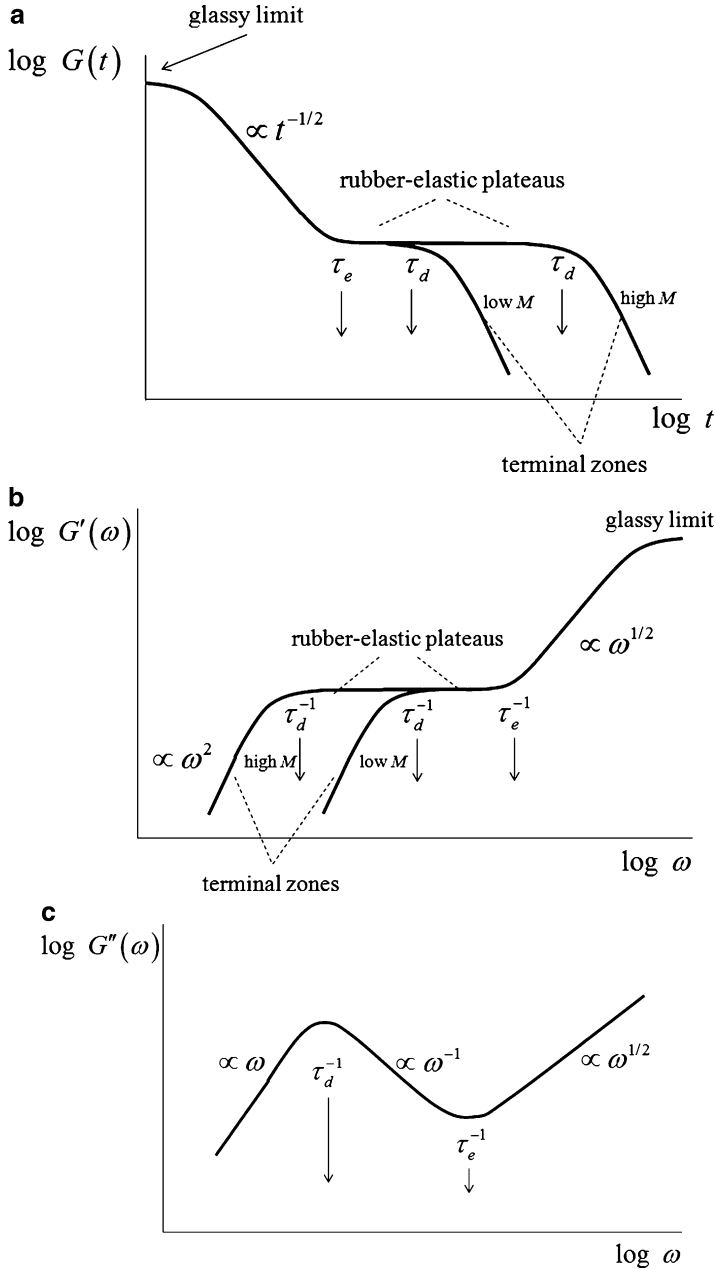


Fig. 5.36 Principal features predicted by the tube/reptation model for mechanical relaxation of (monodisperse) entangled polymers. **(a)** Shear relaxation modulus as a function of time. After the *Rouse zone* characterized by square-root time dependence, the *rubber-elastic plateau* starts at the (molecular-mass independent) entanglement time τ_e and terminates at the disengagement time $\tau_d \propto M^3$. The final drop of the shear relaxation modulus occurs in the *terminal zone*. **(b)** Angular-frequency dependence of the storage modulus G' . The rubber-elastic plateau between τ_d^{-1} and τ_e^{-1} is enframed by the low- and high-frequency limits $G' \propto \omega^2$ and $G' \propto \omega^{1/2}$, respectively. **(c)** Loss modulus G'' as a function of the angular frequency. The respective low- and high-frequency limits are predicted to follow power laws $G'' \propto \omega$ and $G'' \propto \omega^{1/2}$.

(a) *Rouse Zone* $\tau_s \ll (t; \omega^{-1}) \ll \tau_e$

The expressions given in Eqs. (5.191), (5.193), and (5.194) for the relaxation, storage and loss moduli, respectively, apply again. This implies the square root law in Eq. (5.196) valid in the limit $t \ll \tau_R$, of course, since $\tau_e \ll \tau_R = N_K^2 \tau_s = (N_K/N_e)^2 \tau_e = (M/M_e)^2 \tau_e$. The Rouse relaxation time τ_R is given in Eq. (5.140). The following relations are concluded:

$$\left. \begin{aligned} G(t) &\approx \frac{\pi^{1/2}}{2^{3/2}} \frac{\rho N_A k_B T}{M} \left(\frac{\tau_R}{t} \right)^{1/2} \\ G'(\omega) = G''(\omega) &\approx 0.54 \frac{\rho N_A k_B T}{M_e} \sqrt{\omega \tau_e} \end{aligned} \right\} \quad \text{for } \tau_s \ll (t; \omega^{-1}) \ll \tau_e \quad (5.285)$$

For $t = \tau_e$, the shear relaxation modulus adopts the value of the so-called *plateau modulus*:

$$G_{\text{plat}} \approx \frac{\pi^{1/2}}{2^{3/2}} \frac{\rho N_A k_B T}{M} \left(\frac{\tau_R}{\tau_e} \right)^{1/2} = \frac{\pi^{1/2}}{2^{3/2}} \frac{\rho N_A k_B T}{M_K} \frac{b^2}{a^2} \quad (5.286)$$

where M_K is the molecular mass of a Kuhn segment.

(b) *Rubber–Elastic Zone* $\tau_e \ll (t; \omega^{-1}) \ll \tau_d$

The time scale of the rubber–elastic plateau region extends from the entanglement time τ_e (see Eq. 5.263) to the *terminal relaxation time*, that is, the disentanglement time τ_d (see Eq. 5.268). Since stress on a polymer chain will be maintained as long as a part of it is still in the original tube stabilized by entanglement interactions, the stress relaxation process is retarded until the chain reptates out of its original tube [7], [9]. In this view, the decay of the shear relaxation modulus with time is expected to be proportional to the mean probability $\Psi(t)$ that at least one segment is still (or again) confined in its original entanglement constellation:

$$G(t) = G_{\text{plat}} \Psi(t) \quad (5.287)$$

The function $\Psi(t)$ is determined by one-dimensional diffusion along the contour line of the tube. It can consequently be derived from the solution of the one-dimensional version of the diffusion equation (see Eq. 2.167) with appropriate boundary conditions. Performing the required averages over all segments, the relaxation, storage and loss moduli can be shown to obey the relations [7]

$$\left. \begin{aligned} G(t) &\approx \frac{8}{\pi^2} G_{\text{plat}} \sum_{p=1,3,5,\dots} \frac{1}{p^2} \exp \left\{ -\frac{p^2 t}{\tau_d} \right\} \\ G'(\omega) &\approx \frac{8}{\pi^2} G_{\text{plat}} \sum_{p=1,3,5,\dots} \frac{1}{p^2} \frac{(\omega \tau_d)^2}{p^4 + (\omega \tau_d)^2} \\ G''(\omega) &\approx \frac{8}{\pi^2} G_{\text{plat}} \sum_{p=1,3,5,\dots} \frac{1}{p^2} \frac{\omega \tau_d}{p^4 + (\omega \tau_d)^2} \end{aligned} \right\} \quad \text{for } (t; \omega^{-1}) \gg \tau_e \quad (5.288)$$

(as concerns the relationship between $G(t)$, $G'(\omega)$, and $G''(\omega)$, recall the general formalism expressed by Eq. (3.515)).

Table 5.7 Limiting laws for the dynamic mechanical relaxation measurands G, G', G'' as predicted by the tube/reptation model

	Rouse zone (I) _{DE}	Plateau zone (II) _{DE} + (III) _{DE}	Terminal zone (IV) _{DE}
	$\tau_s \ll (t; \omega^{-1}) \ll \tau_e$	$\tau_e \ll (t; \omega^{-1}) \ll \tau_d$	$(t; \omega^{-1}) \gg \tau_d$
$G(t)$	$\frac{\pi^{1/2}}{2^{3/2}} \frac{\rho N_A k_B T}{M} \left(\frac{\tau_R}{t}\right)^{1/2}$	G_{plat}	$\frac{8}{\pi^2} G_{\text{plat}} \exp\left\{-\frac{t}{\tau_d}\right\}$
$G'(\omega)$	$0.54 \frac{\rho N_A k_B T}{M_e} \sqrt{\omega \tau_e}$	G_{plat}	$\frac{\pi^4}{20} G_{\text{plat}} \omega^2 \tau_d^2$
$G''(\omega)$	$0.54 \frac{\rho N_A k_B T}{M_e} \sqrt{\omega \tau_e}$	$G_{\text{plat}}/(\omega \tau_d)$	$\frac{\pi^4}{20} G_{\text{plat}} \omega \tau_d$

The experimental parameters are time (t) and angular frequency (ω)

In the *plateau regime*, that is, for $\tau_e \ll (t; \omega^{-1}) \ll \tau_d$, we can approximate $\exp\{-p^2 t/\tau_d\} \approx 1$ and $(\omega \tau_d)^2 \gg p^4$, so that the relation $\sum_{p=1,3,5,\dots} p^{-2} = \pi^2/8$ can be employed. Under these conditions, the following limits for the moduli are predicted:

$$\left. \begin{aligned} G(t) &\approx G_{\text{plat}} \\ G'(\omega) &\approx G_{\text{plat}} \\ G''(\omega) &\approx \frac{G_{\text{plat}}}{(\omega \tau_d)} \end{aligned} \right\} \quad \text{for } \tau_e \ll (t; \omega^{-1}) \ll \tau_d \quad (5.289)$$

(c) *Terminal Zone* $(t; \omega^{-1}) \gg \tau_d$

Neglecting all sum terms $p^{-2} \exp\{-p^2 t/\tau_d\}$ for $p > 1$ and using $\sum_{p=1,3,5,\dots} p^{-6} = \pi^6/120$ lead to the limiting expressions

$$\left. \begin{aligned} G(t) &\approx \frac{8}{\pi^2} G_{\text{plat}} \exp\left\{-\frac{t}{\tau_d}\right\} \\ G'(\omega) &\approx \frac{\pi^4}{20} G_{\text{plat}} \omega^2 \tau_d^2 \\ G''(\omega) &\approx \frac{\pi^4}{20} G_{\text{plat}} \omega \tau_d \end{aligned} \right\} \quad \text{for } (t; \omega^{-1}) \gg \tau_d \quad (5.290)$$

A schematic graphical representation of the three functions $G(t)$, $G'(\omega)$, and $G''(\omega)$ and their characteristic limits can be found in Fig. 5.36a–c. A survey of the limiting laws is compiled in Table 5.7. Finally, according to Eqs. (3.528) and (5.290), the zero-shear viscosity is expected to obey

$$\eta_0 = \frac{G''(\omega \tau_d \ll 1)}{\omega} = \frac{\pi^4}{20} G_{\text{plat}} \tau_d \propto M^3 \quad (5.291)$$

Experimentally, one is often dealing with broad distributions of molecular masses. Due to the strong molecular-mass dependence inherent to the terminal relaxation time, specific features of dynamic mechanical relaxation will therefore be less pronounced than suggested by model theories. Mechanical relaxation tests should hence be carried out with samples with a polydispersity as small as possible. Examples of such studies can be found in Refs. [73, 74]. The polybutadiene data shown in the diagram in Fig. 5.37 demonstrate that the tube/reptation model accounts

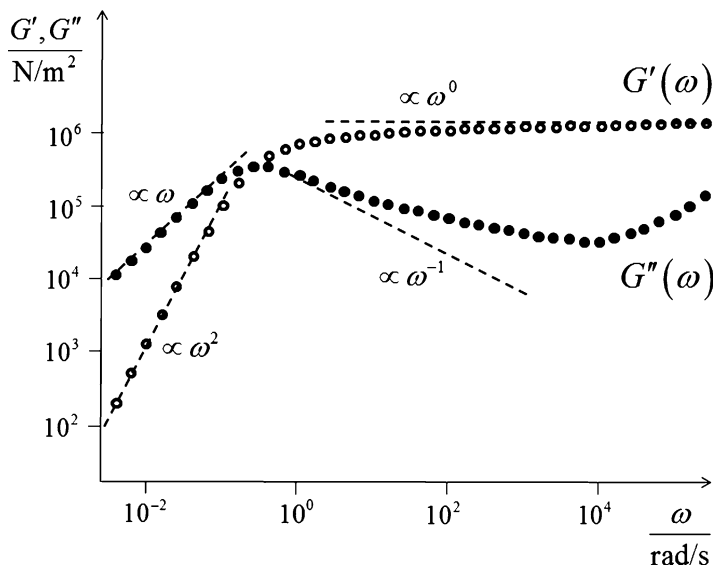


Fig. 5.37 Experimental data for the storage and loss moduli in a practically monodisperse polybutadiene melt of molecular weight 360,000 as reported in Ref. [73]. The *dashed lines* indicate the limits predicted by the tube/reptation model

reasonably well with the long-time dynamics of polymer melts. Shortcomings of the concept notwithstanding revealing themselves in more extended investigations will be discussed in Sect. 5.4.6.7.

5.4.6.6 Tube Diameter

A priori, the tube diameter must be regarded as an adjustable model parameter. It can indirectly be determined by fitting certain expressions predicted by the tube/reptation model to experimental data. A frequently used method is to measure the plateau modulus G_{plat} and evaluate the tube diameter with the aid of Eq. (5.286):

$$a = \frac{\pi^{1/4}}{2^{3/4}} b \left(\frac{\rho N_A k_B T}{M_K G_{\text{plat}}} \right)^{1/2} \quad (5.292)$$

Another possibility is the measurement of the center-of-mass diffusion coefficient D_{cm} which is related to the tube diameter according to Eq. (5.270):

$$a = b N_K \left(\frac{3 \zeta D_{\text{cm}}}{k_B T} \right)^{1/2} \quad (5.293)$$

The parameters in Eqs. (5.292) or (5.293) need then to be estimated from other sources.

Values obtained on this basis are tabulated in Ref. [75] for many polymer species. The range of these empirical data is between about 3 and 8 nm, that is, an order of magnitude larger than the nearest-neighbor distance. Note that the data reported in the literature may be affected somewhat by different conventions for the relevant relations and quantities. A comparison and discussion of this point can be found in Ref. [34].

5.4.6.7 Discussion and Modifications of the Tube/Reptation Model

The tube/reptation model accounts for a series of important features of polymer dynamics. This in particular refers to the long-time behavior beyond the longest Rouse relaxation time including the terminal zone. The quality of description that can be reached on this basis is demonstrated by the mechanical relaxation data in Fig. 5.37. Nevertheless, there are systematic shortcomings of the model which will shortly be discussed in the following points outlining a number of discrepancies with experimental findings.

(a) Center-of-Mass Diffusion and Zero-Shear Viscosity

One of the most obvious discrepancies between prediction and experiment is the molecular-mass dependence expected for the zero-shear viscosity η_0 and the center-of-mass diffusion coefficient D_{cm} of entangled polymer melts. The predictions $\eta_0 \propto \tau_d \propto M^3$ (Eq. 5.291) and $D_{\text{cm}} \propto M^{-2}$ (Eq. 5.270) are contrasted by the experimental findings $\eta_0 \propto M^{3.4 \dots 3.5}$ [76] and $D_{\text{cm}} \propto M^{-2.3}$ [77], respectively.

As concerns field-gradient NMR diffusometry (see Sect. 3.2), the $D_{\text{cm}} \propto M^{-2}$ law predicted for limit (IV)_{DE} appears to be corroborated at first sight by early studies [67, 78–80]. However, there are a number of effects that may influence the outcome of such measurements. The crucial points are the diffusion time probed in the experiments and the molecular mass of the polymer. In order to probe center-of-mass diffusion, the diffusion time must be much longer than the terminal relaxation time, that is, $t \gg \tau_d$ in terms of the tube/reptation model. On the other hand, if the molecular mass is too large, immaterial spin diffusion by flip-flop spin transitions will become perceptible on this time scale as demonstrated in Refs. [81–83]. This limiting immaterial spin diffusion coefficient is about $10^{-15} \text{ m}^2 \text{ s}^{-1}$. That is, the apparent diffusion coefficients acquired in the vicinity of this value tend to be governed by a process other than molecular transport. Safe measurements of center-of-mass diffusion coefficients by field-gradient NMR diffusometry are thus restricted to the limit $D_{\text{cm}} > 10^{-15} \text{ m}^2 \text{ s}^{-1}$ as expected for polymers of sufficiently low molecular mass, say $M_w < 10^5$.

But then, if the diffusion time is not long enough, it may overlap with limit (III)_{DE} where the molecular weight dependence of diffusion is expected to be reduced to $\propto M^{-1/2}$ (see Table 5.6). In this case, the acquired measurand will no longer reflect center-of-mass diffusion exclusively but will be affected by segment diffusion to some degree. A remedy is to employ the correct evaluation formalism

derived in Sect. 5.4.6.3 for the tube/reptation model. With the aid of this analysis, center-of-mass and segment diffusion can clearly be discriminated from each other. In more recent field-gradient NMR diffusometry studies, this has been accounted for with special emphasis on the evaluation of segment diffusion in limits (II)_{DE} and (III)_{DE} [83]. The results will be discussed further down.

(b) *Contour-Length Fluctuation*

An attempt to correct the tube/reptation model with respect to the aforementioned deficiencies is to supplement tube disengagement by *contour-length fluctuation* [7, 84, 85]. The principle is that the contour length will be subject to thermal fluctuations. As a consequence, chain ends will randomly be retracted and extended back and forth so that they thread into new tube conformations without need to move the whole polymer. Fluctuation statistics for many-particle systems says that the chain-end sections subject to this tube renewal process will scale proportional to $\sqrt{M}$ (compare Eq. 5.299). As a result, the combined tube disengagement processes by reptation and contour-length fluctuation may explain the increased molecular weight dependences of the zero-shear viscosity and the center-of-mass diffusion coefficient for molecular masses far above the entanglement molecular mass, $M \gg M_e$. In Ref. [84], it is shown that the zero-shear viscosity is predicted on this basis to obey $\eta_0 \propto M^3 \left[\left(1 - \sqrt{M_e/M}\right)^3 + 5^{-1} (M_e/M)^{3/2} \right]$ which practically coincides with the empirical law $\eta_0 \propto M^{3.4}$ (see Fig. 5.15). Contour-length fluctuation appears also to explain the time dependence of the coherent dynamic structure factor of single polymer chains as acquired with the aid of quasi-elastic neutron scattering as demonstrated in Ref. [86].

(c) *Chain-End Effects*

Contour-length fluctuation suggests increased segment mobility in the fluctuating chain-end sections. Phenomena of this sort have been investigated with the aid of transverse spin relaxation [49, 87]. The transverse relaxation curves of melts of entangled polymers can be analyzed by a rapidly and a slowly decaying component. The different decay rates indicate different segmental mobilities. Fast and slow relaxation decays inversely correspond to low and high fluctuation rates. Thus, the central chain section is thought to be responsible for the rapidly decaying relaxation component, whereas the mobile segment blocks at the chain ends contribute slowly decaying signals.¹⁶ The parameter examined in Ref. [87] as a function of the weight-average molecular mass M_w is the ratio Q of the amplitudes of the slow component (representing the chain ends) and of the total signal.

In the case of *contour-length fluctuation*, chain-end blocks with enhanced mobility are expected to scale characteristically as $M_w^{1/2}$ (see above). The amplitude ratio should hence scale as $Q \propto M_w^{-1/2}$. This is in contrast to the expectation for the so-called *whip model* [87]. In this case, the size of the mobile chain-end blocks is assumed to correspond to the entanglement molecular mass $M_e \approx M_c/2 = \text{const.}$

¹⁶ The increased mobility of chain ends manifests itself also in a locally reduced density: The consequence is an inhomogeneous distribution of the magnetic susceptibility which gives rise to a corresponding broadening of the NMR resonance line (see Ref. [49]).

The prediction on this basis is therefore $Q \propto M_w^{-1}$ [49]. Experimental data for three different polymer species with particularly narrow molecular-mass distribution (polyethylene, polydimethylsiloxane, and polytetrahydrofuran) clearly indicate that the latter case applies. Provided that the different segment mobilities expected for the two models manifest themselves *in the same way* as different transverse relaxation components, these experiments indeed contradict the contour-length fluctuation mechanism in the narrow sense.

A further hint can be obtained by extrapolating the experimental data for $Q = Q(M_w)$ to the value $Q = 1$. Taking the whip model for granted, this limit would mean that the whole signal originates exclusively from the chain-end blocks. The experimental finding actually is $(M_w)_{Q=1} \approx M_c$ for all three polymer species investigated. The conclusion is that the mobile chain-end blocks have a molecular mass of $M_c/2$ each just as anticipated in this model.

(d) Constraint Release

The constraint-release mechanism is thought to erode the tube conformation to some degree well ahead of the disengagement process. Actually, the entangling chains forming the tube are subject to just the same mobility as the polymers considered to be confined in the tube. The consequence could be that a fraction of the entangling chains moves apart and gives space for extended lateral displacements of the tagged chain. Originally, the counterargument was that the shear number of entangling chains forming the tube ensures that constraint release is slow relative to reptative tube disengagement [66]. Nevertheless, a mechanism of this sort is still under discussion up to now [88, 89].

Actually, the constraint-release mechanism is definitely relevant for short polymers near or below M_c : In the realm of the Rouse model of freely draining chains, the constraint-release motions of neighbor chains even prevent the establishment of a tube confinement at all. The question remains how far beyond M_c this process will perceptibly affect chain dynamics. Experimental studies are possible in mixtures of a small percentage of long (“tagged”) polymer chains in a matrix of short polymers of variable molecular mass. In coherent neutron scattering, the distinction is possible by forming the matrix of perdeuterated polymers of the same species. Corresponding experiments have been reported in Ref. [90]. Provided that the matrix chains are short enough relative to the tagged chains, the results are obviously (and not unexpectedly) in favor of the constraint-release effect.

(e) Segment Diffusion

Besides center-of-mass diffusion discussed above, segment diffusion on the time scale of limits (II)_{DE} and (III)_{DE} is of particular interest for tests of predictions of the tube/reptation model. In this regard, one should keep in mind that the propagator for segment diffusion on this time scale is non-Gaussian. That is, the mean-square displacement, that is, the second moment of the propagator, does not contain the full information characteristic for segment diffusion. Rather, the special formalism for the incoherent dynamic structure factor represented by the relationships in Eqs. (5.280), (5.281) and (5.283) must be employed for the evaluation of experimental data and for testing the tube/reptation model in these limits. Actually, some characteristic features could qualitatively be verified in polyethyleneoxide melts

with the aid of field-gradient NMR diffusometry [83]. However, the parameter values needed to describe the experimental data are at substantial variance with known properties of this particular polymer species. It turned out that no consistent description of the data is possible on a quantitative basis.

On the other hand, the diameter of mesoscopic pores confining polymer melts could perfectly be reproduced by fits of Eq. (5.283) to experimental data [69] (see the discussion in Sect. 5.4.8.1). In this sense, the basic idea of the tube/reptation concept has been corroborated provided one replaces the fictitious Doi/Edwards tube by mesoscopic pore confinements as a sort of artificial tube.

(f) *Spin–Lattice Relaxation Dispersion*

Both the harmonic radial potential formalism [40] and the reptation model [62] predict the characteristic power laws $T_1 \propto M^0 \omega^{3/4}$ and $T_1 \propto M^{-1/2} \omega^{1/2}$ for the spin–lattice relaxation dispersion on angular-frequency scales $\tau_l^{-1} < \omega < \tau_R^{-1}$ or $\tau_e^{-1} < \omega < \tau_R^{-1}$ and $\tau_R^{-1} < \omega < \tau_d^{-1}$, respectively (see Tables 5.5 and 5.6). These angular-frequency scales are the realm of field-cycling NMR relaxometry probing the *segment orientation correlation function* as described in Sect. 3.1.4.4. Data for numerous polymer species have been reported in the literature (for a review, see Ref. [49]). In all cases, these laws have never been verified in experiments with *bulk* melts of entangled polymers, at least not in that sequence. The discrepancy is demonstrated by the data in Fig. 5.29, for instance. On this data basis, there is no scope left for these distinct predictions of the tube/reptation concept. It must rather be concluded that the anticipated idealization is too strong to reflect the actual *reorientational* chain dynamics in the frequency range of limits (II)_{DE} and (III)_{DE}.

Instead of the predictions of the reptation model, field-cycling NMR relaxometry data reveal a crossover between power laws $T_1 \propto M^0 \omega^{0.5}$ (high frequencies) and $T_1 \propto M^0 \omega^{0.25}$ (low frequencies) in entangled polymer melts in bulk about the combined frequency scale of limits (II)_{DE} and (III)_{DE}. These results are closely reproduced by the renormalized Rouse formalism outlined in Sect. 5.4.4 (see Table 5.4). Remarkably, it is not only the individual power laws that are rendered by this formalism but also the crossover in just the relevant frequency window.

As in the case of translational segment diffusion in limits (II)_{DE} and (III)_{DE}, a totally different picture arises in polymer melts confined in mesoscopic pores of solid matrices. The spin–lattice relaxation dispersion can then indeed be described by the laws predicted for reptation both with respect to frequency and molecular mass as will be discussed in Sect. 5.4.8.2 [64, 91].

(g) *Limit (III)_{DE} and Thermodynamics*

In general, there is a delicate problem inherent to the reptation model specifically concerning limit (III)_{DE}. On the one hand, the postulation of a tube implies that the interactions among the probe chain and its neighbors are decisive for the formation of the confinement effect on the time scale $t \ll \tau_d$. That is, interchain interactions are supposed to be *strong*. On the other hand, the polymer chains are supposed to move independently in their respective tubes without any essential mutual correlation. This in turn anticipates *weak* interchain interactions. We are thus left with a conflict that cannot be solved in the frame of the laws of statistical physics: In Refs.

[92, 93], it was shown that the entangling matrix chains would form a Doi/Edwards tube only if they fluctuate cooperatively in the strict sense which is not envisioned in this model. In this sense, we are dealing with a subtle conceptual inconsistency that must be tolerated as long as there is no really comprehensive multi-chain theory available.

5.4.7 Local Dynamics

The coarse-grained description of polymer dynamics outlined so far refers to a length scale $\ell \gg b$ which starts at the Kuhn segment level, that is, entities typically consisting of 3–6 monomers. The coarse-grained *length scale* is intimately related to the “coarse-grained” *time scale* $t \gg \tau_s$. The opposite cases, the *short-time* and *short-range scales* around $t \approx \tau_s$ and $\ell \approx b$, respectively, or even the extremes $t \ll \tau_s$ and $\ell \ll b$ are complex and cannot be treated analytically in a straightforward way. Instead of freely jointed phantom chains, the rotational isomerism intrinsic to the valence bond structure must be considered in this case. As a consequence, equations of motion for Kuhn segment-internal dynamics will be nonlinear and, hence, intractable.

Short-range modes and the crossover from short- to coarse-grained modes can however be studied with the aid of computer simulations. An attempt based on a somewhat simplistic model chain was reported in Ref. [40]. In the limit $t \gg \tau_s$, chain dynamics was found to coincide with the predictions of the Rouse model for a freely draining and freely jointed chain, whereas the reorientational restrictions intrinsic to valence bond chains lead to deviations in the opposite limit. This can also be demonstrated with the aid of field-cycling NMR relaxometry in polymer species with τ_s values long enough to be detectable in the experimental frequency window. An example is shown in Fig. 5.38.

As concerns spin–lattice relaxation, it is not only a matter of time or length scales how strong the influence of certain modes is expected. The primary quantity describing fluctuations of intrasegmental dipolar or quadrupolar couplings is the correlation function in Eq. (5.155):

$$G_m(t) = 4\pi(-1)^m \langle Y_{2,m}(t) Y_{2,-m}(0) \rangle \quad (5.294)$$

Short-range modes tend to have larger fluctuation amplitudes of the spherical harmonics. That is, before reaching the coarse-grained time scale, where intermediate- and long-range modes are relevant, a major fraction of the correlation function has already decayed leaving only a relatively small residual correlation. The influence of short-range modes is weighted more strongly than that of long-range modes. Nevertheless, the coarse-grained description is adequate in almost the whole experimental frequency window of field-cycling NMR relaxometry as demonstrated experimentally by the example represented by the data in Fig. 5.24 and theoretically by the analysis in Ref. [94].

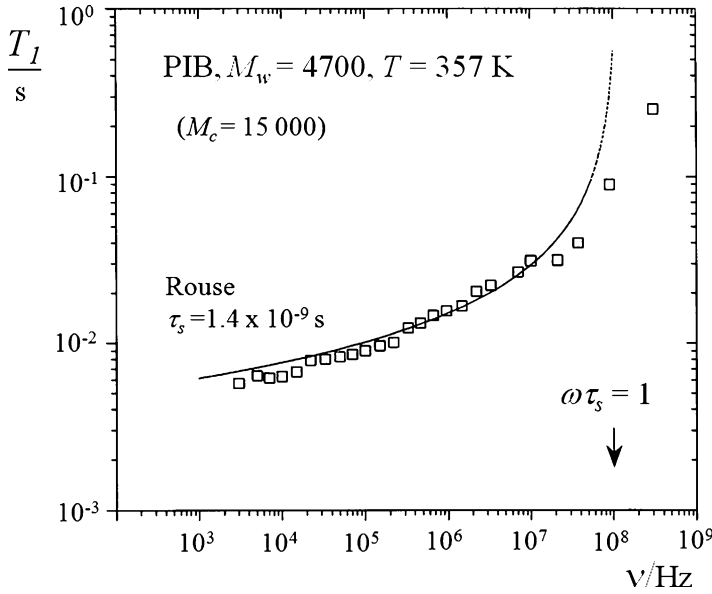


Fig. 5.38 Spin–lattice relaxation dispersion measured in a polyisobutylene (*PIB*) melt [49]. The *solid line* was calculated on the basis of the Rouse model for freely draining polymers, Eq. (5.177). The fitting parameter, that is, the segmental relaxation time $\tau_s = 1.4 \times 10^{-9}$ s, simultaneously limits the range of validity of this concept. The position $\omega\tau_s = 1$ marking this limit is indicated by an *arrow*. Beyond this position on the frequency axis, the theory starts to deviate dramatically from the experimental data

For a more formal consideration, Eq. (5.294) can be factorized according to

$$\mathcal{G}_m(t) = \mathcal{G}_m^{\text{loc}}(t) \mathcal{G}_m^{\text{modes}}(t) \quad (5.295)$$

in contributions by two competing and essentially independent mechanisms, namely, local motions with the correlation function $\mathcal{G}_m^{\text{loc}}(t)$ and chain modes causing correlation decays $\mathcal{G}_m^{\text{modes}}(t)$. The product in Eq. (5.295) combines the probabilities that the fluctuation events have *not yet* taken place in a time t . Furthermore, the (anisotropic and restricted) correlation function for local motions can be split into two terms according to

$$\mathcal{G}_m^{\text{loc}}(t) = \mathcal{G}_m^{\text{loc,red}}(t) + \mathcal{G}_m^{\text{loc}}(\infty) \quad (5.296)$$

$\mathcal{G}_m^{\text{loc}}(\infty) \approx \langle \mathcal{G}_m^{\text{loc}}(t) \rangle_{\tau_s} \approx \text{const}$ is the residual correlation retained *after* the system has experienced local fluctuations over a period in the order of several segment relaxation times τ_s (compare the discussion in the context of Eq. (5.160) in Sect. 5.4.3.7). This quantity thus reflects the anisotropy of local dynamics. $\mathcal{G}_m^{\text{loc,red}}(t)$ is the reduced correlation function accounting for segment-internal processes.

Chain modes are much slower than local motions by definition. That is, there will be little change of the chain-mode correlation function $G_m^{\text{modes}}(t)$ on the time scale on which the reduced correlation function $G_m^{\text{loc,red}}(t)$ decays to zero: $G_m^{\text{modes}}(t \approx \tau_s) \approx G_m^{\text{modes}}(0)$. The total correlation function can thus be expressed as

$$G_m(t) \approx G_m^{\text{loc,red}}(t) G_m^{\text{modes}}(0) + G_m^{\text{loc}}(\infty) G_m^{\text{modes}}(t) \quad (5.297)$$

This approach is also known as *different time-scale limit*.

The spin–lattice relaxation rate resulting from both the local and the chain-mode contribution is consequently a sum of two terms:

$$\frac{1}{T_1} \approx \frac{a_{\text{loc}}}{T_1^{\text{loc}}} + \frac{a_{\text{modes}}}{T_1^{\text{modes}}} \quad (5.298)$$

where a_{loc} and a_{modes} are constants weighting the relative contribution of either process. T_1^{loc} and T_1^{modes} are the respective spin–lattice relaxation times expected for the cases if exclusively local and exclusively chain modes are effective. On a frequency scale $\nu \ll (2\pi\tau_s)^{-1}$ as it is normally relevant for field-cycling NMR relaxometry, Eq. (5.298) can be approximated by $T_1^{-1} \approx a_{\text{modes}}/T_1^{\text{modes}}$ as corroborated and exemplified by the experimental data represented by Figs. 5.24, 5.29 and 5.38.

Let us finish this section by a remark of a more general nature: the chain-mode treatments in the previous sections provide the system-specific long-time tail of the orientation correlation function mentioned in Sect. 1.1.4, while local dynamics is scarcely indicative for effects like entanglements or confinements. Scenarios that are analogous in the sense that local and long-time dynamics must be distinguished will be described in Sect. 6.8.2 for liquid crystals and in Sect. 7.5.2 for adsorbate molecules at surfaces.

5.4.8 Mesoscopic Confinement Effects on Polymer Chain Dynamics (“Corset Effect”)

The so-called corset effect was first identified as a strong change of spin–lattice relaxation dispersion and a strong reduction of relaxation times in polymer melts confined in mesoscopic pores of a solid matrix relative to bulk samples of the same polymer species [45, 64, 91, 95, 96]. These experimental findings thus reveal a strong slowing down of rotational segment dynamics upon mesoscopic confinement. Let us discuss this remarkable phenomenon more specifically with respect to results obtained with the aid of diverse experimental techniques.

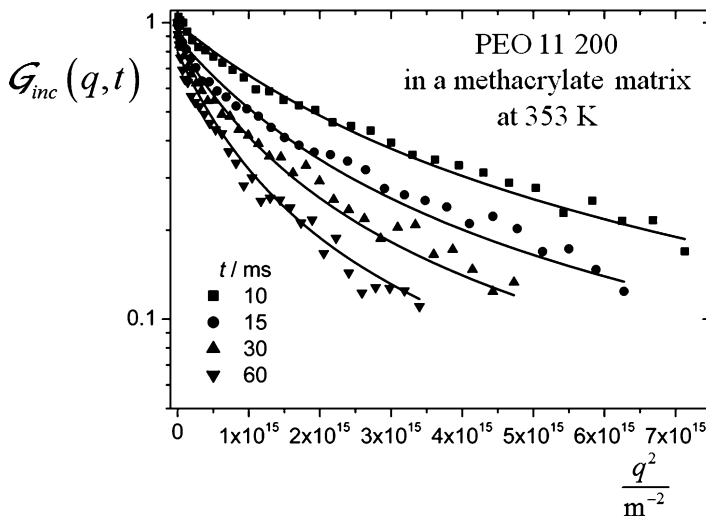


Fig. 5.39 Typical attenuation curves of the stimulated echo amplitude, that is, the incoherent dynamic structure factor $G_{inc}(q, t)$, in poly(ethylene oxide) (PEO) melts confined to pores of a solid methacrylate matrix [69]. The variable is the square of the wave number defined by $q = \gamma g \delta$, where γ is the gyromagnetic ratio, g is the field gradient, and δ is the field-gradient encoding time. The curve parameter is the diffusion time t . The *solid lines* have commonly been fitted to the experimental data set with the aid of Eq. (5.283). The tube diameter determined in this way is $a = (8 \pm 1)$ nm in accordance with the value estimated from the electron micrograph shown in Fig. 5.40. Note that the non-exponentiality of the decay functions indicates that the propagator for segment diffusion is *non-Gaussian*. (Reproduced from Ref. [98] with kind permission of Wiley-VCH 2004)

5.4.8.1 Experimental Results for Translational Diffusion

Figure 5.39 shows a data set for the incoherent dynamic structure factor, Eq. (5.276), as a function of the squared wave number in a system of polyethyleneoxide strands embedded in a practically rigid (cross-linked) polyhydroxyethyl methacrylate (PHEMA) matrix. As outlined above at several occasions, this function characterizes *translational* segment displacements. The particular measuring technique employed for the record of the data in Fig. 5.39 was field-gradient NMR diffusometry.

An electron micrograph visualizing the confined polymer melt is rendered in Fig. 5.40. The preparation of the nanometric poly(ethylene oxide) (PEO) strands in this sample is based on spinodal decomposition and has been described in detail in Ref. [69].

The theoretical curves in Fig. 5.39 represent Eq. (5.283) which was developed in the frame of the tube/reptation model. The almost perfect coincidence with the experimental data corroborates the applicability of the specific (*non-Gaussian*) propagator predicted by the model under the conditions of this particular sample system. Moreover, the dimension of the topological tube constraint a fitted to the

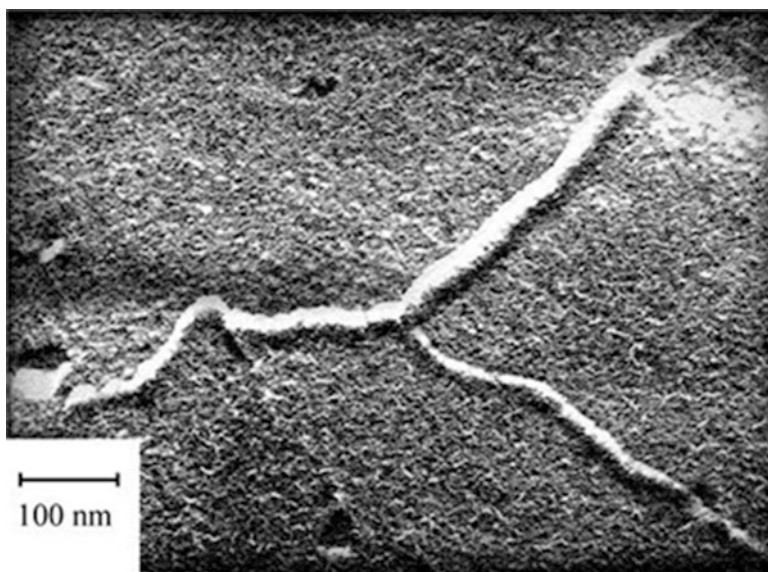


Fig. 5.40 Typical freeze-fracture electron micrograph of PEO strands embedded in a quasi-solid, impenetrable methacrylate matrix (PHEMA) [69]. The mean strand diameter is ca. 8 nm. (Reproduced from Ref. [97] with kind permission of © APS 1999)

data reproduces the real pore diameter as evaluated from the electron micrograph Fig. 5.40 and as determined with the aid of other techniques such as small-angle X-ray scattering [99]. Diffusion measurements of this sort can consequently be used to determine pore diameters as demonstrated in Ref. [69]. The conclusion drawn from the diffusometry results is that the tube/reptation concept works both qualitatively and quantitatively very well if the confining tube is an *artificial* one with really *impenetrable* walls.

5.4.8.2 Experimental Results for Techniques Sensitive to Orientation Correlation Functions

The plots in Fig. 5.41a, b show deuteron spin-lattice relaxation data of linear perdeuterated PEO melts measured under nanometric confinement in PHEMA and as bulk samples, respectively [64]. Recall that deuteron spin-lattice relaxation probes the orientation correlation function in Eq. (5.155) with the advantage that *intermolecular* dipolar interaction is safely negligible in this case relative to *intra-molecular* couplings. That is, it is exclusively sensitive to *rotational* fluctuations. In this sense, deuteron resonance may be preferable to proton resonance for the sake of unambiguity (although equivalent data sets have also been acquired with protons [45]).

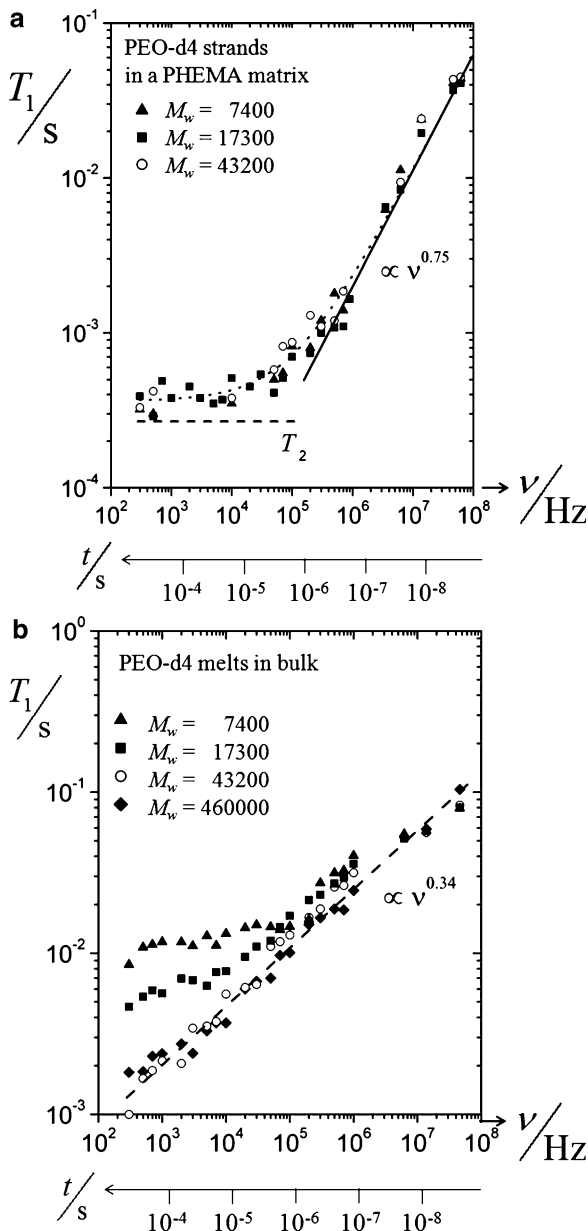


Fig. 5.41 Deuteron spin-lattice relaxation dispersion in perdeuterated PEO confined in 10-nm pores of solid PHEMA at 80 °C (a) and in bulk melts at the same temperature (b). The data have been acquired for a number of different weight-average molecular masses M_w as indicated. The abscissa axes of the plots refer to the deuteron resonance frequency and, for comparison, to the conjugate time scales. The dispersion of the confined polymers at high frequencies corresponds to the law $T_1 \propto M_w^0 \nu^{0.75}$ predicted by Eq. (5.259) for the radial harmonic potential concept and by limit (II)_{DE} of the tube/reptation model as well. The low-frequency plateau observed with the confined polymers indicates that the correlation function implies components decaying more slowly than the magnetization relaxation curves, so that the prerequisites for the Bloch/Wangsness/Redfield relaxation theory outlined in Sect. 3.1.5 are no longer valid in this regime. This is confirmed by the fact that the plateau value corresponds to the transverse deuteron relaxation time T_2 extrapolated from the high-field value measured at 9.4T. (Reproduced from Ref. [64] with kind permission of © Elsevier 1999)

The dispersions of the deuteron spin–lattice relaxation time $T_1(\nu)$ are much steeper when confined in a solid matrix (Fig. 5.41a) than in bulk (Fig. 5.41b) [64]. The values of the spin–lattice and the transverse relaxation times are strongly reduced by up to one order of magnitude. The cogent corollary is that the orientation correlation function decays more slowly in mesoscopically confined polymers than in bulk. Expressed in other terms, this means that segmental reorientation is more anisotropic under confinement than under bulk conditions. In comparison to the translational diffusion data discussed in the previous section, the conclusion is that *rotational* fluctuations of polymer segments are affected by mesoscopic pore confinements already on a molecular length scale whereas *translational* displacements suffer restrictions only at distances approaching the dimension of the pore diameter on the respective time scales of the techniques [100].

Although not always quoted as such, the corset effect, that is, the slowing down of rotational fluctuations of polymers upon mesoscopic confinements, has been revealed in a number of other studies. In Ref. [101], *field-cycling NMR relaxometry* was used to examine poly(ethylene oxide)/sodium montmorillonite nanocomposites. The general tendency in such layered confinement structures is that confinement leads to a more anisotropic character of segment reorientation so that the orientation correlation function decays more slowly at least as concerns its long-time tail [102]. Polybutadiene confined in anodic aluminum oxide matrices (20 and 60 nm) and polydimethylsiloxane restrained to emulsion droplets (200–1,000 nm) were studied with the aid of *multiple-quantum build-up NMR spectroscopy* [103]. Evidence for geometrical confinement effects on polymer chain dynamics independent of the chain length was also observed with the aid of *dielectric relaxation spectroscopy* [104, 105]. The systems examined in this case were poly(propylene glycol) and poly(dimethyl siloxane) in nanoporous glasses. As an intriguing question, the interplay between adsorption and (geometrical) confinement effects was analyzed. Variation of the pore size permitted the clear identification of the geometrical confinement contribution. In this context, it is most important to distinguish the role of *adsorption* at the pore walls as a potential source of phenomena with a similar appearance as the corset effect as discussed in Ref. [106]. Finally, in Ref. [107], a confinement effect in micrometer thick droplets was identified with the aid of *mechanical relaxation* in the sense of an increased terminal relaxation time.

5.4.8.3 Interpretation

The corset effect can be interpreted on different levels. The simplest conclusion one can draw directly from the different slopes of the T_1 dispersion in bulk and under confinement was already mentioned above: It is a different degree of anisotropy of molecular dynamics. The steeper dispersion slope and the reduced transverse relaxation times under confinement mean that the long-time decay of the orientation correlation function is retarded relative to the bulk sample. Segmental isotropization so to speak takes longer. The origin of this retardation can only be a stronger influence of topological constraints hindering rotational rearrangements of chain sections.

As an explanation, it has been suggested that the corset effect can be attributed to a finite-size phenomenon [45]. A well-known law of statistical physics relates the mean-square fluctuation of the particle number in a given volume to the mean number of particles in that volume according to

$$\langle (\delta N_V)^2 \rangle = k_B T \rho_s \kappa_T \langle N_V \rangle \quad (5.299)$$

where ρ_s is the mean (segment) particle number density and κ_T is the isothermal compressibility. Fluctuations in large systems are consequently larger than in small systems. Reducing the system size by confinement thus *reduces* fluctuations. A scaling treatment on this basis suggests that the tube constraints *effective* under mesoscopic confinements are only of the order [45]

$$d \approx \sqrt{b^2 \rho_s k_B T \kappa_T} \quad (5.300)$$

Likewise, in view of the Doi/Edwards reptation model, the fictitious tube is the only source of anisotropy apart from chain connectivity. A rather tight tube diameter must therefore be concluded in the frame of this concept if the strong anisotropy of rotational fluctuations under mesoscopic confinements is to be explained. Actually, the phenomenon was recently confirmed with the aid of computer simulations [108]. In this way, the confinement effect could clearly be reproduced on a time scale beyond $10 \times \tau_s$. In comparison to the polyethyleneoxide data reported in Ref. [45], this is just the time scale where the corset effect becomes perceptible. On the other hand, translational fluctuations as revealed by field-gradient NMR diffusometry and quasi-elastic neutron scattering are obviously not very sensitive to this particular feature of molecular dynamics.

In order to discriminate effects due to polymer–surface interactions on the one hand, and due to purely geometrical confinement on the other, two model scenarios have been simulated in the study reported in Ref. [108]. The conclusion is that surface interactions, as expected, fade away with increasing pore diameter, whereas the collective slowing down of reorientational dynamics upon mesoscopic confinement is much more persistent in this respect. The above interpretation of the corset effect is thus corroborated.

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Chapter 6

Molecular and Collective Dynamics in Liquid Crystals and Other Mesophases

Abstract In a sense, liquid crystals are strongly related to polymers as concerns molecular dynamics. Analytical treatments on the basis of suitable equations of motions result again in solutions based on collective relaxation modes. The features how order-director fluctuations manifest themselves in NMR relaxation experiments and dynamic light scattering will be figured out in detail. Molecular dynamics in lipid bilayers, often considered as biological model membranes, and other layered structures are further examples belonging to this category. This chapter also addresses less common subjects such as shape fluctuations of vesicles and the consequences of the diffusion of structural defects on dielectric relaxation. Finally, the dynamics in the ordered mesophase of poly(dialkylsiloxane) materials will be examined as a relatively exotic but nevertheless most interesting research area.

6.1 Introductory Remarks: Collective Dynamics in Polymers and Liquid Crystals

The crucial strategy we have pursued in the previous chapter was to analyze chain dynamics in isotropic polymer liquids by superimposed relaxation modes. Understanding a polymer chain as a set of elastically *coupled* segments (or more figuratively “beads”), such modes are an expression of *collective motions* of these entities. Molecules in liquid-crystalline materials such as the one schematically depicted in Fig. 6.1 are also elastically *coupled* to their neighbors. It may therefore be suspected that orientational fluctuations in such systems are subject to analogous principles and can again be described in terms of *collective dynamics*.

Notably, we are dealing with *elastic* systems in either case. Elasticity is the crucial prerequisite for the appearance of relaxation modes. Regarding polymers, elasticity refers to variations of the extension of random coils formed by chains or chain sections. Liquid crystals analogously show elastic responses to *bend*, *splay*, or *twist* deformations of the molecular order as illustrated in Fig. 6.2 [1–3]. Here and

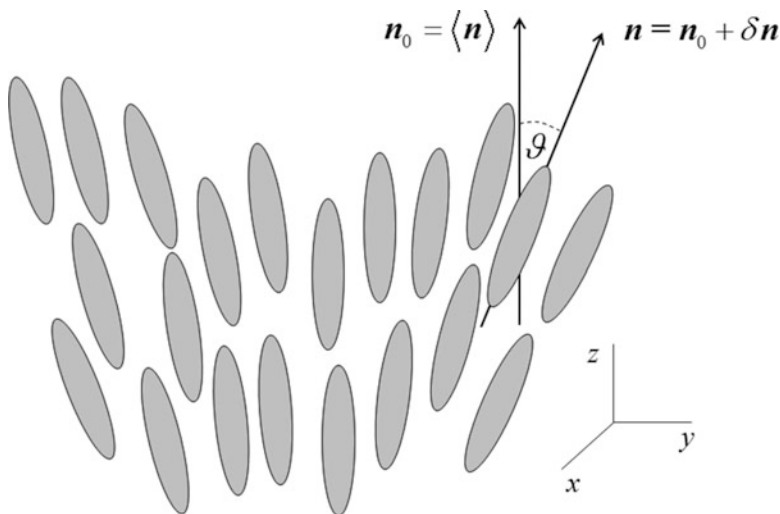


Fig. 6.1 Liquid-crystalline order and schematic representation of the local order director $\mathbf{n} = \mathbf{n}_0 + \delta\mathbf{n}$ at the position $\mathbf{R}$ and time t . The director fluctuates by the inclination vector $\delta\mathbf{n}(\mathbf{R}, t)$ about its temporal average $\mathbf{n}_0 = \langle \mathbf{n} \rangle$. The displayed situation mimics a nematic phase

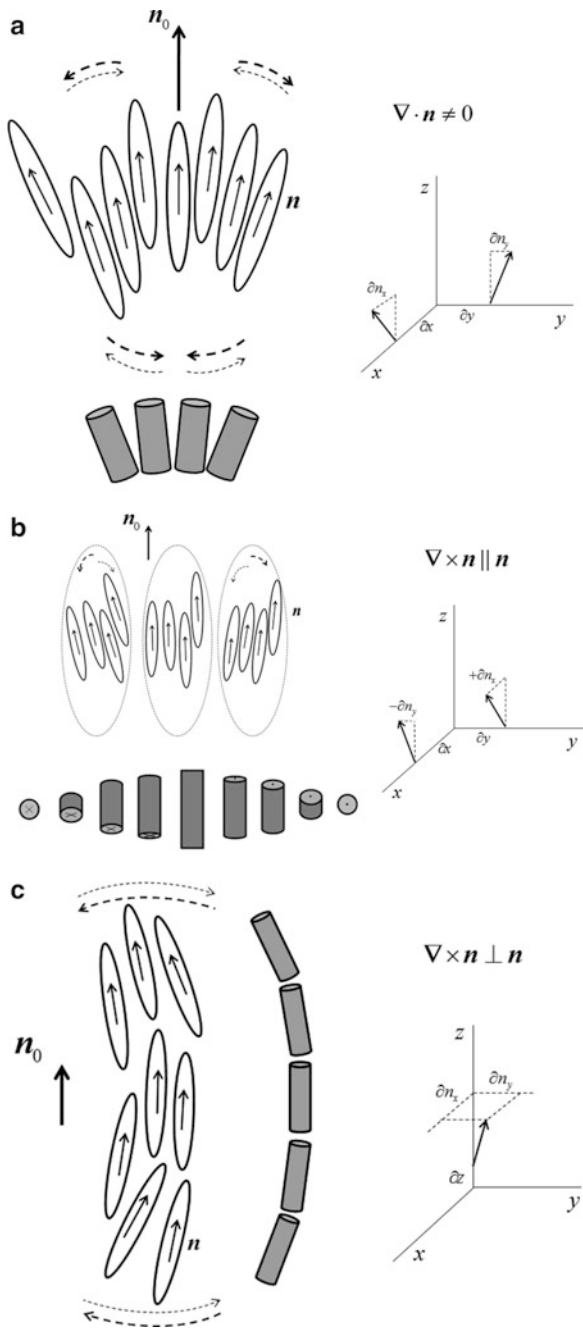
there, elasticity refers to *collectives* which consequently will be subject to a spectrum of superimposed relaxation modes.

The elasticity of freely jointed Kuhn model chains was shown to be of a purely *entropic* nature. This is in contrast to liquid-crystalline materials. Bend, splay, or twist elasticities are largely of an *energetic* origin based on the intermolecular interaction potentials (see Sect. 2.1). Entropic aspects can play a role in addition but are normally of minor importance. The treatment of collective dynamics will therefore deviate somewhat at this point. Nevertheless, the so-called order-director fluctuations of liquid crystals will be shown to be another example of a relaxation-mode analysis of collective dynamics revealing a number of features we are already familiar with.

6.2 Classification of Mesophase Order

The liquid-crystalline state of matter is characterized by a solid-like order as concerns molecular orientation while translational mobility at least partly is retained as in ordinary liquids. The character of the orientational order is *long range* (on a molecular-length scale) and *persistent* (relative to fluctuations of individual molecules). It should not be confused with the temporal short-range order that may arise in isotropic liquids. Long-range order manifests itself by phenomena based on pronounced anisotropic properties. Examples are optical birefringence, dipolar or quadrupolar splitting of NMR lines, quadrupole dips (or

Fig. 6.2 Illustration of elastic deformations in a nematic liquid crystal: (a) “splay,” (b) “twist,” and (c) “bend.” The *left schemes* in (a) and (c) visualize the deformations only in the section coinciding with the drawing plane, for simplicity. In reality, deformations can occur in the third dimension as well



peaks) in spin–lattice relaxation dispersion (see Sect. 3.1.8 and Refs. [4, 5]), and the dipolar-correlation effect (see Sect. 6.6).

Ideally, liquid-crystalline order is *uniform* across the sample. However, there are a number of factors influencing the appearance of order under real conditions. Metastable line singularities, so-called *disclinations*, lead to distortions. Photomicroscopy reveals the so-called birefringent *texture*. Depending on the character of the interaction, molecules near surfaces tend to be aligned parallel or perpendicular to the surface normal so that the confinement topology matters. For theoretical considerations, we will therefore restrict ourselves preferably to areas small enough to be considered uniformly ordered. That is, the dimensions are large on a molecular scale but small relative to the field of view of photomicroscopy.

6.2.1 Ordering Mechanisms

Typical molecules exhibiting liquid-crystalline phases have a rod or disklike shape and contain more or less rigid *mesogenic groups*. Regarding the chemical structure, these groups typically consist of benzene rings or double bond sequences [1–3]. Ordering is then a consequence of the anisotropic intermolecular interaction among mesogenic groups. Parallel lining up is favored for mainly *energetic* reasons. Ordered phases of liquid crystals containing mesogenic groups will be referred to as *type A mesophase*. On the one hand, they can be subdivided into *lyotropic mesophases* adopting orientational order in certain concentration ranges of solutions or dispersions and, on the other, into *thermotropic mesophases* arising in certain temperature ranges. There are a number of molecular-field theories explaining the transition between isotropic and ordered phases thermodynamically. In particular, the order-parameter-based Landau theory [6] and the mean-field concept by Maier and Saupe [7] are well known. Detailed reviews can be found in Refs. [1–3], for example.

The second type of liquid crystals comprises *amphiphilic* molecules in an aqueous environment. There are numerous introductory textbooks on this subject. Examples are Refs. [8–11]. Typical compounds are lipids, soaps, and detergents (also referred to as *surfactants*). Amphiphilic molecules in water tend to be packed in a way that minimizes the contact of the hydrophobic parts of the molecules with water and maximizes the vicinity of water and hydrophilic groups. This so-called *hydrophobic “interaction”* was already described in Sect. 2.1.5 as a mainly entropy-based mechanism. The hydrophobic moiety of the molecules often consist of fatty acid residues with hydrocarbon chains 12–20 carbons long, whereas the hydrophilic groups are polar by nature. Ordering on this basis leads to a parallelization tendency of the hydrocarbon chains. *Mesophases* arising on these grounds can be subsumed as *type B*. The amphiphilic character of the molecules suggests *lyotropic* phase behavior in aqueous environments.

Orientational order can furthermore be established in liquid adsorbate phases by anisotropic interaction with surfaces [12]. This *type C mesophase* refers to

otherwise isotropic liquids or mesogenic liquids in their isotropic phase. When being adsorbed at surfaces of porous media, for example, a *surface-ordered phase* will arise if the interaction with the wall is anisotropic enough to favor a certain orientation of molecular axes relative to the surface. This is also a matter of packing of the molecules in the interface layer. As in all other cases, surface order is the result of the reduced Helmholtz free energy relative to the disordered bulk state.

Finally, there is a class of ordered fluids much less known and less investigated than liquid crystals with mesogenic groups. In the sense of the above classification, these substances are of a totally atypical composition, and their ordered phases are therefore not directly referred to as liquid crystals as such. We mention them nevertheless in the present context since the experimental manifestation of order is phenomenologically the same as with ordinary liquid crystals of type A. In particular, optical birefringence and NMR line splitting can be observed in an analogous way. The systems in question consist of certain flexible polymers capable of numerous rotationally isomeric and energetically equivalent conformations.¹ They are nevertheless capable of ordered mesophases in a certain temperature range below the transition to the isotropic phase [13, 14]. Examples are polydiethylsiloxane and higher homologues thereof. The origin of this type of order is supposed to be of a primarily *entropic* nature since no rigid, rod- or disklike structures are involved. The segmental mobility in the ordered mesophase tends to be *increased* relative to the disordered isotropic phases. Under such conditions, phase space is expected to be populated more extensively in the mesophase than in the isotropic melt. Helmholtz free energy is consequently reduced, so that the mesophase is stabilized thermodynamically. This sort of order in the liquid state will be addressed as *type D mesophase*.

6.2.2 Structural Aspects

Molecular ordering in liquid crystals can adopt different structures, topologies, and geometries. Simple alignment of molecular long axes relative to each other is referred to as *nematic* liquid crystals. Layered arrangements of the aligned molecules are called *smectic*. If the alignment direction and the layer normal coincide, one speaks of *smectic-A phases*. This is in contrast to the *smectic-C* case where the alignment direction is tilted relative to the layer normal. There are a number of further order structures such as the *columnar* and *cholesteric* phases. Depending on the molecular symmetry properties, ordering can also refer to two directions so that the order is *biaxial*. Descriptions of the rich variety of liquid-crystalline phases can be found in more detail in Refs. [1, 2], for example. In the

¹ At this point, it should be noted that this sort of polymers must not be confused with liquid-crystalline side or main-chain polymers which actually contain mesogenic groups leading to ordered phases in analogy to conventional liquid crystals.

subsequent treatments, we will largely focus on *uniaxial nematic* systems which can be considered as paradigm for mesophases.

6.2.3 Order Director and Order Parameter

The direction of orientational order can be described by the (local) order director $\mathbf{n} = \mathbf{n}(\mathbf{R}, t)$. The molecular long axis of a mesogenic molecule at the position $\mathbf{R}$ and at time t is aligned along this dimensionless unit vector. The time dependence is due to fluctuations by collective thermal excitation of the system. The term “collective” refers to the correlation length as a measure of the spatial extent of the cooperatively fluctuating molecules. The director fluctuates about its equilibrium orientation $\mathbf{n}_0(\mathbf{R})$ according to

$$\mathbf{n}(\mathbf{R}, t) = \mathbf{n}_0(\mathbf{R}) + \delta\mathbf{n}(\mathbf{R}, t) \quad (6.1)$$

where the *inclination vector* $\delta\mathbf{n}(\mathbf{R}, t)$ is a local time-dependent disturbance. The equilibrium orientation is given as the long-time average $\mathbf{n}_0(\mathbf{R}) = \langle \mathbf{n}(\mathbf{R}, t) \rangle$ relative to the time scale of order fluctuations. This implies that the mean inclination vector vanishes on that time scale, $\langle \delta\mathbf{n}(\mathbf{R}, t) \rangle = 0$. Figure 6.1 shows a schematic illustration for the nematic case. The director can suitably be defined in terms of the polar angle ϑ (relative to the z -axis of the reference frame) and the azimuthal angle φ (relative to the x -axis in the x/y plane):

$$\mathbf{n}(\varphi, \vartheta) = \begin{pmatrix} \sin \vartheta \cos \varphi \\ \sin \vartheta \sin \varphi \\ \cos \vartheta \end{pmatrix} \quad (6.2)$$

In the case of *uniaxial* liquid crystals, that is, of cylindrically symmetric molecules, it suffices to consider the polar angle ϑ illustrated in Fig. 6.1 as the angle between the molecular axis and $\mathbf{n}_0(\mathbf{R})$. In this case, the degree of orientational order can be characterized by the *order parameter*

$$S_{\text{or}} = \frac{1}{2} \langle 3\cos^2 \vartheta - 1 \rangle \quad (6.3)$$

where the angle ϑ is a thermally fluctuating quantity. The angle brackets indicate an ensemble or – in the ergodic sense – temporal average over all fluctuations affecting the order. The ergodicity condition requires that all orientations occurring in a large

ensemble can also be reached by an individual molecule in the course of time. Ensemble and time averages therefore coincide.²

The order parameter vanishes in the completely disordered and, hence, isotropic phase, $S_{\text{or}} = 0$, whereas the value $S_{\text{or}} = 1$ indicates perfect alignment of molecules. For a typical liquid crystal sample, S_{or} lies between about 0.3 and about 0.8. It decreases as the temperature is raised. In particular, a sharp drop of the order parameter to 0 is observed when the system undergoes a phase transition from a liquid crystalline to the isotropic phase. In more complex system, biaxial liquid-crystalline phases can occur. In this case, two angles are needed to describe the molecular alignment. Instead of a scalar, the order parameter is then a second-rank symmetric and traceless tensor (see, e.g., Ref. [2]).

6.2.4 Alignment in External Fields

As a consequence of anisotropic interactions, liquid-crystalline domains tend to be aligned in certain preferential directions relative to external electric or magnetic fields. Further lining-up mechanisms favoring or opposing the effect of such fields are acoustic fields and alignment relative to surfaces and flow streamlines. In the following, we will restrict ourselves to the discussion of electromagnetic fields as sources of alignment.

6.2.4.1 Magnetic Fields

As concerns the polarizing effect of magnetic fields, there is a certain analogy to the electric case already referred to in Sect. 3.9.1. The analogue to the electric equilibrium polarization $\mathbf{P}_0$ is the equilibrium magnetization $\mathbf{M}_0$, that is, total magnetic dipole moment per unit volume. $\mathbf{M}_0$ is related to the magnetic flux density $\mathbf{B}$ effective in the material by

$$\mathbf{M}_0 = \frac{\chi_m}{\mu_0(1 + \chi_m)} \mathbf{B} \approx \frac{\chi_m}{\mu_0} \mathbf{B} \quad (6.4)$$

where μ_0 is the magnetic field constant, and χ_m is the *magnetic susceptibility* of the material. In *diamagnetic* media which are of primary interest in the present context,

² This is in contrast to partly immobilized systems such as isotropic polymer networks, for example (see Sect. 5.3): The temporal average of the restricted orientations of a mesh-chain suggests a *finite* value of the mean second-order Legendre polynomial in Eq. (6.3) while the (powdery) ensemble average over all mesh chains *vanishes*. Ergodicity is violated, and the term “order” is ill-defined in this case. On the other hand, if the network is strongly stretched so that ensemble and time averages of mesh orientations approach each other, the term “order” may be appropriate in turn.

we can approximate the above expression here and in the following according to $|\chi_m| \ll 1$:

Note that

$$\mathbf{B} = \mu_r \mathbf{B}_0 \quad (6.5)$$

is the flux density effective *in the material*, whereas $\mathbf{B}_0$ is understood as the external flux density measured *in a vacuum*. The *relative permeability* μ_r of the material is related to the magnetic susceptibility χ_m by

$$\mu_r = 1 + \chi_m \quad (6.6)$$

For diamagnetism, the relative permeability is less than 1, $\mu_r < 1$, so that $\chi_m < 0$. That is, the magnetization is directed *opposite* to the flux density. Equation (6.4) is the magnetic counterpart of Eq. (3.541). Likewise, Eq. (6.6) finds its parallel in Eq. (3.542). The magnetic energy density of an *isotropic* diamagnetic material exposed to a magnetic flux density $\mathbf{B}$ is given by

$$\frac{\partial W_m}{\partial V} = - \int_0^B M'_0 dB' = - \frac{\chi_m}{\mu_0} \int_0^B B' dB' = - \frac{1}{2} \frac{\chi_m}{\mu_0} B^2 \quad (6.7)$$

where we have made use of the linear variation of the magnetization $M'_0 = (\chi_m/\mu_0) B'$ with the magnetic flux density.³

Since we are dealing with *anisotropic* molecule/field interactions, the magnetic susceptibility and the relative permeability must be replaced by second-rank tensors. In the case of *uniaxial* nematics, that is, for symmetry of the magnetic susceptibility about one molecular axis referred to by the symbol $\parallel$, the magnetic susceptibility tensor has the principal-axes structure

$$\chi_m = \begin{pmatrix} \chi_{m,\perp} & 0 & 0 \\ 0 & \chi_{m,\perp} & 0 \\ 0 & 0 & \chi_{m,\parallel} \end{pmatrix} \quad (6.8)$$

The components parallel and normal to the molecular symmetry axis are denoted by $\chi_{m,\parallel}$ and $\chi_{m,\perp}$, respectively. The *anisotropy of the magnetic susceptibility* is defined by the parameter

$$\Delta\chi_m = \chi_{m,\parallel} - \chi_{m,\perp} \quad (6.9)$$

³Note that there is a subtle difference between, on the one hand, the energy of a (variable) magnetization, Eq. (6.7) multiplied by the volume, and the Zeeman energy of a (fixed) nuclear dipole in a magnetic field, Eq. (3.2), on the other!

In terms of the uniaxial susceptibility tensor Eq. (6.8), the relation between the magnetization (averaged over thermal fluctuations of the order director) and the external flux density, Eq. (6.4), adopts the analogous form

$$\begin{aligned}
 \mathbf{M}_0 &\approx \frac{1}{\mu_0} \chi_m \mathbf{B} \\
 &= \frac{1}{\mu_0} \left(\chi_{m,\perp} B_x \mathbf{u}_x + \chi_{m,\perp} B_y \mathbf{u}_y + \chi_{m,\parallel} B_z \mathbf{u}_z \right) \\
 &= \frac{\chi_{m,\perp}}{\mu_0} \mathbf{B} + \frac{\Delta \chi_m}{\mu_0} (\mathbf{n}_0 \cdot \mathbf{B}) \mathbf{u}_z
 \end{aligned} \tag{6.10}$$

where $\mathbf{u}_x, \mathbf{u}_y, \mathbf{u}_z$ are unit vectors along the x, y, z directions of the principal-axes system of the susceptibility tensor and where the mean order director $\mathbf{n}_0$ coincides with the z -direction. The potential-energy density Eq. (6.7) must correspondingly be modified according to

$$\frac{\partial W_m}{\partial V} = -\frac{1}{2} \frac{\chi_{m,\perp}}{\mu_0} B^2 - \frac{1}{2} \frac{\Delta \chi_m}{\mu_0} (\mathbf{n}_0 \cdot \mathbf{B})^2 \tag{6.11}$$

The first term on the right-hand side is obviously not influenced by the director orientation relative to the magnetic field and is therefore irrelevant with respect to alignments. It is rather the second term that determines the preferential orientation of the vectors $\mathbf{n}_0$ and $\mathbf{B}$ relative to each other.

Equation (6.11) is the decisive contribution to the density of Helmholtz free energy in regard to the interaction between mesogenic molecules and magnetic fields,

$$\begin{aligned}
 \frac{\partial A_{H,m}}{\partial V} &= \frac{\partial W_m}{\partial V} - T \frac{\partial S}{\partial V} \\
 &= \frac{1}{2} \frac{\chi_{m,\perp}}{\mu_0} B^2 - \frac{1}{2} \frac{\Delta \chi_m}{\mu_0} (\mathbf{n}_0 \cdot \mathbf{B})^2 - T \frac{\partial S}{\partial V}
 \end{aligned} \tag{6.12}$$

provided that the variation of the entropy S upon alignment is minor. The term $-\Delta \chi_m (\mathbf{n}_0 \cdot \mathbf{B})^2 / (2\mu_0)$ thus represents the field alignment tendency which competes with thermal fluctuations of the director. If the anisotropy of the magnetic susceptibility is positive, $\Delta \chi_m > 0$, the Helmholtz free energy will adopt a minimum for parallel or antiparallel orientations. In the opposite case, $\Delta \chi_m < 0$, an alignment perpendicular to the external magnetic field is favored.

6.2.4.2 Electric Fields

Alignment of liquid crystals in external electric fields obeys quite analogous laws. The electric field strength $\mathbf{E}$ effective *in the material* is related to the field strength $\mathbf{E}_0$ measured *in vacuum* by

$$\mathbf{E}_0 = \underline{\varepsilon}_r \mathbf{E} \quad (6.13)$$

where $\underline{\varepsilon}_r$ is the tensor of the relative permittivity of the material. With the electric susceptibility tensor $\underline{\chi}_e = \underline{\varepsilon}_r - \underline{u}$, the electric counterpart of Eq. (6.4), that is, the electric polarization as a function of the external electric field strength, reads

$$\mathbf{P}_0 = \varepsilon_0 \underline{\chi}_e \mathbf{E} \quad (6.14)$$

ε_0 is the electric field constant, and $\underline{u}$ is the unit tensor. The electric energy density of an *isotropic* material exposed to an external electric field would accordingly be given by

$$\frac{\partial W_e}{\partial V} = - \int_0^E \mathbf{P}'_0 dE' = -\varepsilon_0 \chi_e \int_0^E E' dE' = -\frac{1}{2} \varepsilon_0 \chi_e E^2 \quad (6.15)$$

where χ_e is the isotropic susceptibility. Referring to *anisotropic* media such as uniaxial nematic phases, we must distinguish the respective components parallel and normal to the molecular symmetry axis $\chi_{e,\parallel}$ and $\chi_{e,\perp}$. As a parameter, the *anisotropy of the electric susceptibility* is defined by

$$\Delta\chi_e = \chi_{e,\parallel} - \chi_{e,\perp} \quad (6.16)$$

The electric counterpart to the Helmholtz free-energy density Eq. (6.12) thus is

$$\begin{aligned} \frac{\partial A_{H,e}}{\partial V} &= \frac{\partial W_e}{\partial V} - T \frac{\partial S}{\partial V} \\ &= -\frac{1}{2} \varepsilon_0 \chi_{e,\perp} E_0^2 - \frac{1}{2} \varepsilon_0 \Delta\chi_e (\mathbf{n}_0 \cdot \mathbf{E}_0)^2 - T \frac{\partial S}{\partial V} \end{aligned} \quad (6.17)$$

with the same consequences as mentioned above in the magnetic case.

6.3 Elasticity of Uniaxial Nematic Liquid Crystals

Molecules in liquid-crystalline phases are elastically coupled. This in particular refers to molecular orientations. In the bulk state, perfect alignment corresponds to a minimum of Helmholtz free energy. Deviations arise in the static sense by certain boundary conditions at confining surfaces, and, dynamically, because of thermal excitation of the elastic system. Mesogenic molecules in liquid-crystalline phases thus form a system of two- or three-dimensional, elastically coupled oscillators being able to perform collective excitations. In the limit of small disturbances,

linear relations between the restoring forces and deformations are warranted. Not unlike lattice dynamics of solid crystals, one can then analyze the collective reorientation dynamics as a superposition of normal modes with wave vectors $\mathbf{q}$ [15, 16].

In the *continuum limit*, we do not distinguish between individual molecules. The local directors $\mathbf{n} = \mathbf{n}(\mathbf{R})$ thus form an elastically coupled vector field as a continuous function of the position $\mathbf{R} = \mathbf{R}(x, y, z)$. In the absence of any thermal excitation, the director vector field would be uniformly directed along a single direction. However, as soon as thermal energy is “fed” into the system, the directors will fluctuate leading to *elastic deformations*. In this respect, one speaks of fluctuating *curvature strain* of the director field. The three types of curvature strain, that is, *splay*, *twist*, and *bend* to be distinguished in the following are illustrated in Fig. 6.2.

For an analytical definition of curvature strain, we consider a position at the origin of the reference frame, $\mathbf{R} = 0$, and assume that the director at this location is aligned along the z -direction:

$$\mathbf{n}(0) = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad (6.18)$$

Small shifts along the three coordinate axes will cause changes of the orientation of the director. As the basis of the approach to be pursued in the following, let us now expand the components of $\mathbf{n} = \mathbf{n}(\mathbf{R})$ around the origin in a Taylor series and truncate it after the linear term with an accuracy of the order $o(R^2)$:

$$n_i(\mathbf{R}) = n_i(0) + \sum_{j=1}^3 R_j \left(\frac{\partial n_i}{\partial R_j} \right)_{R=0} + o(R^2) \quad (6.19)$$

The subscripts $i = 1, 2, 3$ and $j = 1, 2, 3$ correspond to the respective space directions x, y, z . Since $\mathbf{n}(\mathbf{R})$ has a maximum at the origin $\mathbf{R} = 0$ according to Eq. (6.18), all three derivatives of the z -component vanish at this position, that is, $(\partial n_z / \partial R_j)_{R=0} = 0$. The explicit expansions of the three components thus take the form

$$\begin{aligned} n_x(\mathbf{R}) &= \left(\frac{\partial n_x}{\partial x} \right)_{R=0} x + \left(\frac{\partial n_x}{\partial y} \right)_{R=0} y + \left(\frac{\partial n_x}{\partial z} \right)_{R=0} z + o(R^2) \\ n_y(\mathbf{R}) &= \left(\frac{\partial n_y}{\partial x} \right)_{R=0} x + \left(\frac{\partial n_y}{\partial y} \right)_{R=0} y + \left(\frac{\partial n_y}{\partial z} \right)_{R=0} z + o(R^2) \\ n_z(\mathbf{R}) &= 1 + o(R^2) \end{aligned} \quad (6.20)$$

where we are now using the identities $R_x \equiv x$, $R_y \equiv y$, and $R_z \equiv z$.

On this basis, we can define the *curvature strain* components at the origin as the coefficients in Eq. (6.20). They can be assorted into three groups:

$$\begin{aligned}
s_1 &= \left(\frac{\partial n_x}{\partial x} \right)_{R=0} & s_2 &= \left(\frac{\partial n_y}{\partial y} \right)_{R=0} & \text{“splay”} \\
t_1 &= - \left(\frac{\partial n_y}{\partial x} \right)_{R=0} & t_2 &= \left(\frac{\partial n_x}{\partial y} \right)_{R=0} & \text{“twist”} \\
b_1 &= \left(\frac{\partial n_x}{\partial z} \right)_{R=0} & b_2 &= \left(\frac{\partial n_y}{\partial z} \right)_{R=0} & \text{“bend”}
\end{aligned} \tag{6.21}$$

The meaning of this classification “becomes obvious when considering the schemes in Fig. 6.2. *Splay deformations* arise if the director is modified by variations $+\partial n_x$ and/or $+\partial n_y$ upon offsets $+\partial x$ and $+\partial y$ away from the origin, respectively. This explicates the attribute “splay.” The condition for this sort of deformation can consequently be expressed by

$$s_1 + s_2 = \left(\frac{\partial n_x}{\partial x} \right)_{R=0} + \left(\frac{\partial n_y}{\partial y} \right)_{R=0} = \nabla \cdot \mathbf{n} \neq 0 \tag{6.22}$$

Twist deformations by contrast are defined by changes $-\partial n_y$ and/or $+\partial n_x$ in lateral distances $+\partial x$ and $+\partial y$, respectively. Note the change of both the signs and the allocation of subscripts relative to splay deformations. This obviously corresponds to a “twist” of the director *around* the z -axis. The condition is therefore based on a vectorial rotation operation according to

$$-(t_1 + t_2) = \left(\frac{\partial n_y}{\partial x} \right)_{R=0} - \left(\frac{\partial n_x}{\partial y} \right)_{R=0} = \mathbf{n} \cdot (\nabla \times \mathbf{n}) \neq 0 \quad \text{or} \quad \nabla \times \mathbf{n} \parallel \mathbf{n} \tag{6.23}$$

Finally, the *bend deformation* is characterized by differences ∂n_x and/or ∂n_y in a distance ∂z along the z -axis. The director “bends” *away* from the z -axis. The vector condition is consequently

$$b_1^2 + b_2^2 = \left(\frac{\partial n_x}{\partial z} \right)_{R=0}^2 + \left(\frac{\partial n_y}{\partial z} \right)_{R=0}^2 = [\mathbf{n} \times (\nabla \times \mathbf{n})]^2 = \mathbf{n} \cdot \nabla \mathbf{n} \neq 0 \quad \text{or} \quad \nabla \times \mathbf{n} \perp \mathbf{n} \tag{6.24}$$

where we have made use of a variant of the Weber relation $\mathbf{n} \times (\nabla \times \mathbf{n}) = \frac{1}{2} \nabla n^2 - (\mathbf{n} \cdot \nabla) \mathbf{n}$ (see Eq. 4.29) and $\nabla n^2 = 0$.

Concurrent to the expansion and linear approximation of the director components Eq. (6.20), the elastic contribution to the Helmholtz free-energy density, $\partial A_{\text{H,elast}}/\partial V$, can formally be expanded according to

$$\frac{\partial A_{\text{H,elast}}}{\partial V} \approx \sum_{i=1}^6 k_i a_i + \frac{1}{2} \sum_{i=1}^6 \sum_{j=1}^6 k_{ij} a_i a_j \tag{6.25}$$

The coefficients k_i and $k_{ij} = k_{ji}$ are constants to be specified in the further treatment. The quantities a_i are the six *curvature strain components* defined above in Eq. (6.21). They have been renamed according to

$$a_1 \equiv s_1; \quad a_2 \equiv t_2; \quad a_3 \equiv b_1; \quad a_4 \equiv -t_1; \quad a_5 \equiv s_2; \quad a_6 \equiv b_2 \quad (6.26)$$

The number of terms in the expansion Eq. (6.25) can be reduced substantially by taking advantage of the symmetry properties inherent to uniaxial nematic liquid crystals [1–3]: (1) *invariance of $\partial A_{H, \text{elast}}/\partial V$ under rotation about the z-axis*; (2) *invariance of $\partial A_{H, \text{elast}}/\partial V$ under director inversion, $\mathbf{n} \leftrightarrow -\mathbf{n}$* , provided that the mesogenic molecules are nonpolar (as it is usually the case); and (3) *invariance of $\partial A_{H, \text{elast}}/\partial V$ under reflection in planes containing the z-axis*. Furthermore, surface-related contributions are irrelevant for the *bulk* behavior. Under all these conditions, the density of the curvature-elastic contribution to Helmholtz free energy can be expressed in the reduced form

$$\frac{\partial A_{H, \text{elast}}}{\partial V} = \frac{1}{2} \left\{ \underbrace{\hat{K}_1 (\nabla \cdot \mathbf{n})^2}_{\text{splay}} + \underbrace{\hat{K}_2 [\mathbf{n} \cdot (\nabla \times \mathbf{n})]^2}_{\text{twist}} + \underbrace{\hat{K}_3 [\mathbf{n} \times (\nabla \times \mathbf{n})]^2}_{\text{bend}} \right\} \quad (6.27)$$

This expression is usually referred to as *Frank/Oseen free-energy density*. In terms of the derivative relations for the deformations specified in Eqs. (6.22), (6.23), and (6.24), the total free energy can be spelt out as

$$A_{H, \text{elast}} = \frac{1}{2} \int_{\text{Vol}} \left\{ \underbrace{\hat{K}_1 \left(\frac{\partial n_x}{\partial x} + \frac{\partial n_y}{\partial y} \right)^2}_{\text{splay}} + \underbrace{\hat{K}_2 \left(\frac{\partial n_x}{\partial y} - \frac{\partial n_y}{\partial x} \right)^2}_{\text{twist}} + \underbrace{\hat{K}_3 \left[\left(\frac{\partial n_x}{\partial z} \right)^2 + \left(\frac{\partial n_y}{\partial z} \right)^2 \right]}_{\text{bend}} \right\} dV \quad (6.28)$$

where the integral covers the whole sample volume. The (positive) coefficients $\hat{K}_i$ are the respective *curvature-elastic constants* for the three types of deformations illustrated in Fig. 6.2.

We note that all three terms in Eq. (6.28) have the format “elastic constant times the square of a curvature strain.” This analytical structure reflects the fact that, for sufficiently small curvature strain, the system will comply to *Hookean relations* between stress or torque on the one hand and strain on the other. As a consequence, there will be a *square* dependence of the elastic deformation energy on the curvature strain.

In nematic liquid crystals, the three elastic constants are usually of the same order of magnitude. For further treatments of a possibly more qualitative but at any rate tractable nature, the formalism can therefore be simplified by the *one-constant approximation*

$$\hat{K} \approx \hat{K}_1 \approx \hat{K}_2 \approx \hat{K}_3 \quad (6.29)$$

In this case, the density of the elastic Helmholtz free energy takes the form [1]

$$\frac{\partial A_{\text{H,elast}}}{\partial V} = \frac{1}{2} \hat{K} \{ (\nabla \cdot \mathbf{n})^2 + (\nabla \times \mathbf{n})^2 \} \quad (6.30)$$

6.4 Order-Director Fluctuations in Nematic Liquid Crystals

Let us resume the discussion we started in Sect. 6.1: The elastic properties of liquid crystals elucidated above suggest *collective* relaxation modes in the sense that the order director fluctuates about its equilibrium orientation $\mathbf{n}_0 = \langle \mathbf{n}(\mathbf{R}, t) \rangle$ (see Fig. 6.1). In the Hookean, that is, *linear* stress–strain elasticity regime of liquid-crystalline systems, one therefore expects a superposition of relaxation modes in close analogy to the derivation of Rouse modes in the case of freely draining polymers.

Consider a cuboid-shaped probe volume in a nematic liquid crystal as sketched in Fig. 6.3. The probe volume is thought to be located within a bulk sample so that no anchoring energy at confining walls needs to be taken into account. The dynamics in this sort of system is best treated on the basis of the Langevin equation of motion (see Sect. 2.4.3). The problem is considerably simplified by the following conditions: (1) As mentioned before, the molecules are *elastically* coupled to their nearest neighbors. The *one-constant approximation*, that is, Eq. (6.29), is assumed.⁴ (2) The number of molecules on the length scale of interest be large enough, $N \gg 1$, to permit a treatment in the *continuum limit*. (3) The resistance of the liquid crystal against shearing is characterized by the (constant) viscosity η .

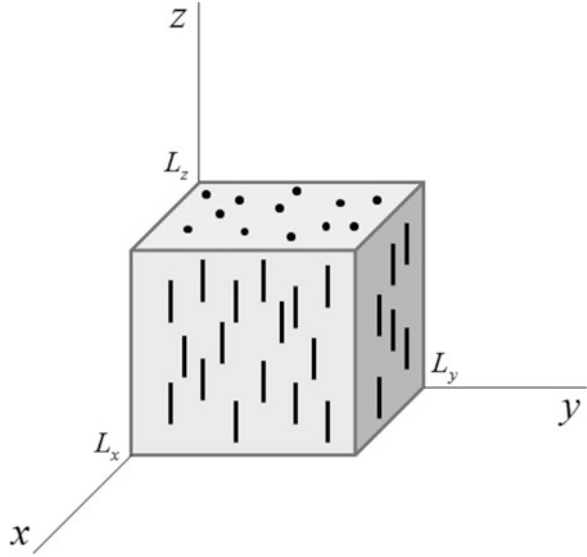
In principle, we have already established an equation of motion of this sort, namely, Eq. (5.103), the basis of the Rouse model. Since we are now dealing with *orientational* fluctuations instead of *translational* displacements of the moving objects, the equation of motion is now composed of *shear stresses* in place of simple *forces*.⁵ The local frictional shear stress is given by

$$\boldsymbol{\tau}_\eta = -\eta \frac{\partial \delta \mathbf{n}}{\partial t} \quad (6.31)$$

⁴ A treatment differentiating all three Frank elastic constants will follow in Sect. 6.7.2.

⁵ From a molecular point of view, shear stress can also be interpreted as torque per unit volume with a vector direction perpendicular to shear stress.

Fig. 6.3 Probe volume in a nematic liquid crystal. The shape is assumed to be a cuboid of dimension $L_x \times L_y \times L_z$. The edges are aligned along the three space directions where the z -direction coincides with the equilibrium director $\mathbf{n}_0$. Since the probe volume is thought to be part of a bulk sample, no anchoring energy at confining walls needs to be taken into account



where η is the effective (dynamic) viscosity of the liquid crystal, and $\partial\delta\mathbf{n}/\partial t$ is the reorientation rate. The local elastic shear stress due to coupling to the nearest neighbors is⁶

$$\boldsymbol{\tau}_{\text{elast}} = \hat{K} \nabla^2 \delta \mathbf{n} \quad (6.32)$$

The Laplace operator ∇^2 in principle represents the three-dimensional version of the quasi-one-dimensional problem considered in Eq. (5.104) for the crossover from discrete objects to the *continuum* limit.

Finally, the local stochastic shear stress due to thermal impacts on the mesogenic molecules is represented by $\boldsymbol{\tau}_{\text{stoch}}(\mathbf{R}, t)$. Under the assumptions of the Langevin formalism, the sum of all these shear stresses must be zero:

$$\boldsymbol{\tau}_\eta + \boldsymbol{\tau}_{\text{elast}} + \boldsymbol{\tau}_{\text{stoch}} = \hat{K} \nabla^2 \delta \mathbf{n} - \eta \frac{\partial \delta \mathbf{n}}{\partial t} + \boldsymbol{\tau}_{\text{stoch}} = 0 \quad (6.33)$$

This equation of motion can be rewritten in the more convenient form

$$\frac{\partial \delta \mathbf{n}}{\partial t} = \frac{\hat{K}}{\eta} \nabla^2 \delta \mathbf{n} + \frac{1}{\eta} \boldsymbol{\tau}_{\text{stoch}} \quad (6.34)$$

⁶ Contrary to the usual representation [1], it was argued in Ref. [17] that the right-hand side of Eq. (6.32) should in principle be supplemented by a term $-\hat{K}(\mathbf{n} \cdot \nabla^2 \mathbf{n})\mathbf{n}$, that is, by a vector aligned along the director $\mathbf{n} = \mathbf{n}_0 + \delta \mathbf{n}$. Since we are referring here to shear deformations in lateral directions, that is, orientational fluctuations, this term will not be pursued any further.

where the terms on the right-hand side are the contributions to the local reorientation rate.

There is a further mechanism that can be assumed to contribute *independently* to this rate. Since liquid crystals are fluids, translational diffusion can be an efficient process so-to-speak for the “relocation of molecular orientation” from position to position via material *transport*. The transport equation specific for this contribution is

$$\frac{\partial \delta \mathbf{n}}{\partial t} = D \nabla^2 \delta \mathbf{n} \quad (6.35)$$

in analogy to Fick’s second law given in Eq. (2.167). D is the diffusion coefficient of the mesogenic molecules. Adding the right-hand side to Eq. (6.34) gives the final equation of motion to be solved for order-director fluctuations:

$$\frac{\partial \delta \mathbf{n}}{\partial t} = \left(\frac{\widehat{K}}{\eta} + D \right) \nabla^2 \delta \mathbf{n} - \frac{1}{\eta} \boldsymbol{\tau}_{\text{stoch}} \quad (6.36)$$

The Neumann boundary condition at the surfaces of the probe volume (see Fig. 6.3) is

$$\left. \frac{\partial \delta \mathbf{n}}{\partial x_i} \right|_{\text{surface}} = 0 \quad (6.37)$$

where the coordinates x_i refer to the three space directions. This condition states that no coupling to the exterior of the probe volume is anticipated. That is, the ensemble of mesogenic molecules in the probe volume is considered to be isolated.

Equation (6.36) can be solved with the aid of a normal-mode analysis in complex form. Since we are now dealing with a three-dimensional problem (in contrast to the related Rouse scenario in Sect. 5.4.3.2), the integration over the probe volume must refer to all three space directions. In vectorial form, the dimensionless normal coordinates are defined by

$$\delta \tilde{\mathbf{n}}(\mathbf{q}, t) = \frac{1}{V} \int_{\text{vol}} \delta \mathbf{n}(\mathbf{R}, t) \exp\{-i\mathbf{q} \cdot \mathbf{R}\} d^3 R \quad (6.38)$$

that is, by the spatial Fourier transform of $\delta \mathbf{n}(\mathbf{R}, t)$. The quantity $\mathbf{q}$ is the wave vector of the normal modes. The probe volume amounts to $V = L_x L_y L_z$ (see Fig. 6.3). The vector $\mathbf{R}$ with the components x, y, z indicates the position in the probe volume at which the inclination vector $\delta \mathbf{n}(\mathbf{R}, t)$ is regarded. In the following, we will refer to a discrete set of normal modes complying with the matching condition with respect to the probe volume dimensions:

$$q_x L_x = v\pi; \quad q_y L_y = v\pi; \quad q_z L_z = v\pi \quad (v = 1, 2, 3, \dots) \quad (6.39)$$

On the other hand, the continuum limit requires $q_\alpha \ll \ell^{-1}$ ($\alpha = x, y, z$), where ℓ represents the relevant dimension of the molecules.

Multiplying Eq. (6.36) on both sides from left by $V^{-1} \exp\{-i\mathbf{q} \cdot \mathbf{R}\}$, integrating all terms according to $\int_0^{L_x} \int_0^{L_y} \int_0^{L_z} \dots dxdydz$, and substituting the respective terms by the normal coordinate $\delta\tilde{\mathbf{n}}(\mathbf{q}, t)$ give

$$q^2 \left(\frac{\widehat{K}}{\eta} + D \right) \delta\tilde{\mathbf{n}}(\mathbf{q}, t) + \frac{\partial}{\partial t} \delta\tilde{\mathbf{n}}(\mathbf{q}, t) - \tilde{\boldsymbol{\tau}}(\mathbf{q}, t) = 0 \quad (6.40)$$

where, after integration by parts, we have taken into account the boundary and matching conditions Eqs. (6.35) and (6.39), respectively. The function

$$\tilde{\boldsymbol{\tau}}(\mathbf{q}, t) = \frac{1}{\eta V} \int_0^{L_z} \int_0^{L_y} \int_0^{L_x} \boldsymbol{\tau}_{\text{stoch}}(\mathbf{R}, t) \exp\{-i\mathbf{q} \cdot \mathbf{R}\} dxdydz \quad (6.41)$$

is still of a purely stochastic nature. That is, the temporal cross-correlation function between $\tilde{\boldsymbol{\tau}}(\mathbf{q}, t)$ and any other function vanishes. Exploiting this property, we can evaluate the autocorrelation functions of the normal coordinates:

$$c(\mathbf{q}, t) = \langle \delta\tilde{\mathbf{n}}(\mathbf{q}, t) \cdot \delta\tilde{\mathbf{n}}^*(\mathbf{q}, 0) \rangle \quad (6.42)$$

The superscript * indicates the conjugate complex form. The scalar product of $\delta\tilde{\mathbf{n}}^*(\mathbf{q}, 0)$ with each of the terms in Eq. (6.40) and the formation of the ensemble average $\langle \dots \rangle$ leads to

$$q^2 \left(\frac{\widehat{K}}{\eta} + D \right) c(\mathbf{q}, t) + \frac{\partial}{\partial t} c(\mathbf{q}, t) - \underbrace{\langle \tilde{\boldsymbol{\tau}}(\mathbf{q}, t) \cdot \delta\tilde{\mathbf{n}}^*(\mathbf{q}, 0) \rangle}_{=0} = 0 \quad (6.43)$$

The remaining terms form a linear differential equation with constant coefficients. The solution is

$$c(\mathbf{q}, t) = c(\mathbf{q}, 0) \exp\{-t/\tau_q\} \quad (6.44)$$

with the initial value

$$c(\mathbf{q}, 0) = \langle |\delta\tilde{\mathbf{n}}(\mathbf{q})|^2 \rangle \quad (6.45)$$

and the normal-mode relaxation time

$$\tau_q = \frac{1}{\left(\frac{\widehat{K}}{\eta} + D\right)q^2} \quad (6.46)$$

Let us now determine the temporal correlation function of the inclination vector (in this context interpreted as a complex quantity): $\langle \delta \mathbf{n}(\mathbf{R}, t) \cdot \delta \mathbf{n}^*(\mathbf{R}, 0) \rangle$. The normal-coordinate transformation inverse to Eq. (6.38) is

$$\delta \mathbf{n}(\mathbf{R}, t) = \sum_{\mathbf{q}} \delta \tilde{\mathbf{n}}(\mathbf{q}, t) \exp\{i\mathbf{q} \cdot \mathbf{R}\} \quad (6.47)$$

where the sum runs over all $\mathbf{q}$ vectors matching the conditions in Eq. (6.39). Forming the correlation function on this basis and inserting Eq. (6.44) gives

$$\begin{aligned} \langle \delta \mathbf{n}(\mathbf{R}, t) \cdot \delta \mathbf{n}^*(\mathbf{R}, 0) \rangle &= \sum_{\mathbf{q}} \sum_{\mathbf{q}'} \langle \delta \tilde{\mathbf{n}}(\mathbf{q}, t) \cdot \delta \tilde{\mathbf{n}}^*(\mathbf{q}', 0) \rangle \exp\{i(\mathbf{q} - \mathbf{q}') \cdot \mathbf{R}\} \delta_{\mathbf{q}\mathbf{q}'} \\ &= \sum_{\mathbf{q}} \left\langle |\delta \tilde{\mathbf{n}}(\mathbf{q})|^2 \right\rangle \exp\{-t/\tau_q\} \end{aligned} \quad (6.48)$$

The Kronecker symbol $\delta_{\mathbf{q}\mathbf{q}'}$ reflects that normal modes with wave vectors deviating from each other are uncorrelated. The fluctuations of the inclination vector are composed of a superposition of all normal modes complying to the matching conditions Eq. (6.39). In the sum remaining in the above expression, the relaxation functions $\exp\{-t/\tau_q\}$ are weighted by the mean square fluctuation $\left\langle |\delta \tilde{\mathbf{n}}(\mathbf{q})|^2 \right\rangle$ which is a Boltzmann average over the squared amplitudes of the mode with wave vector $\mathbf{q}$.

$\left\langle |\delta \tilde{\mathbf{n}}(\mathbf{q})|^2 \right\rangle$ can consequently be evaluated with the aid of the *equipartition theorem* of thermodynamics [1]: The mean thermal energy of deformations having a *square* dependence of the elastic energy on the curvature strain (see Eq. 6.28) will be $k_B T/2$. Thus, each normal-mode – notabene – component for a given wave vector independently contributes this amount. Elastic couplings exist in all three space directions so that normal modes contribute with all three components in principle. Since only fluctuations *transverse* to the director $\mathbf{n}_0 = \langle \mathbf{n}(\mathbf{R}, t) \rangle$ are relevant for the orientation of molecules, it suffices to consider the x and y components only. Assuming the one-constant approximation Eq. (6.29) thus leads to

$$\left\langle |\delta \tilde{\mathbf{n}}(\mathbf{q})|^2 \right\rangle = \frac{2k_B T}{V \widehat{K} q^2} \quad (6.49)$$

In volumes V large relative to molecular dimensions, the sum in Eq. (6.48) can be converted to an integral in the continuum limit according to

$$\sum_{\mathbf{q}} \dots \rightarrow \frac{V}{(2\pi)^3} \int \dots 4\pi q^2 d\mathbf{q} \quad (6.50)$$

where $\left[V / (2\pi)^3 \right] 4\pi q^2 d\mathbf{q}$ is the number of states in the volume element $4\pi q^2 d\mathbf{q}$ of the $\mathbf{q}$ space. The combination of Eqs. (6.49) and (6.50) with (6.48) results in the *correlation function of order-director fluctuations* (ODF)

$$\langle \delta n_x(t) \delta n_x(0) \rangle + \langle \delta n_y(t) \delta n_y(0) \rangle = \frac{k_B T}{\pi^2 \hat{K}} \int_{q_l}^{q_h} \exp \left\{ - \left(\frac{\hat{K}}{\eta} + D \right) q^2 t \right\} d\mathbf{q} \quad (6.51)$$

where we have inserted the normal-mode relaxation times given in Eq. (6.46). The upper cutoff limit of the integral, $q_h = 2\pi/\lambda_{\min}$, corresponds to a wavelength $\lambda_{\min}$ approaching the dimension of the molecules (where the continuum limit breaks down). The lower limit $q_l = 2\pi/\lambda_{\max}$ reflects the maximum mode wavelength $\lambda_{\max}$ corresponding to the nematic domain size. In contrast to the one-constant approximation, a formalism based on all Frank elastic constants will be needed for the treatment of dynamic light scattering. An outline in this regard follows in Sect. 6.7.2.

6.5 Spin–Lattice Relaxation Dispersion in Nematic Liquid Crystals

The theory of order-director fluctuations leads to some characteristic predictions for the frequency dependence (or *dispersion*) of spin–lattice relaxation times or rates. NMR relaxometry is therefore one of the main techniques employed for studies of the dynamics in liquid crystals. As the simplest scenario, let us consider a nematic liquid crystal consisting of molecules containing practically isolated pairs of protons. The protons of the representative pair to be regarded in the following are assumed to be separated by a vectorial distance $\mathbf{a}$ on the long axis of the molecules. The dominating interaction between the two protons will be *intramolecular* dipolar coupling, whereas intermolecular interactions are of minor importance and can be neglected. The treatment therefore refers to a representative *ensemble of dipolar-coupled two-spin systems* (see the discussion in Sect. 3.1.5.3).

For positive anisotropy of the magnetic susceptibility, $\Delta\chi_m > 0$, the mean order director will be aligned along the external magnetic flux density, that is, $\mathbf{n}_0 \parallel \mathbf{B}_0$. The problem is now to derive a formalism for spin–lattice relaxation based on the collective orientational fluctuation modes discussed in the previous section [15, 18–22].

Since the magnitude of the director obeys

$$|\mathbf{n}| = |\mathbf{n}_0 + \delta\mathbf{n}| = 1 \quad (6.52)$$

and since the director is assumed to be parallel to the internuclear vector, $\mathbf{n} \parallel \mathbf{a}$, the dipolar Hamiltonian Eq. (3.87) can be rewritten in the form

$$\mathcal{H}_d = \frac{\mu_0}{4\pi} (\hbar\gamma)^2 \frac{1}{a^3} \{\mathbf{I}_1 \cdot \mathbf{I}_2 - 3(\mathbf{I}_1 \cdot \mathbf{n})(\mathbf{I}_2 \cdot \mathbf{n})\} = f_d \sum_{k=-2}^2 F^{(k)} \mathcal{O}^{(k)} \quad (6.53)$$

$\mathbf{I}_1$ and $\mathbf{I}_2$ are the spin vector operators of the coupled protons (with the spin quantum number $I = 1/2$). For like spins, the factor f_d is defined by $f_d = \mu_0 \hbar^2 \gamma^2 / 4\pi$, where μ_0 is the magnetic field constant, γ is the gyromagnetic ratio, and $\hbar$ is Planck's constant divided by 2π . The spatial functions $F^{(k)}$ and the spin operator terms $\mathcal{O}^{(k)}$ are defined in Eqs. (3.90) and (3.91), respectively.

The Cartesian components of the director specifying the molecular orientation can be expressed in terms of spherical coordinates according to

$$\begin{aligned} n_x &= \sin \vartheta \cos \varphi \\ n_y &= \sin \vartheta \sin \varphi \\ n_z &= \cos \vartheta \end{aligned} \quad (6.54)$$

The angles are defined in Fig. 6.4. Furthermore defining the complex relations

$$\begin{aligned} n_x + in_y &= \sin \vartheta \exp\{+i\varphi\} \\ n_x - in_y &= \sin \vartheta \exp\{-i\varphi\} \end{aligned} \quad (6.55)$$

leads to the following expressions for the functions $F^{(k)}(\varphi, \vartheta)$ in Eq. (6.53):

$$\begin{aligned} F^{(0)}(\vartheta) &= a^{-3} (1 - 3\cos^2 \vartheta) = a^{-3} (1 - 3n_z^2) = -\sqrt{\frac{16\pi}{5}} \frac{1}{a^3} Y_{2,0}(\vartheta) \\ F^{(+1)}(\varphi, \vartheta) &= a^{-3} \sin \vartheta \cos \vartheta \exp\{-i\varphi\} = a^{-3} n_z (n_x - in_y) = \sqrt{\frac{8\pi}{15}} \frac{1}{a^3} Y_{2,-1}(\varphi, \vartheta) \\ F^{(-1)}(\varphi, \vartheta) &= a^{-3} \sin \vartheta \cos \vartheta \exp\{+i\varphi\} = a^{-3} n_z (n_x + in_y) = -\sqrt{\frac{8\pi}{15}} \frac{1}{a^3} Y_{2,+1}(\varphi, \vartheta) \\ F^{(+2)}(\varphi, \vartheta) &= a^{-3} \sin^2 \vartheta \exp\{-2i\varphi\} = a^{-3} (n_x - in_y)^2 = \sqrt{\frac{32\pi}{15}} \frac{1}{a^3} Y_{2,-2}(\varphi, \vartheta) \\ F^{(-2)}(\varphi, \vartheta) &= a^{-3} \sin^2 \vartheta \exp\{+2i\varphi\} = a^{-3} (n_x + in_y)^2 = \sqrt{\frac{32\pi}{15}} \frac{1}{a^3} Y_{2,+2}(\varphi, \vartheta) \end{aligned} \quad (6.56)$$

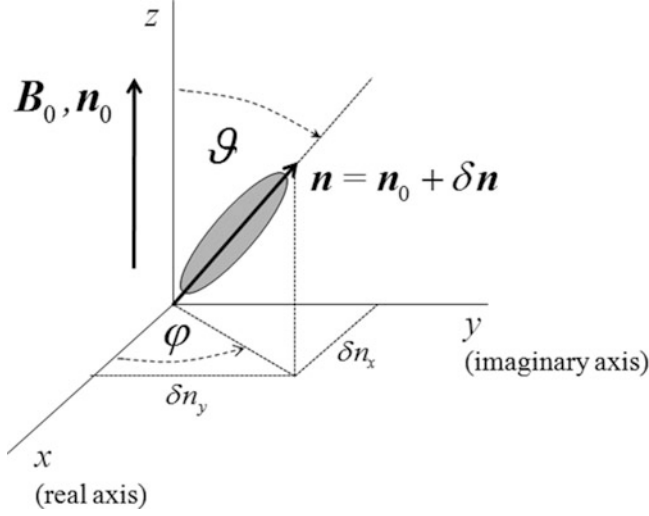


Fig. 6.4 Spherical and Cartesian coordinates of the molecular orientation vector $\mathbf{n} = \mathbf{n}_0 + \delta \mathbf{n}$ relative to the order director $\mathbf{n}_0$ and the external flux density $\mathbf{B}_0$. The *complex plane* is indicated

For the sake of completeness, we have also specified the equivalent representations in terms of second-degree spherical harmonics. Inserting the spin operator terms $\mathcal{O}^{(k)}$ given in Eq. (3.91), the dipolar Hamiltonian Eq. (6.53) can be rewritten on this basis in a form adequate for order-director fluctuations:

$$\begin{aligned}
 \mathcal{H}_d &= \mathcal{H}_d^{\text{secular}} + H_d^{\text{non-secular}} \\
 \mathcal{H}_d^{\text{secular}} &= \frac{\mu_0}{4\pi} (\hbar\gamma)^2 \underbrace{a^{-3}(1 - 3n_z^2)}_{F^{(0)}} \underbrace{\{I_{1z}I_{2z} - 4^{-1}(I_1^+I_2^- + I_1^-I_2^+)\}}_{\mathcal{O}^{(0)}} \\
 \mathcal{H}_d^{\text{non-secular}} &= -\frac{\mu_0}{4\pi} (\hbar\gamma)^2 \left[\underbrace{a^{-3}n_z(n_x - in_y)}_{F^{(+1)}} \underbrace{(3/2)\{I_1^+I_{2z} + I_{1z}I_2^+\}}_{-\mathcal{O}^{(+1)}} + \right. \\
 &\quad \left. \underbrace{a^{-3}(n_x - in_y)^2}_{F^{(+2)}} \underbrace{(3/4)I_1^+I_2^+}_{-\mathcal{O}^{(+2)}} + \text{cc} \right] \quad (6.57)
 \end{aligned}$$

“cc” means *conjugate complex*. The spin raising and lowering operators are defined in Eq. (3.92). In that context, it was shown that spin–lattice relaxation of *like* spins is mediated specifically by *non-secular* terms, so that we can restrict ourselves to the contribution by $\mathcal{H}_d^{\text{non-secular}}$.

For spin–lattice relaxation, merely the fluctuating, that is, time dependent part of the director,

$$\mathbf{n}(t) = \mathbf{n}_0 + \delta \mathbf{n}(t) \quad (6.58)$$

is of interest. Since the mean director $\mathbf{n}_0$ is aligned along $\mathbf{B}_0$ so that $n_{0z} = 1$ and $n_{0x} = n_{0y} = 0$, we can replace the relevant terms in Eq. (6.56) by

$$\begin{aligned} n_z(t) [n_x(t) \pm i n_y(t)] &= n_z(t) [\delta n_x(t) \pm i \delta n_y(t)] \\ [n_x(t) \pm i n_y(t)]^2 &= [\delta n_x(t) \pm i \delta n_y(t)]^2 \end{aligned} \quad (6.59)$$

For small fluctuations $\delta n_x \ll 1$, $\delta n_y \ll 1$ (or equivalently $\vartheta \ll 1$), the z -component, $n_z(t) = \cos \vartheta$, will be of order 1. Neglecting the quadratic fluctuation terms leads to the reduced form of the non-secular dipolar Hamiltonian effective in nematic liquid crystal domains aligned along $\mathbf{B}_0$:

$$\mathcal{H}_d^{\text{non-secular}} \approx -\frac{\mu_0}{4\pi} (\hbar\gamma)^2 \left[\underbrace{a^{-3} n_z (\delta n_x - i \delta n_y)}_{F^{(+1)}} \underbrace{(3/2) \{I_1^+ I_{2z} + I_{1z} I_2^+\}}_{-\mathcal{O}^{(+1)}} \right] + \text{cc} \quad (6.60)$$

This expression contains merely single-quantum spin transition operators whereas the double-quantum terms containing operators $\mathcal{O}^{(\pm 2)}$ are negligible for fluctuations small enough. A discussion of this point and an extension of the formalism for large fluctuations, that is, for higher-order terms, can be found in Ref. [23].

On the time scale of the correlation decay by order-director fluctuations, the limit $\vartheta \ll 1$ will be relevant, so that we can set $n_z(t)n_z(0) \approx 1$. With the definitions

$$\begin{aligned} \delta n_-(t) &\equiv \delta n_x(t) - i \delta n_y(t) \\ \delta n_+(0) &\equiv \delta n_x(0) + i \delta n_y(0) \end{aligned} \quad (6.61)$$

the only (*orientation*) correlation function pertinent in the present context can thus be written as

$$\begin{aligned} G_1(t) &= \langle F^{(1)}(t) F^{(-1)}(0) \rangle = \frac{1}{a^6} \frac{8\pi}{15} \langle Y_{2,-1}(t) Y_{2,+1}(0) \rangle \\ &= \frac{1}{a^3} n_z (\delta n_x - i \delta n_y) \\ &= \frac{1}{a^6} \langle n_z(t) [\delta n_x(t) - i \delta n_y(t)] n_z(0) [\delta n_x(0) + i \delta n_y(0)] \rangle \\ &\approx \frac{1}{a^6} \langle \delta n_-(t) \delta n_+(0) \rangle = \frac{2}{a^6} \langle \delta n_x(t) \delta n_x(0) \rangle \end{aligned} \quad (6.62)$$

where $\alpha = x$ or y . There is no contribution of a correlation function $G_2(t)$ for orders $m = \pm 2$ of spherical harmonics as in ordinary relaxation scenarios (see the discussions in Sects. 3.1.5.7 and 3.1.7). Note furthermore that the relations $\langle \delta n_x(t) \delta n_x(0) \rangle = \langle \delta n_y(t) \delta n_y(0) \rangle$ and $\langle \delta n_x(t) \delta n_y(0) \rangle = \langle \delta n_y(t) \delta n_x(0) \rangle$ are valid in the uniaxial case assumed here. The normalized version of Eq. (6.62) is

$$\mathcal{G}_1(t) = \frac{\langle F^{(+1)}(t)F^{(-1)}(0) \rangle}{\langle |F^{(+1)}|^2 \rangle} = -4\pi \langle Y_{2,+1}(t)Y_{2,-1}(0) \rangle = \frac{\langle \delta n_x(t)\delta n_x(0) \rangle}{\langle (\delta n_x)^2 \rangle} \quad (6.63)$$

(see Eqs. 3.128 and 3.130). In this way, the dipolar NMR correlation function has been expressed in terms of the order-director correlation function $\langle \delta n_x(t)\delta n_x(0) \rangle$.

Inserting Eqs. (6.51) into (6.62) gives

$$G_1(t) = \frac{2}{a^6} \frac{k_B T}{\pi^2 \widehat{K}} \int_{q_1}^{q_h} \exp \left\{ - \left(\frac{\widehat{K}}{\eta} + D \right) q^2 t \right\} dq \quad (6.64)$$

for the dipolar-correlation function and

$$J^{(1)}(\omega) = \frac{4}{a^6} \frac{k_B T}{\pi^2 \widehat{K}} \int_{q_1}^{q_h} dq \int_0^\infty dt \exp \left\{ - \left(\frac{\widehat{K}}{\eta} + D \right) q^2 t \right\} \cos\{\omega t\} \quad (6.65)$$

for the spectral density as the Fourier transform of $G_1(t)$. Substituting this in Eq. (3.138) for a two-spin-1/2-ensemble leads to the following expression for the spin–lattice relaxation rate of uniaxial nematic liquid crystals subjected to collective orientation fluctuations:

$$\frac{1}{T_1} = \frac{9}{2} \left(\frac{\mu_0}{4\pi} \right)^2 \gamma^4 \hbar^2 \frac{1}{a^6} \frac{k_B T}{\pi^2 \widehat{K}} \int_{q_1}^{q_h} dq \int_0^\infty dt \exp \left\{ - \left(\frac{\widehat{K}}{\eta} + D \right) q^2 t \right\} \cos\{\omega t\} \quad (6.66)$$

Neglecting the size of the molecules that is assuming the limit $q_h \rightarrow \infty$ and considering an “infinite” domain size corresponding to the limit $q_1 \rightarrow 0$, the integrals can be evaluated. The angular-frequency dependence of the spin–lattice relaxation rate is then predicted to obey

$$\frac{1}{T_1} = \frac{9}{2^{5/2}} \left(\frac{\mu_0}{4\pi} \right)^2 \gamma^4 \hbar^2 \frac{1}{a^6} \frac{k_B T}{\pi^2 \widehat{K}} \left(\frac{\widehat{K}}{\eta} + D \right)^{-1/2} \omega^{-1/2} \quad (6.67)$$

The characteristic $\omega^{-1/2}$ dispersion predicted by this expression for a range where collective reorientation modes dominate has been verified in several field-cycling NMR relaxometry studies [24–29]. A typical substance showing uniaxial nematic phases is 4-octyl-4'-cyanobiphenyl (8CB). Spin–lattice relaxation data recorded in this system are plotted in Fig. 6.5 in comparison to the isotropic phase. In the latter case, no frequency dependence is observed as expected in the absence of collective orientation fluctuation modes.

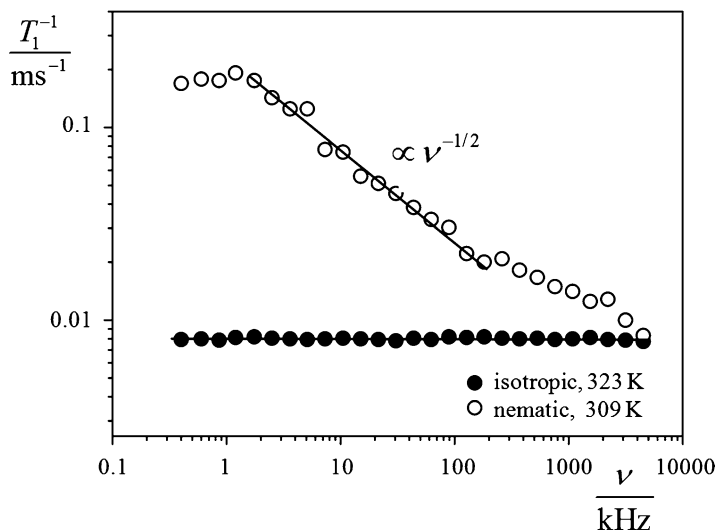


Fig. 6.5 Comparison of the proton spin–lattice relaxation rate T_1^{-1} as a function of the frequency ν in the nematic and in the isotropic phase of 4-octyl-4'-cyanobiphenyl (8CB). The inverse square-root law of the spin–lattice relaxation rate $T_1^{-1} \propto \nu^{-1/2}$ in the nematic phase indicates the dominance of order-director fluctuations as predicted by Eq. (6.67). The deviations at very high and very low frequencies are on the one hand due to local motions (rotational diffusion about the molecular long axis) and reflect the cutoff at long mode wavelengths owing to finite domain sizes, on the other. The isotropic phase does not show any frequency dependence in the experimental window since order-director fluctuations are absent (and local motions are extremely fast) (Reprinted from Ref. [26] with kind permission of © Elsevier 2004)

For the sake of completeness, it should be noted that owing to the different nature of the relevant spectral density functions, the rotating-frame relaxation rate $T_{1\rho}^{-1}$ (compare Eq. 3.154) does not show any perceptible frequency dispersion in the range where Eq. (6.67) for the laboratory-frame spin–lattice relaxation rate applies. The reason for the different dispersion behavior is that T_1 is governed by fluctuations of the spherical harmonic $Y_{2,1}$, whereas $T_{1\rho}$ depends predominantly on $Y_{2,0}$. For small orientational fluctuations, the leading term of an expansion of $Y_{2,0}$ becomes independent of time in contrast to that of the expansion of $Y_{2,1}$. Independence of time on the correlation function level means independence of the frequency of the Fourier conjugate functions. For more details, see Ref. [26].

The fact that the collective reorientational motions by order-director fluctuations are composed of overdamped hydrodynamic modes can also be demonstrated by measuring the spin–lattice relaxation dispersion while sonicating the liquid-crystalline sample intensely and selectively at a certain frequency within the NMR measuring range [27]. A pronounced effect on the spin–lattice relaxation rate can be stated. Remarkably, the influence is distributed over the whole spectrum of ODF modes although the irradiation of the sound was focused on an extremely narrow frequency band. That is, the elastic energy selectively fed into the system is

spontaneously dissipated to all available degrees of motional freedom and therefore to the whole frequency range probed in these experiments. The detailed theory of this phenomenon has been elaborated in Ref. [28].

The result represented by Eq. (6.67) is based on the (for nematic phases adequate) approach that the elastic constants for splay, bend, and twist distortions are more or less the same. This is in contrast to layered structures such as smectic phases and lipid bilayers where the elastic constants tend to be strongly anisotropic. We will come back to scenarios of this sort in Sect. 6.8.

6.6 The Dipolar-Correlation Effect for Nematic Order-Director Fluctuations

A further technique suitable for studies of order and order-director fluctuations is based on the dipolar-correlation effect described in Sect. 3.5 [30]. The basic RF pulse sequence is shown in Fig. 3.36. If necessary, it can be supplemented by 180° pulses in the middle of each τ_1 interval in order to eliminate undesired chemical-shift offset effects as discussed in Ref. [31].

As concerns the time dependence, the normalized ODF correlation function Eq. (6.63) can be identified with the temporal correlation function of the dipolar-modulated resonance frequencies, $\mathcal{G}_\omega(\tau)$. Inserting Eq. (6.51) gives

$$\mathcal{G}_\omega(\tau) = \frac{1}{q_h - q_l} \int_{q_l}^{q_h} \exp \left\{ - \left(\frac{\hat{K}}{\eta} + D \right) q^2 \tau \right\} dq \quad (6.68)$$

where τ is the relevant time variable. The symbols have the same meaning as above: q_h and q_l are the upper and lower cutoff wave numbers, $\hat{K}$ is the elastic constant in the one-constant approximation, η is the effective viscosity, and D is the diffusivity. In the following, we will neglect the limitation by molecular dimensions, so that we can set $q_l \approx 0$. Substituting furthermore the integration variable q by the *normal-mode relaxation time*, Eq. (6.46), $\tau_q = \left[\left(D + \hat{K}/\eta \right) q^2 \right]^{-1}$, converts Eq. (6.68) to

$$\mathcal{G}_\omega(\tau) = \frac{\sqrt{\tau_\ell}}{2} \int_{\tau_\ell}^{\infty} \tau_q^{-3/2} \exp \left\{ - \frac{\tau}{\tau_q} \right\} d\tau_q \quad (6.69)$$

The lower limit of the integration interval, $\tau_\ell = \left(D + \hat{K}/\eta \right)^{-1} q_h^{-2}$, is defined as the shortest mode correlation time. In this context, “shortest” means “shortest *beyond the motional-averaging regime*” as discussed in Sect. 3.5.1: Modes contributing to motional averaging are irrelevant for the dipolar-correlation effect.

Let us now refer to the formalism for the dipolar-correlation effect outlined in Sect. 3.5.4. The temporal correlation function $\bar{G}_d(\tau)$ must be replaced by $\bar{G}_\omega(\tau)$ given in Eq. (6.69), and the correlation time τ_c must correspondingly be substituted by τ_q (Eq. 6.46). The coefficients C_1 and C_2 defined in Eq. (3.401) are renamed as $\hat{C}_1$ and $\hat{C}_2$, respectively, and adopt the new forms

$$\begin{aligned}\hat{C}_1 &= \frac{\sqrt{\tau_\ell}}{2} \int_{\tau_\ell}^{\infty} \sqrt{\tau_q} \left(\exp\left\{-\frac{2\tau_1}{\tau_q}\right\} - 2 \exp\left\{-\frac{\tau_1}{\tau_q}\right\} + 1 \right) \left(1 - \exp\left\{-\frac{\tau_2}{\tau_q}\right\} \right) d\tau_q \\ \hat{C}_2 &= \frac{\sqrt{\tau_\ell}}{2} \int_{\tau_\ell}^{\infty} \sqrt{\tau_q} \left(\exp\left\{-\frac{2\tau_1}{\tau_q}\right\} - 2 \exp\left\{-\frac{\tau_1}{\tau_q}\right\} + 1 \right) \exp\left\{-\frac{\tau_2}{\tau_q}\right\} d\tau_q\end{aligned}\quad (6.70)$$

with the RF pulse intervals τ_1 and τ_2 of the stimulated-echo sequence shown in Fig. 3.36.

On this basis, the dipolar-correlation quotient, Eq. (3.400), adapted to order-director fluctuations is predicted to obey

$$Q_{dc} = \frac{1}{2} \exp\left\{-\frac{1}{4} \langle \delta \bar{\Omega}_d^2 \rangle \hat{C}_1\right\} \left(1 + \cos\{\langle \bar{\Omega}_d \rangle \tau_1\} \exp\left\{-\frac{1}{2} \langle \delta \bar{\Omega}_d^2 \rangle \hat{C}_2\right\} \right) \quad (6.71)$$

$\langle \bar{\Omega}_d \rangle$ is the effective residual dipolar-coupling constant. The average represented by angle brackets refers to the experimental time scale of the RF pulse sequence. $\langle \delta \bar{\Omega}_d^2 \rangle$ is the mean squared fluctuation of the residual dipolar-coupling constant on that time scale. For discussion purposes, the coefficients $\hat{C}_1$ and $\hat{C}_2$ can be rewritten as

$$\begin{aligned}\hat{C}_1 &= \frac{\sqrt{\tau_\ell}}{2} \int_{\tau_\ell}^{\infty} \sqrt{\tau_q} \left(1 - \exp\left\{-\frac{\tau_1}{\tau_q}\right\} \right)^2 \left(1 - \exp\left\{-\frac{\tau_2}{\tau_q}\right\} \right) d\tau_q \\ \hat{C}_2 &= \frac{\sqrt{\tau_\ell}}{2} \int_{\tau_\ell}^{\infty} \sqrt{\tau_q} \left(1 - \exp\left\{-\frac{\tau_1}{\tau_q}\right\} \right)^2 \exp\left\{-\frac{\tau_2}{\tau_q}\right\} d\tau_q\end{aligned}\quad (6.72)$$

The integration variable τ_q can suitably be substituted by $x = \tau_2/\tau_q$ so that

$$\begin{aligned}\hat{C}_1 &= \frac{\tau_2^{3/2} \sqrt{\tau_\ell}}{2} F_1 \\ \hat{C}_2 &= \frac{\tau_2^{3/2} \sqrt{\tau_\ell}}{2} F_2\end{aligned}\quad (6.73)$$

where

$$F_1 = \int_0^{\tau_2/\tau_\ell} x^{-5/2} \left(1 - \exp\left\{-\frac{x\tau_1}{\tau_2}\right\}\right)^2 (1 - \exp\{-x\}) dx$$

$$F_2 = \int_0^{\tau_2/\tau_\ell} x^{-5/2} \left(1 - \exp\left\{-\frac{x\tau_1}{\tau_2}\right\}\right)^2 \exp\{-x\} dx$$
(6.74)

A typical experimental situation is characterized by the limit $\tau_1 \ll \tau_2$ for the RF pulse intervals (see Fig. 3.36). The integral represented by F_2 converges already when x approaches a value of the order 1. We may therefore assume $x\tau_1/\tau_2 \ll 1$. Let us now consider a number of special cases in the frame of this limit.

If $\tau_1 \ll \tau_2 \ll \tau_\ell$, the functions F_1 and F_2 in Eq. (6.74) can be approximated by

$$F_1 \approx \left(\frac{\tau_1}{\tau_2}\right)^2 \int_0^{\tau_2/\tau_\ell} x^{1/2} dx = \frac{2}{3} \tau_1^2 \tau_2^{-1/2} \tau_\ell^{-3/2}$$

$$F_2 \approx \left(\frac{\tau_1}{\tau_2}\right)^2 \int_0^{\tau_2/\tau_\ell} x^{-1/2} dx = 2 \tau_1^2 \tau_2^{-3/2} \tau_\ell^{-1/2}$$
(6.75)

where we have used the lowest-order approximations

$$e^{-x} \approx 1; \quad 1 - e^{-x} \approx x; \quad \left(1 - e^{-x\tau_1/\tau_2}\right)^2 \approx \left(\frac{\tau_1}{\tau_2}\right)^2 x^2$$
(6.76)

The dipolar-correlation quotient thus becomes

$$Q_{dc} \approx \frac{1}{2} \exp\left\{-\frac{1}{4} \langle \delta \bar{\Omega}_d^2 \rangle \frac{\tau_2 \tau_1^2}{3 \tau_\ell}\right\} \left(1 + \cos\{\langle \bar{\Omega}_d \rangle \tau_1\} \exp\left\{-\frac{1}{2} \langle \delta \bar{\Omega}_d^2 \rangle \tau_1^2\right\}\right)$$
(6.77)

On the other hand, if $\tau_1 \ll \tau_\ell \ll \tau_2$, the functions F_1 and F_2 can be represented on the same level of approximation by

$$F_1 \approx \left(\frac{\tau_1}{\tau_2}\right)^2 \int_0^{\tau_2/\tau_\ell} x^{-1/2} (1 - e^{-x}) dx \approx \left(\frac{\tau_1}{\tau_2}\right)^2 \left(2\sqrt{\frac{\tau_2}{\tau_\ell}} - \sqrt{\pi}\right)$$

$$F_2 \approx \left(\frac{\tau_1}{\tau_2}\right)^2 \int_0^\infty x^{-1/2} e^{-x} dx = \sqrt{\pi} \left(\frac{\tau_1}{\tau_2}\right)^2$$
(6.78)

The upper integration boundary has been replaced by ∞ in all cases where the integrand implies an exponentially decaying factor. On this basis, the dipolar-correlation quotient for order-director fluctuations can be approximated by

$$Q_{dc} \approx \frac{1}{2} \exp \left\{ -\frac{1}{4} \langle \delta \bar{\Omega}_d^2 \rangle \tau_1^2 \left(1 - \frac{1}{2} \sqrt{\frac{\pi \tau_\ell}{\tau_2}} \right) \right\} \\ \times \left(1 + \cos \{ \langle \bar{\Omega}_d \rangle \tau_1 \} \exp \left\{ -\frac{1}{4} \langle \delta \bar{\Omega}_d^2 \rangle \tau_1^2 \sqrt{\frac{\pi \tau_\ell}{\tau_2}} \right\} \right) \quad (6.79)$$

Finally, in the case $\tau_\ell \ll \tau_1 \ll \tau_2$, the functions F_1 and F_2 take the approximate forms

$$F_1 \approx \int_0^\infty x^{-5/2} \left(1 - e^{-x \tau_1 / \tau_2} \right)^2 (1 - e^{-x}) dx \approx \frac{8}{3} \sqrt{\pi} (\sqrt{2} - 1) \left(\frac{\tau_1}{\tau_2} \right)^{3/2} - \sqrt{\pi} \left(\frac{\tau_1}{\tau_2} \right)^2 \\ F_2 \approx \left(\frac{\tau_1}{\tau_2} \right)^2 \int_0^\infty x^{-1/2} e^{-x} dx = \sqrt{\pi} \left(\frac{\tau_1}{\tau_2} \right)^2 \quad (6.80)$$

With these relations, the dipolar-correlation quotient adopts the form

$$Q_{dc} \approx \frac{1}{2} \exp \left\{ -\frac{1}{4} \langle \delta \bar{\Omega}_d^2 \rangle \tau_1^2 \left(\sqrt{\frac{\tau_\ell}{\tau_1}} - \frac{1}{2} \sqrt{\frac{\pi \tau_\ell}{\tau_2}} \right) \right\} \\ \times \left(1 + \cos \{ \langle \bar{\Omega}_d \rangle \tau_1 \} \exp \left\{ -\frac{1}{4} \langle \delta \bar{\Omega}_d^2 \rangle \tau_1^2 \sqrt{\frac{\pi \tau_\ell}{\tau_2}} \right\} \right) \quad (6.81)$$

In macroscopically ordered systems, the term $\cos \{ \langle \bar{\Omega}_d \rangle \tau_1 \}$ in the above equations for the dipolar-correlation quotient has a finite value [30]. The consequence is that the dipolar-correlation quotient is undulated with the angular frequency $\langle \bar{\Omega}_d \rangle$ as a function of the RF pulse spacing τ_1 . In simple cases, that is, if dipolar coupling is determined by a distinct dipole–dipole distance a , and if the director is aligned preferentially along the external magnetic field, the effective residual dipolar-coupling constant is directly related to the order parameter S_{or} , Eq. (6.3), according to

$$\langle \bar{\Omega}_d \rangle = -\frac{3\mu_0 \gamma^2 \hbar}{8\pi a^3} \langle 3\cos^2 \vartheta - 1 \rangle = -\frac{3\mu_0 \gamma^2 \hbar}{4\pi a^3} S_{or} \quad (6.82)$$

Figure 6.6 shows dipolar-correlation quotient data of 4'-*n*-pentyl-4-cyanobiphenyl (5CB), a typical liquid-crystalline material exhibiting a nematic phase. The data are plotted as a function of the first pulse spacing τ_1 with the second pulse spacing τ_2 as a curve parameter. The order in the nematic phase reveals itself as a pronounced modulation pattern.

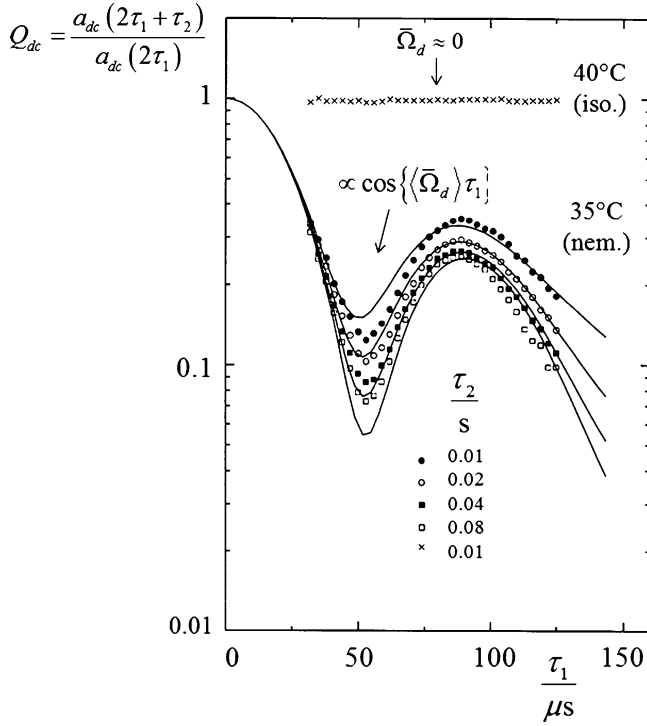


Fig. 6.6 Dipolar-correlation quotient $Q_{dc} = a_{dc}(2\tau_1 + \tau_2)/a_{dc}(2\tau_1)$ (see Eq. 3.388) of 4'-n-pentyl-4-cyanobiphenyl (5CB) as a function of the first RF pulse interval τ_1 of the stimulated-echo sequence depicted in Fig. 3.36. The data were measured in the nematic and the isotropic phases at 35 and 40°C, respectively. The curve parameter is the second RF pulse interval τ_2 . In the isotropic phase, motional-averaging levels the dipolar-coupling constant almost completely. There is no residual dipolar coupling, $\bar{\Omega}_d \approx 0$, so that no perceptible dependence on τ_1 arises: $Q_{dc} \approx 1$. In this case, the signals correspond to ordinary spin echoes as described in Sect. 3.2.2 (in the absence of field gradient pulses). By contrast, the nematic phase is characterized by a strong undulation of the τ_1 dependence of Q_{dc} . The undulations reflect the effective residual dipolar-coupling and order term $\cos\{\langle\bar{\Omega}_d\rangle\tau_1\}$ indicative for macroscopic order. The *solid lines* represent a least-square fit of Eq. (6.79) valid in the limit $\tau_1 \ll \tau_\ell \ll \tau_2$. The shortest mode correlation time accessible in these experiments was fitted to be 3.9 ms. In reality much faster processes occur, of course. However, these are subject to motional averaging and do not contribute to the dipolar-correlation effect (Reprinted from Ref. [30] with kind permission of © AIP 1995)

In the above analysis, we have anticipated that the order director is aligned along the magnetic flux density so that there is no distribution of director orientations within the sample. This assumption is certainly justified for the experimental example represented by Fig. 6.6. In cases, where the orientation of the (local) director is determined by random surfaces or other distortions, things are different: The echo signals will then be superpositions of contributions from different director orientations. That is, the angle α in Eq. (3.361) and consequently the effective residual dipolar-coupling constant $\langle\bar{\Omega}_d\rangle$ will be distributed over a certain range. We are thus dealing with powder averages. This in particular refers to the cosine term in the expressions for the dipolar-correlation quotient. If the distribution is completely

random, the powder average vanishes due to destructive superposition, $\langle \cos \{ \langle \hat{\Omega}_d \rangle \tau_1 \} \rangle_{\text{powder}} \approx 0$. It will then not be possible to observe order-based undulations of experimental data.

Notabene, the absence of the modulation phenomenon on these grounds must not be confused with motional averaging (as it is relevant for the isotropic-phase data of 5CB plotted in Fig. 6.6). Even in a disordered amorphous solid, that is, if molecular motions are completely frozen in, no undulation of this sort would appear. Powder averaging of order undulations can be demonstrated in liquid crystals confined in mesoscopic porous glasses as studied in Ref. [32]. Depending on the pore size, the director tends to be oriented by the local surface rather than by the magnetic field. On a mesoscopic length scale, the liquid crystal may still be ordered, but macroscopically it forms a disordered system so that the powder average tends to vanish. As a further consequence of the confinement, the distribution of director fluctuation modes is restricted to the pore size in contrast to bulk samples [32]. That is, the distribution in Eq. (6.69) will be truncated correspondingly.

6.7 Dynamic Light Scattering in Nematic Liquid Crystals

6.7.1 The Scattering Mechanism Dominating in Liquid Crystals

As outlined in Sect. 3.7, dynamic light scattering is caused by the local electric polarization oscillating under the influence of the electric field of the incident light. The amplitudes of the polarization, $\hat{\mathbf{P}}(\mathbf{R}, t)$, and of the incident electric field, $\hat{\mathbf{E}}(\mathbf{R})$, effective in the sample material are related as

$$\hat{\mathbf{P}}(\mathbf{R}, t) = \varepsilon_0 \chi_e(\mathbf{R}, t) \hat{\mathbf{E}}(\mathbf{R}) \quad (6.83)$$

in analogy to Eq. (3.458). $\chi_e(\mathbf{R}, t)$ is the locally fluctuating electric susceptibility tensor for optical frequencies, and ε_0 is the electric field constant. Since we are referring to amplitudes, the time dependences in Eq. (6.83) exclusively originate from the fluctuating susceptibility tensor. This expression can alternatively be expressed in terms of the relative dielectric tensor

$$\underline{\varepsilon}_r = \underline{u} + \chi_e \quad (6.84)$$

where $\underline{u}$ is the unit tensor. The fluctuating part is in both cases the same and reflects varying optical properties in the material as a consequence of thermal excitations.

The light deflected by scattering thus fluctuates because of spatial as well as temporal fluctuations of the susceptibility tensor. The amplitude of the electric field strength of the scattered light obeys the proportionality

$$\hat{\mathbf{E}}'(\mathbf{R}, t) \propto \hat{\mathbf{P}}(\mathbf{R}, t) = \varepsilon_0 \chi_e(\mathbf{R}, t) \hat{\mathbf{E}}(\mathbf{R}) \quad (6.85)$$

Owing to the second-rank tensor property of χ_e , the wave polarization⁷ of the scattered light will be different from that of the incident light.

The fact that we are using the tensor version of the susceptibility instead of the scalar quantity employed in Eq. (3.458) indicates the crucial difference between light scattering in isotropic liquids (as considered in Sect. 3.7) and in ordered liquid-crystalline phases: The reason for scattering in nematic phases is not so much fluctuation of the density. The dominating source is rather *collective fluctuations of the orientation of anisotropic molecules* [33]. Experimentally, this origin of light scattering reveals itself by a pronounced angular distribution and rotated wave polarizations.

To account for the cylinder-symmetric tensor properties of the susceptibility in uniaxial nematics, it is favorable to refer to the (director-fixed) principal-axes representation

$$\chi_e = \begin{pmatrix} \chi_{e,\perp} & 0 & 0 \\ 0 & \chi_{e,\perp} & 0 \\ 0 & 0 & \chi_{e,\parallel} \end{pmatrix} \quad (6.86)$$

where $\chi_{e,\perp}$ concerns field directions perpendicular to the director $\mathbf{n}$, that is, the long (and symmetry) axis of the molecules, and $\chi_{e,\parallel}$ accounts for the parallel case. The anisotropy of the electric susceptibility is characterized by $\Delta\chi_e$ as defined in Eq. (6.16).

The *orientation* of the local susceptibility tensor fluctuates as a consequence of the dynamics of the order director. According to Eqs. (6.38) and (6.47), the components of the normal coordinates are given by

$$\begin{aligned} n_x(\mathbf{R}, t) &= \sum_q \tilde{n}_x(\mathbf{q}, t) \exp\{i\mathbf{q} \cdot \mathbf{R}\} \\ n_y(\mathbf{R}, t) &= \sum_q \tilde{n}_y(\mathbf{q}, t) \exp\{i\mathbf{q} \cdot \mathbf{R}\} \end{aligned} \quad (6.87)$$

The Fourier conjugates of these relations are

$$\begin{aligned} \tilde{n}_x(\mathbf{q}, t) &= \frac{1}{V} \int_{\text{vol}} n_x(\mathbf{R}, t) \exp\{-i\mathbf{q} \cdot \mathbf{R}\} d^3R \\ \tilde{n}_y(\mathbf{q}, t) &= \frac{1}{V} \int_{\text{vol}} n_y(\mathbf{R}, t) \exp\{-i\mathbf{q} \cdot \mathbf{R}\} d^3R \end{aligned} \quad (6.88)$$

where V is the sample volume.

⁷ Note that we distinguish between *electric polarization* $\hat{\mathbf{P}}$ and *wave polarization*. The latter is defined by the orientation of the electric field vector $\hat{\mathbf{E}}$.

In contrast to the one-constant approximation assumed for the NMR applications above, we will now distinguish all three Frank elastic constants $\hat{K}_1$ (splay), $\hat{K}_2$ (twist), and $\hat{K}_3$ (bend). The square derivative terms in the Frank/Oseen free energy Eq. (6.28),

$$A_{H,\text{elast}} = \frac{1}{2} \int_{\text{Vol}} \left\{ \hat{K}_1 \left(\frac{\partial n_x}{\partial x} + \frac{\partial n_y}{\partial y} \right)^2 + \hat{K}_2 \left(\frac{\partial n_x}{\partial y} - \frac{\partial n_y}{\partial x} \right)^2 + \hat{K}_3 \left[\left(\frac{\partial n_x}{\partial z} \right)^2 + \left(\frac{\partial n_y}{\partial z} \right)^2 \right] \right\} d^3R \quad (6.89)$$

can be evaluated with the aid of the Fourier relations given in Eq. (6.87). For example

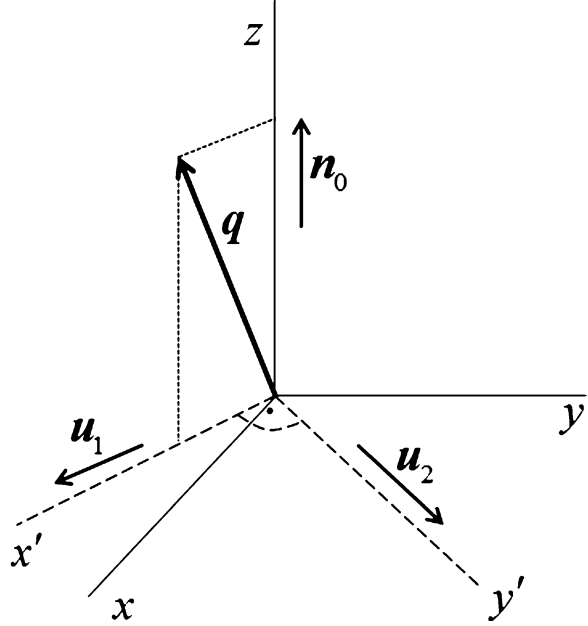
$$\begin{aligned} \int_{\text{vol}} \frac{\partial n_x}{\partial x} \frac{\partial n_x^*}{\partial x} d^3R &= \int_{\text{vol}} \sum_{\mathbf{q}} \sum_{\mathbf{q}'} \tilde{n}_x(\mathbf{q}) \tilde{n}_x^*(\mathbf{q}') q_x q'_x \exp\{i(\mathbf{q} - \mathbf{q}') \cdot \mathbf{R}\} d^3R \\ &= V \sum_{\mathbf{q}} |\tilde{n}_x(\mathbf{q})|^2 q_x^2 \\ \int_{\text{vol}} \frac{\partial n_x}{\partial x} \frac{\partial n_y^*}{\partial y} d^3R &= \int_{\text{vol}} \sum_{\mathbf{q}} \sum_{\mathbf{q}'} \tilde{n}_x(\mathbf{q}) \tilde{n}_y^*(\mathbf{q}') q_x q'_y \exp\{i(\mathbf{q} - \mathbf{q}') \cdot \mathbf{R}\} d^3R \\ &= V \sum_{\mathbf{q}} \sum_{\mathbf{q}'} \tilde{n}_x(\mathbf{q}) \tilde{n}_y^*(\mathbf{q}') q_x q_y \end{aligned} \quad (6.90)$$

etc. The two factors into which the squares in the integrals in Eq. (6.89) can be split are discriminated by different wave-vector symbols $\mathbf{q}$ and $\mathbf{q}'$. The integrals vanish for $\mathbf{q} \neq \mathbf{q}'$. The second relation in Eq. (6.90) indicates that x and y mode components are mixed in this representation, in contrast to the z -component which remains independent of both transverse contributions. This problem can be remedied by the coordinate transformation to be described in the following section.

6.7.2 Eigenmodes of Order-Director Fluctuations for Different Frank Elastic Constants

For the further treatment, we choose the reference frame depicted in Fig. 6.7. It permits us to describe order-director fluctuations by two independent eigenmodes of the director fluctuations [34]. The z -axis of the new, $\mathbf{q}$ -specific reference frame is again aligned along $\mathbf{n}_0$. The transverse axes, x' , y' , are rotated about the z -axis in such a way that the wave vector $\mathbf{q}$ is coplanar to the plane spanned by the new x' -axis and the z -axis. The directions of the x' - and y' -axes are defined by the unit vectors $\mathbf{u}_1$ and $\mathbf{u}_2$, respectively. Relative to this frame, the components of the vector $\mathbf{q}$ are $q_{x'} \equiv q_{\perp}$, $q_{y'} = 0$, and $q_{z'} \equiv q_{\parallel}$.

Fig. 6.7 Reference frame x', y' for decoupled eigenmodes $\delta\tilde{n}_1(\mathbf{q}), \delta\tilde{n}_2(\mathbf{q})$



The transverse components of $\tilde{n}(\mathbf{q}, t)$ relative to the new frame, that is, the eigenmodes $\tilde{n}_{x'}(\mathbf{q}, t) \equiv \delta\tilde{n}_1(\mathbf{q}, t)$ and $\tilde{n}_{y'}(\mathbf{q}, t) \equiv \delta\tilde{n}_2(\mathbf{q}, t)$, are aligned along the unit vectors $\mathbf{u}_1$ and $\mathbf{u}_2$, respectively, so that

$$\delta\tilde{n}(\mathbf{q}, t) = \delta\tilde{n}_1(\mathbf{q}, t)\mathbf{u}_1 + \delta\tilde{n}_2(\mathbf{q}, t)\mathbf{u}_2 \quad (6.91)$$

With the identities $\tilde{n}_{x'}(\mathbf{q}, t) \equiv \delta\tilde{n}_1(\mathbf{q}, t)$ and $\tilde{n}_{y'}(\mathbf{q}, t) \equiv \delta\tilde{n}_2(\mathbf{q}, t)$, the Frank/Oseen free energy takes the form

$$A_{\text{H,elast}} = \frac{1}{2} V \sum_{\mathbf{q}} \left[|\delta\tilde{n}_1(\mathbf{q})|^2 (\hat{K}_1 q_{\perp}^2 + \hat{K}_3 q_{\parallel}^2) + |\delta\tilde{n}_2(\mathbf{q})|^2 (\hat{K}_2 q_{\perp}^2 + \hat{K}_3 q_{\parallel}^2) \right] \quad (6.92)$$

Equation (6.92) tells us that the two eigenmodes contribute *independently* to the elastic energy. The eigenmode $\delta\tilde{n}_1(\mathbf{q}, t)$ undulates along the x' -axis with the unit vector $\mathbf{u}_1$ in the $(\mathbf{n}_0, \mathbf{q})$ plane. It entails a combination of splay and bend deformations with an effective elastic constant composed of the Frank constants $\hat{K}_1$ and $\hat{K}_3$. On the other hand, the eigenmode $\delta\tilde{n}_2(\mathbf{q}, t)$ varying along the unit vector $\mathbf{u}_2$ in the plane $(\mathbf{n}_0, \mathbf{u}_2)$ normal to $(\mathbf{n}_0, \mathbf{q})$ concerns twist and bend deformations so that the effective elastic constant implies the Frank constants $\hat{K}_2$ and $\hat{K}_3$.

In terms of eigenmodes, the correlation function of normal coordinates, Eq. (6.42), can be split into two independent contributions according to

$$\begin{aligned}
c(\mathbf{q}, t) &= \langle \delta \tilde{\mathbf{n}}(\mathbf{q}, t) \cdot \delta \tilde{\mathbf{n}}^*(\mathbf{q}, 0) \rangle \\
&= \langle \delta \tilde{n}_1(\mathbf{q}, t) \delta \tilde{n}_1^*(\mathbf{q}, 0) \rangle + \langle \delta \tilde{n}_2(\mathbf{q}, t) \delta \tilde{n}_2^*(\mathbf{q}, 0) \rangle
\end{aligned} \tag{6.93}$$

The eigenmode correlation functions $\langle \delta \tilde{n}_1(\mathbf{q}, t) \delta \tilde{n}_1^*(\mathbf{q}, 0) \rangle$ and $\langle \delta \tilde{n}_2(\mathbf{q}, t) \delta \tilde{n}_2^*(\mathbf{q}, 0) \rangle$ can be derived analogous to the treatment outlined in Sect. 6.4. In particular, the independent character of the two eigenmodes permits us to establish two independent equations of motion analogous to Eq. (6.43) but modified with respect to the effective elastic constants and viscosity parameters. The solutions are the eigenmode correlation functions

$$\langle \delta \tilde{n}_1(\mathbf{q}, t) \delta \tilde{n}_1^*(\mathbf{q}, 0) \rangle = \langle |\delta \tilde{n}_1(\mathbf{q})|^2 \rangle \exp \left\{ -\frac{t}{\tau_q^{(1)}} \right\} \tag{6.94}$$

and

$$\langle \delta \tilde{n}_2(\mathbf{q}, t) \delta \tilde{n}_2^*(\mathbf{q}, 0) \rangle = \langle |\delta \tilde{n}_2(\mathbf{q})|^2 \rangle \exp \left\{ -\frac{t}{\tau_q^{(2)}} \right\} \tag{6.95}$$

The mean square fluctuations can be derived on the basis of the equipartition theorem as already utilized in the context of Eq. (6.49). The results are

$$\langle |\delta \tilde{n}_1(\mathbf{q})|^2 \rangle = \frac{k_B T}{V(\bar{K}_1 q_\perp^2 + \bar{K}_3 q_\parallel^2)}; \quad \langle |\delta \tilde{n}_2(\mathbf{q})|^2 \rangle = \frac{k_B T}{V(\bar{K}_2 q_\perp^2 + \bar{K}_3 q_\parallel^2)} \tag{6.96}$$

Likewise, the mode relaxation times given in Eq. (6.46) for the one-constant approximation are now converted to the eigenmode relaxation times

$$\tau_q^{(1)} = \frac{\eta_q^{(1)}}{\bar{K}_1 q_\perp^2 + \bar{K}_3 q_\parallel^2}; \quad \tau_q^{(2)} = \frac{\eta_q^{(2)}}{\bar{K}_2 q_\perp^2 + \bar{K}_3 q_\parallel^2} \tag{6.97}$$

where $\eta_q^{(1)}$ and $\eta_q^{(2)}$ are wave-number dependent viscosities effective for the two eigenmodes (for details, e.g., see Ref. [34]). Note that we have omitted the self-diffusion coefficient D in this expression in contrast to Eq. (6.46). The reason is that light scattering is caused by entities much larger than molecular-length scales. Translational diffusion is therefore not expected to affect the scattering correlation functions perceptibly (in contrast to the NMR applications described above).

6.7.3 First- and Second-Order Correlation Functions

The primary quantity acquired in dynamic light-scattering experiments is the second-order correlation function

$$G_2(\tau) \equiv \frac{\langle I'(\mathbf{q}_s, t + \tau) I'(\mathbf{q}_s, t) \rangle}{\langle I'(\mathbf{q}_s, t) \rangle^2} \quad (6.98)$$

formed by a digital autocorrelator from the fluctuating intensity $I'(\mathbf{q}_s, t)$ of the scattered light at two different instants. The scattering vector $\mathbf{q}_s = \mathbf{k} - \mathbf{k}'$ is the difference of the wave vectors of the incident and the scattered light, $\mathbf{k}$ and $\mathbf{k}'$, respectively (see Eq. 3.467). The second-order correlation function is linked to the first-order correlation function,

$$G_1(\tau) \equiv \frac{\langle \tilde{E}'(\mathbf{q}_s, t + \tau) \tilde{E}'^*(\mathbf{q}_s, t) \rangle}{\langle |\tilde{E}'(\mathbf{q}_s, t)|^2 \rangle} \quad (6.99)$$

via the Siegert relation Eq. (3.489), $G_2(\tau) = 1 + [G_1(\tau)]^2$. The intensity $I'(\mathbf{q}_s, t)$ of the scattered light is related to the electric field $\tilde{E}'(\mathbf{q}_s, t)$ according to $I'(\mathbf{q}_s, t) \propto |\tilde{E}'(\mathbf{q}_s, t)|^2$, where $\tilde{E}'(\mathbf{q}_s, t)$ is the spatial Fourier transform of the amplitude of the scattered light, $\hat{E}'(\mathbf{R}, t)$.

The electric field amplitude arriving at the detector depends on three conditions apart from the geometric setup of the experiment: (1) According to Eq. (6.16), the amplitudes $\hat{E}'(\mathbf{R}, t)$ and $\hat{\mathbf{P}}(\mathbf{R}, t)$ are proportional to each other. Large polarization amplitudes cause large scattered light amplitudes, and large fluctuations of the electric polarization stipulate large fluctuations of the secondary waves. The maximum scattering effect will be determined by the anisotropy of the susceptibility $\Delta\chi_e$. The electric polarization fluctuates owing to reorientations of the susceptibility tensor, and this in turn fluctuates as a consequence of the order-director eigenmodes. Therefore, intimate relationships among the temporal correlation functions of the amplitudes of light and electric polarization, on the one hand, and the eigenmode correlation function Eq. (6.93), on the other, can be expected. (2) The condition for finite intensities of scattered light at the detector far away from the sample is that the scattering vector $\mathbf{q}_s = \mathbf{k} - \mathbf{k}'$ matches the wave vector of the eigenmodes:

$$\mathbf{q} = \mathbf{q}_s \quad (6.100)$$

In the following, the symbol $\mathbf{q}$ can therefore be used homonymously for either quantity. (3) The light-wave polarizations before and after scattering must be taken into account. Light-scattering experiments are usually carried out with a polarizer in the incident beam and an analyzer before the detector. Let the wave polarization direction of the polarizer be characterized by the unit vector $\mathbf{i}$ and that of the analyzer by the unit vector $\mathbf{f}$. Only light components matching both directions will then contribute to the intensity acquired in the detector [33, 35].

The resulting second-order correlation function

$$G_2(\tau) = 1 + C \sum_{\alpha=1,2} \frac{[(\mathbf{i} \cdot \mathbf{u}_\alpha) f_{\parallel} + i_{\parallel}(\mathbf{f} \cdot \mathbf{u}_\alpha)]^2}{\hat{K}_\alpha q_{\perp} + \hat{K}_3 q_{\parallel}} \exp\left\{-\frac{t}{\tau_q^{(\alpha)}}\right\} \quad (6.101)$$

depends on the eigenmode relaxation functions Eqs. (6.94) and (6.95) in the expected way [34, 36, 37]. C is a constant implying the anisotropy $\Delta\chi_e$ of the electric susceptibility tensor. $\mathbf{u}_\alpha$ represents the two unit vectors defined in Fig. 6.7. $f_{\parallel}$ and $i_{\parallel}$ are the components of $\mathbf{f}$ and $\mathbf{i}$, respectively, along the z -axis, that is, along the equilibrium director $\mathbf{n}_0$. In this way, the dynamic features of order-director fluctuations reveal themselves via the exponential decay functions with the mode relaxation times $\tau_q^{(\alpha)}$ as time constants (Eq. 6.97). Typical experimental data exemplifying this formalism can be found in Refs. [38, 39].

6.8 Spin Relaxation in Smectic Liquid Crystals and Lamellar Systems

6.8.1 Collective Fluctuations in Smectic Liquid Crystals

Typical representatives of this class of layered molecular order are smectic-A phases and lipid bilayers. The structure of such systems stipulates that the Frank elastic constants strongly deviate from each other. Unlike the treatment of spin–lattice relaxation in nematic liquid crystals, the one-constant approximation will be totally inappropriate. We are now dealing with pseudo two-dimensional systems where bending deformations are suppressed. The usual approach is in this case the limit $\hat{K}_3 \ll \hat{K}_1 \approx \hat{K}_2$ for the Frank elastic constants. That is, the dominating contributions to order fluctuations are splay and twist deformations. Modifying the theory in Sect. 6.5 accordingly leads to a *linear* frequency dependence of the spin–lattice relaxation time [15, 40–43]

$$T_1(\omega) \propto \omega \quad (6.102)$$

in contrast to the square-root frequency dependence predicted in Eq. (6.67) for nematic liquid crystals. Experimental data supporting Eq. (6.102) can be found in Ref. [25], for instance. As in the nematic case, the frequency range where this law applies is limited by the dimensions of the molecules on the one hand and of the liquid-crystalline domains on the other.

A further reduction of the elastic constants effective for order-director fluctuations is expected for uni-lamellar systems such as lipid bilayers, where no elastic coupling between different layers exists. The Helmholtz free energy will then be governed solely by the splay elastic term with the Frank constant $\hat{K}_1$. Hydrodynamic modes are accordingly restricted to the plane of the lamellae. Wave vectors perpendicular to that

plane vanish. In this case, the spin–lattice relaxation rate originating from order-director fluctuations is predicted to obey [44]

$$\frac{1}{T_1} \propto S_{\text{or}}^2 \frac{k_B T}{\hat{K}_1} \frac{1}{\omega} \quad (6.103)$$

The quantity S_{or} is the order parameter defined in Eq. (6.3). Experimental field-cycling NMR relaxometry data [45] recorded in phospholipid membranes are in accordance with the frequency dependence predicted by this relation.

This particular spin–lattice relaxation dispersion is relevant on a frequency scale where order-director fluctuations dominate. In principle, the range of validity is enframed by local molecular processes governing spin–lattice relaxation at high frequencies and by a cutoff at low frequencies due to the finite size and the curvature of the molecular layers. Apart from the latter restriction, experimental artifacts at low frequencies may conceal the dispersion behavior inherent to Eqs. (6.102) or (6.103). This problem arises if field-cycling NMR relaxometry experiments are carried out without taking care of the adiabatic condition for the crossover from the high-field limit, where the external magnetic field dominates, to the low-field case governed by local fields due to secular spin interactions. A discussion can be found in Ref. [29].

6.8.2 Distinction of Local and Collective Molecular Motions

Typical representatives of amphiphilic molecular species forming bilayers in aqueous environments are di-palmitoyl and di-myristoyl lecithin. These molecules consist on the one hand of polar headgroups forming the interface layer to the surrounding water and, on the other hand, of fatty acid residues with 16 and 14 carbon groups, respectively. A schematic representation of lipid bilayers and the alkane chain part formed by the fatty acid residues is depicted in Fig. 2.10. Since alkane chains form the largest part of lipids, we will refer specifically to this section of the bilayers when speaking of local motions in the present context. An experimental analysis of the NMR signals arising from the fatty acid residues, the polar headgroups, and the water phase has been reported in Ref. [46].

For protons, the relaxation mechanism is predominantly due to intramolecular dipolar interaction. Intermolecular contributions tend to be negligible at short times as argued for the similar scenario of polymer dynamics in Ref. [47]. Spin–lattice relaxation thus reflects the time evolution of intramolecular dipolar-correlation functions for two essentially independent processes, namely, $G_{\text{loc}}(t)$ describing *local*, intramolecular processes and $G_{\text{ODF}}(t)$ representing *collective* order-director fluctuations. Unlike ordinary nematic and smectic-A liquid crystals consisting mainly of rigid mesogenic groups, there is significant internal mobility in lipid bilayers due to fluctuating rotational isomerism. The dynamic behavior is correspondingly complex.

The partial correlation functions $G_{\text{loc}}(t)$ and $G_{\text{ODF}}(t)$ are adequately interpreted as probabilities that the fluctuation events leading to loss of correlation have *not yet* taken place in a time t . The total correlation function can consequently be formed as the product

$$G(t) = G_{\text{loc}}(t)G_{\text{ODF}}(t) \quad (6.104)$$

expressing the probability that neither local nor collective reorientations have yet taken place. The (anisotropic and restricted) correlation function for local motions can be split into two terms according to

$$G_{\text{loc}}(t) = G_{\text{loc}}^{\text{red}}(t) + G_{\text{loc}}(\infty) \quad (6.105)$$

$G_{\text{loc}}(\infty) = \text{const}$ is the residual correlation retained *after* the system has experienced local fluctuations over a long time. This quantity thus reflects the anisotropy of local dynamics. $G_{\text{loc}}^{\text{red}}(t)$ is the reduced correlation function representing the dynamic characteristics local motions.

Since order-director fluctuations as a collective phenomenon are much slower than local motions of individual alkane chains, we can assume that $G_{\text{ODF}}(t) \approx G_{\text{ODF}}(0)$ on the time scale on which the reduced correlation function $G_{\text{loc}}^{\text{red}}(t)$ decays to zero. That is, the total correlation function can be expressed in the *different-time-scale limit* as

$$G(t) \approx G_{\text{loc}}^{\text{red}}(t)G_{\text{ODF}}(0) + G_{\text{loc}}(\infty)G_{\text{ODF}}(t) \quad (6.106)$$

The effective relaxation rate consequently results as a sum of two terms

$$\frac{1}{T_1} \approx \frac{a_{\text{loc}}}{T_1^{\text{loc}}} + \frac{a_{\text{ODF}}}{T_1^{\text{ODF}}} \quad (6.107)$$

where a_{loc} and a_{ODF} are constants weighting the relative contribution of either process. T_1^{loc} and T_1^{ODF} would be the spin–lattice relaxation times for the two processes *in the absence* of the other motional component. In fact, the crossover of spin–lattice relaxation from (fast) local to (slow) collective molecular motions predicted by Eq. (6.107) was experimentally demonstrated in Refs. [45, 48] for lipid bilayers.

In this context, a word of caution may be appropriate. The above sum of weighted relaxation rates for the two contributing dynamic processes assumed here is not of general validity. In the literature of spin relaxation in liquid crystals and similar systems, interpretations by such sums of relaxation rates are sometimes attempted, where the relaxation rates are thought to represent different dynamic model mechanisms simultaneously acting on the spins. This cannot be done without further reasoning. It is most important to note that sums like that in Eq. (6.107) make only sense if the different-time-scale limit is warranted. The correlation

function for superimposed dynamic processes is primarily a *product* (see Eq. 6.104) rather than a *sum* of partial correlation functions. If the different-time-scale limit does not apply, the correlation function cannot be analyzed in the sense of Eq. (6.106).

The subject discussed above is also an example of the problem already addressed in Sect. 1.1.4: Local motions must be distinguished from the collective modes revealing themselves as the system-specific long-time tail of the orientation correlation function. In analogous form, this complex of problems implies dynamics of polymers (see Sect. 5.4.7) and reorientational fluctuations of adsorbate molecules at pore-space surfaces (see Sect. 7.5.2).

6.8.3 Local Motions in the Alkane Chain Phase of Lipid Bilayers

Local motions of individual molecules in lipid bilayers cannot be described as mere rotational diffusion of the whole molecule. The reason is that the alkane “tails” of lipid molecules consist of flexible saturated hydrocarbon chains with numerous degrees of motional freedom. This is a consequence of rotational (or gauche/trans) isomerism about carbon–carbon bonds as already discussed in the context of polymer dynamics in Chap. 5. The terms “trans” and “gauche” rotamers of saturated hydrocarbon chains are explained in Fig. 5.3.

A model picture based on this isomerism is one-dimensional diffusion of structural defects along the hydrocarbon chains restricted by two reflecting barriers at the polar headgroups. As illustrated in Fig. 2.10, the headgroups terminate the bilayer at both surfaces. This defect diffusion scenario has already been described in Sect. 3.9.4 as an example giving rise to specific dielectric relaxation features. A *defect* can be a rotamer such as a so-called kink, for example, a rotamer sequence gauche[−]–trans–gauche⁺ (g[−]tg⁺), or a more extended torsion. In both cases, the defect is assumed to be able to diffuse back and forth along the hydrocarbon chain. Dipolar-coupled spin pairs will be reoriented when a defect happens to arrive at this particular position. The original orientation will be reestablished once the defect has diffused apart. In this way, dipolar coupling among spins fluctuates with a rate and a statistics determined by translational diffusion of structural defects. A schematic representation of this scenario is shown in Fig. 3.51: A defect of width b on a linear alkane chain is confined between two reflecting barriers in a distance d .

Two-time constants characteristic for this model and the system can be defined as mean diffusion times over the lengths b and d defining the geometry of the problem. According to the one-dimensional version of Einstein’s relation Eq. (2.169), the average interval a spin pair remains deflected from its undistorted orientation during the passage of a defect thus is

$$\tau_b = \frac{b^2}{2D} \quad (6.108)$$

where D is the defect diffusion coefficient. On the other hand, the diffusion time a defect needs in the average to travel the distance d between the reflecting headgroups is

$$\tau_{dd} = \frac{d^2}{2D} \quad (6.109)$$

In terms of this restricted defect diffusion model, the (reduced) spectral density, that is, the NMR analogue to the dielectric formalism referred to in Eq. (3.571), was established in the form of the following three limits [49]:

$$I_{\text{loc}}(\omega) = \begin{cases} \frac{2}{3} (\tau_b^{1/2} \tau_{dd}^{1/2} - \tau_b) & \text{for } \omega \tau_{dd} \ll 1 \\ \frac{\tau_{dd} \tau_b^{1/2} - 2 \tau_b \tau_{dd}^{1/2}}{(\tau_{dd}^{1/2} - \tau_b^{1/2})^2} \omega^{-1/2} & \text{for } \omega \tau_b \ll 1 \ll \omega \tau_{dd} \\ \frac{\tau_{dd}^{1/2}}{\tau_{dd}^{1/2} \tau_b^{1/2} - \tau_b} \omega^{-3/2} & \text{for } \omega \tau_b \gg 1 \end{cases} \quad (6.110)$$

On this basis, the spin–lattice relaxation rate can be evaluated with the relation

$$\frac{1}{T_1} = \left(\frac{\mu_0}{4\pi} \right)^2 \frac{3}{20r^6} \gamma^4 \hbar^2 [I(\omega_0) + 4I(2\omega_0)] \quad (6.111)$$

(see Eq. 3.139 for spins $I = 1/2$). The distance between the spins of a dipolar-coupled pair is denoted by r . Plots of the frequency and temperature dependences expected on this basis can be found in Fig. 3.52.

Note that the square-root frequency dependence predicted for the spin–lattice relaxation time in the intermediate angular-frequency range $\tau_{dd}^{-1} \ll \omega \ll \tau_b^{-1}$ must not be confused with the same dispersion predicted for nematic order fluctuations in Eq. (6.67). As a matter of fact, local and collective motions can display identical features although they are of an entirely different nature. In the present case, the spectral density due to collective order-director fluctuations which may potentially be superimposed to the local defect diffusion process is rather expected to follow the frequency dependence suggested by Eq. (6.103). In the different-time scale limit, Eq. (6.106) can then be employed to take both mechanisms into account. In this case, the high-frequency dispersion would be governed by local defect diffusion while collective chain fluctuations reveal themselves at low frequencies.

The alkane chains in di-palmitoyl lecithin are composed of 16 carbon atoms each. The dimensions of lipid bilayers are very well known from X-ray studies such as that reported in Ref. [50]. The distance between the polar headgroups is $d \approx 3.8$ nm. Assuming a g^-tg^+ rotational isomer, a so-called “kink,” as diffusing defect, one estimates a defect width of roughly $b \approx 0.25$ nm (see the projection of main-chain bond lengths in alkanes specified in Fig. 5.2). On this basis, the ratio between the two characteristic time constants is predicted as $\tau_{dd}/\tau_b \approx 230$. With these parameters, experimental findings for the frequency and temperature dependences

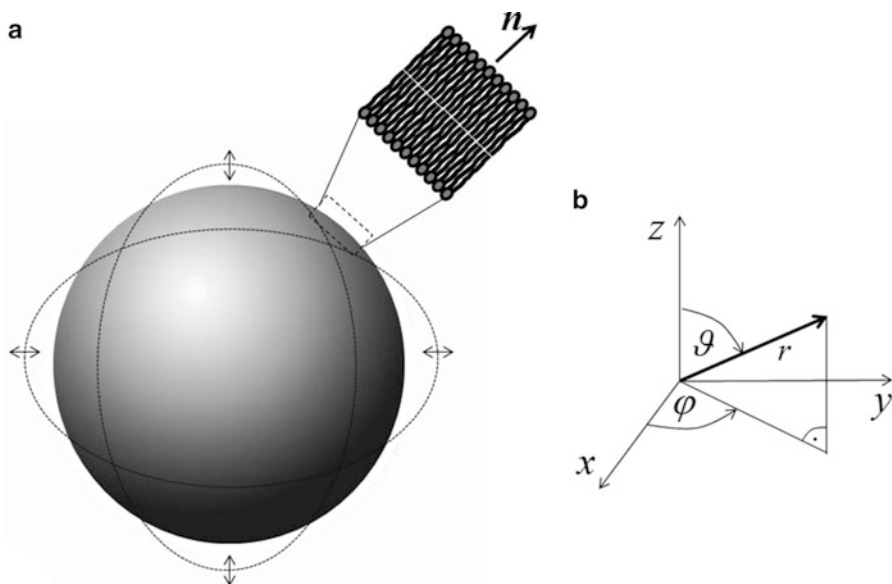


Fig. 6.8 (a) Schematic representation of shape fluctuations of mono-lamellar vesicles. The lamella is assumed to consist of a single lipid bilayer in an aqueous environment as illustrated in the partial view at the *top*. The lipid molecules consist of polar headgroups at both lipid–water interfaces enframing the alkane chain phase. The *spherical* shape in the ground state is thermally excited by modes altering the contour of the vesicle. The *ellipsoidal lines* indicate typical first harmonics of such fluctuations. In reality, the shape is composed of a superposition of a weighted set of all possible higher harmonics. (b) Spherical coordinates used for the description of shape fluctuations, where the origin is assumed in the sphere center

of the spin–lattice relaxation time can very well be reproduced. For details, see Ref. [48]. It may be of interest in this context that the restricted defect diffusion model can also be employed for the interpretation and description of local chain dynamics in amorphous polymers as demonstrated in Ref. [51].

6.8.4 Shape Fluctuations of Vesicles

The treatment of order-director fluctuations in smectics, membranes, and (multilamellar) lipid vesicles referred to in Sect. 6.8.1 anticipates that the lamellae are stacked. In this sense, they are thought to form bulk media [44]. However, vesicles consisting of a single or only a few lipid bilayers are mesoscopic objects with structurally elastic properties [52, 53]. That is, order-director fluctuations manifest themselves as thermally excited *shape fluctuations* which can be considered as overdamped hydrodynamic modes of the object. A schematic representation of a vesicle and its shape fluctuations is shown in Fig. 6.8a.

Unlike the liquid-crystalline mono-domains considered so far, the local order director varies with the position on the spherical shape of the vesicle. Spin relaxation due to order-director fluctuations in lipid bilayers in vesicles therefore needs a special consideration [54–56]. The mechanism will shortly be referred to as *shape fluctuation*.

In the case of such fluctuations, that is, deviations from the spherical shape, the local distance from the center to the surface of the vesicle will be distorted according to

$$r(t) = r_0[1 + \varepsilon(\vartheta, \varphi, t)] \quad (6.112)$$

where r_0 is the radius of the undistorted sphere, and the deviation $\varepsilon(\vartheta, \varphi, t)$ describes its fluctuations [55, 56]. The polar and azimuthal angles ϑ and φ are defined in Fig. 6.8b. In the following, the problem will be to relate $\varepsilon(\vartheta, \varphi, t)$ with order-director fluctuations in the sense of the considerations in the previous sections. For this purpose, we tacitly distinguish the *explicit* time dependence of $\varepsilon(\vartheta, \varphi, t)$ for a *given* coordinate set ϑ, φ from the *implicit* time dependence of the local order-director $\mathbf{n}(\vartheta, \varphi)$ via the coordinates ϑ, φ .

The equilibrium order director $\mathbf{n}_0(\vartheta, \varphi)$ of the lipid bilayer forming the vesicle is no longer unidirectional as in the case of planar lamellar or smectic systems. It is rather oriented in radial direction normal to the (undistorted) vesicle surface and thus depends on the polar and azimuthal angles ϑ and φ . Under the action of shape fluctuations, the local director

$$\mathbf{n}(\vartheta, \varphi) = \mathbf{n}_0(\vartheta, \varphi) + \delta\mathbf{n}(\vartheta, \varphi) \quad (6.113)$$

for the instantaneous shape of the vesicle will deviate by the local order-director fluctuation (ODF) vector $\delta\mathbf{n}(\vartheta, \varphi)$ from the radial direction. The time dependence of the director is implicitly involved in its spherical components measured in radial, polar, and azimuthal directions. In the undistorted case the respective components are $n_{0r} = 1$, $n_{0\vartheta} = 0$ and $n_{0\varphi} = 0$. Likewise, the spherical components of the ODF vector $\delta\mathbf{n}(\vartheta, \varphi)$ are δn_r , δn_ϑ and δn_φ .

The local ODF vector $\mathbf{n}(\vartheta, \varphi)$ is a function of the deviation $\varepsilon(\vartheta, \varphi, t)$. In order to find corresponding relations, we refer to the nabla operator expressed in spherical coordinates:

$$\nabla \dots = \frac{\partial \dots}{\partial r} \mathbf{u}_r + \frac{1}{r} \frac{\partial \dots}{\partial \vartheta} \mathbf{u}_\vartheta + \frac{1}{r \sin \vartheta} \frac{\partial \dots}{\partial \varphi} \mathbf{u}_\varphi \quad (6.114)$$

where $\mathbf{u}_r$, $\mathbf{u}_\vartheta$ and $\mathbf{u}_\varphi$ are the respective unit vectors in radial, polar, and azimuthal directions (see Ref. [57], for instance). For director fluctuations, we are particularly interested in the polar and azimuthal components

$$\nabla_\vartheta \dots = \frac{\partial \dots}{\partial \vartheta}; \quad \nabla_\varphi \dots = \frac{1}{\sin \vartheta} \frac{\partial \dots}{\partial \varphi} \quad (6.115)$$

where we have set $r \approx 1$ and have omitted the length unit, for simplicity. The (dimensionless) *arc lengths* of the polar and azimuthal components of the director are then

$$\delta n_{\vartheta}^{(\text{arc})} = -\nabla_{\vartheta} \varepsilon; \quad \delta n_{\varphi}^{(\text{arc})} = -\nabla_{\varphi} \varepsilon \quad (6.116)$$

The minus signs indicate that the tangential director components are negative for positive derivatives and vice versa. The weighting factor $(\sin \vartheta)^{-1}$ in the expression for ∇_{φ} accounts for the variation of the arc length of an azimuthal-angle element $\partial \varphi$ as a function of the polar angle ϑ . Finally, the ODF vector components measured *in radians* are

$$\delta n_{\vartheta} = -\frac{\nabla_{\vartheta} \varepsilon}{M}; \quad \delta n_{\varphi} = -\frac{\nabla_{\varphi} \varepsilon}{M} \quad (6.117)$$

where

$$M = \sqrt{(1 + \varepsilon)^2 + \left(\delta n_{\vartheta}^{(\text{arc})}\right)^2 + \left(\delta n_{\varphi}^{(\text{arc})}\right)^2} \quad (6.118)$$

is the magnitude of the (dimensionless) distance from the origin to the tip of the ODF vector. In the limit of *small* shape fluctuations, that is, $|\varepsilon| \ll 1$, $|\delta n_{\vartheta}^{(\text{arc})}| \ll 1$ and $|\delta n_{\varphi}^{(\text{arc})}| \ll 1$, we can approximate Eq. (6.118) by $M \approx 1$. The components of the ODF vector can thus be approached by

$$\delta n_{\vartheta}(\vartheta, \varphi) \approx -\nabla_{\vartheta} \varepsilon(\vartheta, \varphi) = -\frac{\partial \varepsilon(\vartheta, \varphi)}{\partial \vartheta} \quad (6.119)$$

and

$$\delta n_{\varphi}(\vartheta, \varphi) \approx -\nabla_{\varphi} \varepsilon(\vartheta, \varphi) = -\frac{1}{\sin \vartheta} \frac{\partial \varepsilon(\vartheta, \varphi)}{\partial \varphi} \quad (6.120)$$

The next step is to expand the (dimensionless) deviation $\varepsilon(\vartheta, \varphi, t)$ in Eq. (6.112) in a series of spherical harmonics:

$$\varepsilon(\vartheta, \varphi, t) = \sum_{l=2}^{\infty} \sum_{m=-l}^{+l} \varepsilon_{l,m}(t) Y_{l,m}(\vartheta, \varphi) \quad (6.121)$$

The sum indices l and m number the modes to which the vesicle shape will be subjected. The complex coefficients $\varepsilon_{l,m}(t)$ characterize the set of normal modes of which shape fluctuations are composed. That is, the explicit time dependence of the fluctuating deviations $\varepsilon(\vartheta, \varphi, t)$ is exclusively represented by these coefficients.

The outer sum starts at $l = 2$ since lower degrees of spherical harmonics do not contribute to order-director fluctuations: The degree $l = 0$, that is, $Y_{0,0} = (4\pi)^{-1}$, means a uniform increase or decrease of the vesicle radius without variation of the local director orientations, whereas the case $l = 1$, $m = 0, \pm 1$ merely produces a uniform displacement of the whole vesicle.

The combination of Eqs. (6.119), (6.120), and (6.121) requires the derivations of spherical harmonics. For this purpose, we exploit the known relations for the (dimensionless) ladder operators L^+ , L^- of angular momentum (see, e.g., Ref. [57]). In spherical coordinates, these operators are defined by

$$\begin{aligned} L^+ \dots &= e^{+i\varphi} \left(\frac{\partial \dots}{\partial \vartheta} + i \cot \vartheta \frac{\partial \dots}{\partial \varphi} \right) \\ L^- \dots &= e^{-i\varphi} \left(-\frac{\partial \dots}{\partial \vartheta} + i \cot \vartheta \frac{\partial \dots}{\partial \varphi} \right) \end{aligned} \quad (6.122)$$

On this basis, the derivations in Eqs. (6.119) and (6.120) can be expressed by

$$\begin{aligned} \nabla_{\vartheta} &= \frac{\partial}{\partial \vartheta} = \frac{1}{2} (e^{-i\varphi} L^+ - e^{+i\varphi} L^-) \\ \nabla_{\varphi} &= \frac{1}{\sin \vartheta} \frac{\partial}{\partial \varphi} = \frac{1}{2i \cos \vartheta} (e^{-i\varphi} L^+ + e^{+i\varphi} L^-) \end{aligned} \quad (6.123)$$

That is, the polar and azimuthal components of the nabla operator have been traced back to the action of the ladder operators. As concerns spherical harmonics, the effect of the raising and lowering operators L^+ , L^- is

$$L^{\pm} Y_{l,m} = \sqrt{l(l+1) - m(m \pm 1)} Y_{l,m \pm 1} \quad (6.124)$$

provided that $|m \pm 1| \leq l$. Otherwise, the result of the operation will be 0. That is, the ladder operators produce spherical harmonics of an order raised or lowered by one. Of course, the azimuthal component of the nabla operator could just as well be applied to spherical harmonics according to

$$\nabla_{\varphi} Y_{l,m} = \frac{1}{\sin \vartheta} \frac{\partial}{\partial \varphi} Y_{l,m} = i \frac{m}{\sin \vartheta} Y_{l,m} \quad (6.125)$$

Combining Eqs. (6.119), (6.120), (6.121) and (6.123), (6.124), (6.125) leads to

$$\begin{aligned} \delta n_{\vartheta}(\vartheta, \varphi) &= -\frac{1}{2} (e^{-i\varphi} L^+ - e^{+i\varphi} L^-) \sum_{l=2}^{\infty} \sum_{m=-l}^{+l} \varepsilon_{l,m}(t) Y_{l,m}(\vartheta, \varphi) \\ \delta n_{\varphi}(\vartheta, \varphi) &= i \frac{1}{\sin \vartheta} \sum_{l=2}^{\infty} \sum_{m=-l}^{+l} m \varepsilon_{l,m}(t) Y_{l,m}(\vartheta, \varphi) \end{aligned} \quad (6.126)$$

The coefficients $\varepsilon_{l,m}(t)$ are fluctuating functions of time, so that $\delta n_\vartheta(\vartheta, \varphi)$ and $\delta n_\varphi(\vartheta, \varphi)$ fluctuate equally. On this basis, we can form the temporal correlation functions $\langle \delta n_\vartheta(t) \delta n_\vartheta^*(0) \rangle$ and $\langle \delta n_\varphi(t) \delta n_\varphi^*(0) \rangle$ of the transverse ODF vector components. The angle brackets represent ensemble averages implying integrations of the type $\int_0^{2\pi} d\varphi \int_0^\pi d\vartheta \dots$. The sum terms arising after evaluation of the operations in Eq. (6.126) are composed of sine and cosine functions of φ and ϑ . The orthogonality of these terms (compare Eq. 3.199) eliminates contributions by cross-correlations between different degrees and orders l, m . The correlation functions of the components Eq. (6.126) can finally be represented by the common form [55, 56]

$$\begin{aligned} \langle \delta n_\vartheta(t) \delta n_\vartheta^*(0) \rangle &= \langle \delta n_\varphi(t) \delta n_\varphi^*(0) \rangle \\ &= \frac{1}{8\pi} \sum_{l=2}^{l_{\max}} l(l+1)(2l+1) \langle \varepsilon_{l,m}(0) \varepsilon_{l,m}^*(t) \rangle \end{aligned} \quad (6.127)$$

The coefficients in the sum originate from the known relation $\sum_{m=-l}^{+l} m^2 = l(l+1)(2l+1)/3$. Terms linear in m cancel. Note that the correlation function $\langle \varepsilon_{l,m}(0) \varepsilon_{l,m}^*(t) \rangle$ – despite the specification in the subscripts – merely depends on the degree l , but not on the order m . This factor therefore did not matter in the evaluation of the sum over m resulting in Eq. (6.127). The fact that the above ODF correlation functions were found to be independent of the coordinates φ and ϑ reflects the equivalence of all positions on the vesicle. The upper sum limit $l_{\max}$ is determined by the width of the molecules below which the continuum limit starts to fail.

If the shape fluctuations are small enough, we can make use of the linear approach already employed in Eq. (6.62). The dipolar orientation correlation function can then be expressed in analogous form by the correlation functions of the transverse order-director components:

$$\begin{aligned} G_1(t) &\approx \frac{1}{a^6} \left[\langle \delta n_\vartheta(t) \delta n_\vartheta^*(0) \rangle + \langle \delta n_\varphi(t) \delta n_\varphi^*(0) \rangle \right] \\ &= \frac{1}{4\pi a^6} \sum_{l=2}^{l_{\max}} l(l+1)(2l+1) \langle \varepsilon_{l,m}(0) \varepsilon_{l,m}^*(t) \rangle \end{aligned} \quad (6.128)$$

where a is the nearest dipole–dipole distance. The result of a mode analysis for elastic spherical shells is [55, 56]

$$\langle \varepsilon_{l,m}(0) \varepsilon_{l,m}^*(t) \rangle = \langle |\varepsilon_{l,m}|^2 \rangle \exp\{-t/\tau_l\} \quad (6.129)$$

with the mean square fluctuation

$$\langle |\varepsilon_{l,m}|^2 \rangle = \frac{k_B T}{\hat{K}(l+2)(l-1)(l^2 + l + \sigma)} \quad (6.130)$$

and the mode relaxation times

$$\tau_l = \frac{\eta r_0^3}{\hat{K}} \frac{(2l+1)(2l^2 + 2l - 1)}{l(l+1)(l+2)(l-1)(l^2 + l + \sigma)} \quad (6.131)$$

η is the viscosity of the aqueous medium surrounding the vesicles, and $\hat{K}$ is the effective elastic constant of the lipid bilayer. σ is a parameter taking the surface tension into account.

The Fourier conjugate of Eq. (6.128), the spectral density

$$\begin{aligned} J^{(1)}(\omega) &= \int_{-\infty}^{\infty} G_1(t) \exp\{-i\omega t\} dt \\ &= \frac{1}{4\pi a^6} \int_{-\infty}^{\infty} \left[\sum_{l=2}^{l_{\max}} l(l+1)(2l+1) \langle |\varepsilon_{l,m}|^2 \rangle \exp\{-t/\tau_l\} \right] \exp\{-i\omega t\} dt \end{aligned} \quad (6.132)$$

permits us to calculate the spin–lattice relaxation rate in the lipid bilayers via the reduced version of Eq. (3.138):

$$\frac{1}{T_1} = \left(\frac{\mu_0}{4\pi} \right)^2 \frac{3}{2} \gamma^4 \hbar^2 I(I+1) J^{(1)}(\omega) \quad (6.133)$$

I is the spin quantum number of the nuclei under consideration. The second-order spectral density $J^{(2)}(2\omega)$ does not matter in this context as already argued in Sect. 6.5. The level of approximation is the same as employed in the derivation of Eq. (6.66). On this basis, a *linear* angular-frequency dependence, $T_1 \propto \omega$, is predicted by this formalism over a wide range just as in the case of smectic liquid crystals (see Eq. 6.102) [55].

A further reorientation mechanism potentially contributing to spin relaxation in vesicles is *translational diffusion* as a reorientation process. Such a mechanism has already been implied in the treatment of ODF modes of nematic liquid crystals (see Sect. 6.4). In the present case, translational diffusion may be even more important because of the spherical shape of vesicles. A detailed treatment and discussion can be found in Refs. [54, 58]. The mechanism is also referred to as *reorientation mediated by translational displacements* (RMTD). We will encounter a number of other applications of this sort in Chap. 7.

Shape fluctuations and RMTD processes are relatively slow. The much faster motions of a local nature will therefore dominate at relatively high frequencies as

discussed in Sect. 6.8.3. On the broad frequency scale of field-cycling NMR relaxometry ranging down to the kHz regime, the superimposed effect of all contributions mentioned above might be relevant. Corresponding data have been interpreted in this way in Ref. [59]. Transverse relaxation has been examined with the same objective in Ref. [60]. Finally, it should be noted that the dynamic structure factor for shape fluctuations of vesicles has been developed on a similar basis in Ref. [53]. Corresponding results for neutron or light scattering are predicted.

6.9 Type D Mesophases of Poly(Dialkylsiloxanes)

Let us finally resume the discussion started in Sect. 6.2.1 and turn to the somewhat exotic form of ordered liquids, namely, type D mesophases. The first example of this sort was discovered in linear polydiethylsiloxane (PDES), that is, a silicon-based organic polymer having $-\text{CH}_2\text{CH}_3$ side groups. The ordered phase appears in a certain temperature interval between the solid and the isotropic melt phases. All higher homologues of PDES show the same or even more pronounced order phenomena [14, 61]. As flexible polymers, they are to be distinguished from the species forming nematic liquid crystals due to mesogenic groups in the main chain or in side chains [62]. We are thus dealing with ordered phases of polymers *without mesogenic groups*.

Figure 6.9 shows spin–lattice relaxation dispersion data for PDES both in the isotropic and in the mesomorphic phase [63]. The dispersion in the isotropic phase is governed by the same empirical power laws found in melts of non-mesogenic PDMS (side groups: $-\text{CH}_3$) and other polymer species (see Ref. [64] and Fig. 5.29). In the mesophase, two power law regimes were found as well, but with larger exponents and a crossover frequency shifted by a factor of about 10 (after correction for the different temperatures) to a lower value. The low-frequency dispersion regime $T_1 \propto \nu^{0.25 \pm 0.05}$ of the isotropic phase is converted to the power law $T_1 \propto \nu^{0.45 \pm 0.05}$ found in the mesophase. Likewise, the law $T_1 \propto \nu^{0.5 \pm 0.05}$ valid at medium frequencies in the isotropic phase finds its counterpart $T_1 \propto \nu^{0.73 \pm 0.05}$ for the ordered phase. Note that there is no dependence on the molecular mass. That is, the relevant chain modes refer in any case to a time scale below the longest Rouse relaxation time.

The exponents of the before mentioned power laws cannot be identified with those predicted for order-director fluctuations in nematic (Eq. 6.67) and smectic (Eq. 6.102) phases, respectively. They rather suggest chain modes modified owing to chain ordering. This conclusion is corroborated by the identical frequency dispersion of the spin–lattice relaxation times T_1 and $T_{1\rho}$ in the laboratory and in the rotating frames, respectively: If the order in the PDES mesophase would be of a nematic nature and the fluctuations causing dispersion region II consequently would be of the ODF type, the frequency dispersion of $T_{1\rho}$ should vanish while

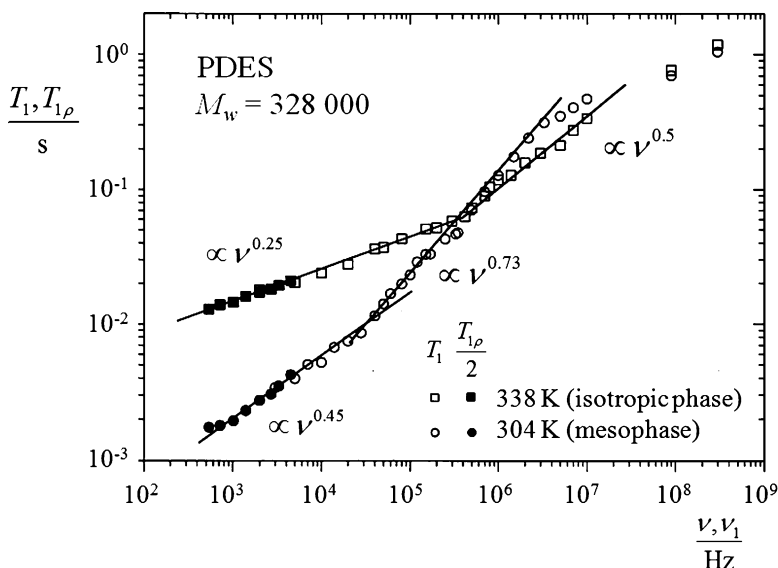


Fig. 6.9 Proton spin–lattice relaxation times in the laboratory system (T_1) and in the rotating frame ($T_{1\rho}$) of polydiethylsiloxane (PDES) melts in the isotropic and mesomorphic phases as a function of the frequency, ν and ν_1 are the frequencies effective in the laboratory and in the rotating frame, respectively. The spin–lattice relaxation dispersion data of the isotropic phase are characterized by proportionalities $\propto \nu^{0.25}$ and $\propto \nu^{0.5}$ and refer to the molecular-weight-independent chain-mode regimes we know already from ordinary entangled polymer melts (e.g., see the data in Fig. 5.29). In the (ordered) mesomorphic phase, the dispersion slopes are much steeper. They follow power laws $\propto \nu^{0.45}$ and $\propto \nu^{0.73}$ with a crossover frequency shifted to a lower value than in the isotropic phase. Beyond the power law regimes, the influence of local motions (including side chain motions) becomes gradually visible at the highest frequencies (Reproduced from Ref. [63] with kind permission of © ACS 1994)

that of T_1 is retained (see the discussion in the context of Eq. 6.67). Obviously, this is not the case.

For comparison, the information that can be deduced from the dipolar-correlation effect is of particular interest [65]. Despite the macroscopic order in the mesophase, the characteristic undulations of the dipolar-correlation factor as a function of the pulse spacing τ_1 (see Fig. 6.6) have not been observed. This fact indicates that a powdery order-director distribution must exist in the sample. In Ref. [65], it was furthermore argued that the sample consists of defect enriched, that is, less ordered areas, and, on the other hand, of domains ordered to a higher degree. Polymer segments in these two areas should be subject to different mobilities, and their (temperature dependent) populations fluctuate both temporally and spatially. It was found that the exchange times between the two mobility states range between 0.1 and 1.0 s in the mesomorphic temperature range, so that the exchange process between the two environments is slow compared with the transverse relaxation rates. As a consequence of slow exchange, two NMR signal components arise

which can be assigned to the two areas.⁸ One may furthermore suspect that the different power law regimes of spin–lattice relaxation correlate with the two segment phases. Studies based on two-dimensional relaxation-correlation maps (see Sect. 3.4.5), as they have now become popular for investigations of complex systems [66], may be helpful for elucidating this question.

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⁸This is in contrast to spin–lattice relaxation. In this case, flip-flop spin diffusion (see the discussion following Eqs. 5.169 and 5.247) as an additional exchange mechanism mediates averaging over all heterogeneities. Spin–lattice relaxation curves therefore tend to decay mono-exponentially in a wide range, whereas transverse relaxation is subject to a superposition of virtually two exponential functions.

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Chapter 7

Dynamics at Fluid Solid Interfaces: Porous Media and Colloidal Particles

Abstract This chapter could be entitled “molecular motions in complex media” as well. The point is that the systems of interest can be defined by the existence of fluid–solid interfaces. Surface-related phenomena are therefore of central interest. There is an endless list of examples belonging to this category in principle. Emphasis will be laid on porous glasses, fine-particle agglomerates, biopolymer solutions, lipid bilayers, biological tissue, etc. The predominant purpose of this chapter is to elaborate a well-classified scheme of the key mechanisms determining molecular dynamics in the presence of fluid–solid interfaces. This includes adsorption and exchange kinetics, translational and rotational diffusion, and liquid/vapor coexistence phenomena. Effects due to fluid–wall interactions on the one hand and, on the other hand, owing to geometric confinement in mesoscopic pore spaces will thoroughly be discriminated.

7.1 Survey and Some Definitions

Dynamics in porous media is a multi-faceted field of confusing complexity. Before treating a number of selected scenarios typical for this application field, let us therefore begin with a list of fundamental definitions and distinctions.

The dynamic phenomena treated so far were predominantly characterized either by *coherent transport* (Chap. 4) or *collective* relaxation modes (Chaps. 5 and 6). None of these properties apply to the systems of interest in this chapter. We are rather dealing with motions of individual molecules of fluids in varying environments and subjected to interactions with surfaces of pore walls or colloid particles. We thus arrive at the least concerted type of molecular motions. Unlike the corset effect on polymer dynamics discussed in Sect. 5.4.8, this implies that we are now restricting ourselves to *small* molecules with little or no internal degrees of motional freedom. The typical medium of interest in the present context is a fluid being either exclusively in the liquid phase or coexisting in liquid and gaseous phases. The question is how the bulk dynamic properties of the fluid are changed, owing to the presence of

solid surfaces and a (possibly random) pore space topology. The length scale of interest is usually specified as “mesoscopic” which ranges from atomistic lengths up to micrometers.

7.1.1 Characterization of Pore Spaces

Before proceeding, let us first resume the discussion led in Sect. 4.9.1, where a number of basic parameters for the characterization of pore spaces have been defined [1]. In the following, we will speak of “pore spaces” irrespective of whether this refers to a compact porous medium or a bed of particles or particle agglomerates in general. As the most elementary quantity characterizing confinements, we know already the *porosity*, that is, the ratio of the pore-space volume and the volume of the total system:

$$\Pi = \frac{V_{\text{pores}}}{V_{\text{total}}} \quad (7.1)$$

As a characteristic measure of the topological pore-space constraints, the *tortuosity* has been introduced in Sect. 4.9.1. This quantity is sometimes defined as the mean ratio of the shortest path length, $\ell_{i,f}$, and the straight distance between an initial starting and a finishing point, $r_{i,f}$ (see Fig. 7.1):

$$\tau = \left\langle \frac{\ell_{i,f}}{r_{i,f}} \right\rangle \quad (7.2)$$

Where $\ell_{i,f}$ is the *chemical distance* between the starting and finishing points. Since we will be dealing with diffusion and relaxation problems in the following, we will prefer another definition which is in frequent use as well: The *diffusive tortuosity*

$$\tau_{\text{diff}} = \frac{D_0}{D_{\text{eff}}} \quad (7.3)$$

is the quotient of the diffusion coefficients effective in bulk, D_0 , and under pore-space confinement, D_{eff} , on a length scale exceeding the correlation length (see below). This definition is of a more practical nature and should not be confused with that given in Eq. (7.2).

Another quantity we have encountered before is the *correlation length* of a macroscopically isotropic pore space. This parameter characterizes the decay of the spatial pore-space correlation function. Considering pairs of positions $\mathbf{R}_1$ and $\mathbf{R}_2$ in the sample, the following correlation function can be defined:

$$G(\mathbf{r}) = \langle w(\mathbf{R}_1)w(\mathbf{R}_2) \rangle = \langle w(0)w(\mathbf{r}) \rangle \quad (7.4)$$

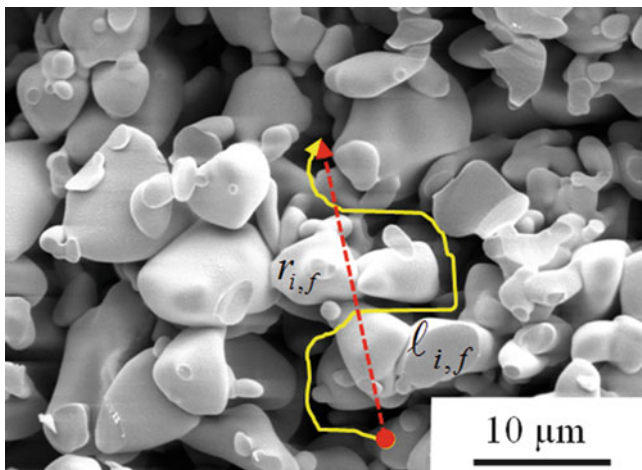


Fig. 7.1 Scanning electron micrograph of a typical porous silica glass (product name VitraPor #5, nominal pore size 1–1.6 μm) (Reproduced from Ref. [2] with kind permission of © Wiley-VCH 2009)

The position $\mathbf{R}_1$ is assumed inside the pore space whereas $\mathbf{R}_2$ can be anywhere within the sample, inside or outside of the pore space. $\mathbf{r} = \mathbf{R}_2 - \mathbf{R}_1$ is the distance vector between the two positions. The function $w(\mathbf{R})$ equals 1 if the volume element around $\mathbf{R}$ is located in the pore space and vanishes otherwise. The angle brackets represent an average over an ensemble of position pairs. On this basis, a *correlation length* can be defined by

$$\begin{aligned}\xi &= [\mathcal{G}(0) - \mathcal{G}(\infty)]^{-1} \int_0^\infty [\mathcal{G}(\mathbf{r}) - \mathcal{G}(\infty)] d\mathbf{r} \\ &= [1 - \Pi]^{-1} \int_0^\infty [\mathcal{G}(\mathbf{r}) - \Pi] d\mathbf{r}\end{aligned}\quad (7.5)$$

(where we formally assume an infinitely extended sample). x is an arbitrary coordinate and line-integration axis. The direction does not matter since the medium is assumed to be isotropic in this respect. On length scales much larger than ξ , the pore network adopts homogeneous coarse-grain properties.

Note that a somewhat different definition of the correlation length is often used in the frame of percolation theory as already mentioned in Sect. 4.9.1. Percolation theory [3] is of a largely mathematical character but models many features of random pore networks. Percolation clusters can therefore be taken as a paradigm for random pore spaces especially with respect to transport. We have encountered this strategy in Chap. 4 at diverse occasions.

7.1.2 Adsorption Versus Restricted-Geometry Effects

Spatial restrictions of fluids and interactions with surfaces give rise to a rich variety of dynamic phenomena which are absent under bulk conditions. In the following, *adsorption* and *restricted-geometry* effects will be distinguished as the key to the understanding of molecular dynamics in such systems. Actually, this differentiation has already been discussed in Sect. 5.4.8.3 in the context of the corset effect on the dynamics of mesoscopically confined polymers.

Adsorption of fluid molecules matters if the interaction with solid surfaces is attractive so that molecules tend to reside temporarily in bound (and possibly ordered) states at the surfaces. The binding energy, that is, the strength of the adsorption effect, is a matter of the mutual interaction affinity of adsorbate and surface chemical groups. In the following, we will roughly distinguish *polar/polar* and *nonpolar/polar* interactions as classes with antithetic tendencies in this respect.

Even in the complete absence of adsorption, that is, if the fluid/wall interaction is inert or repulsive, purely *geometrical effects* due to pore-space restrictions and tortuosity are expected. Phenomena of this sort are particularly evident in the context of translational diffusion.

7.1.3 Categories of Restricted-Geometry Effects on Translational Diffusion

In cases where fluid/wall interactions are neutral or even repulsive, adsorption will be irrelevant. Diffusion on a length scale approaching the pore dimension will then be subject to normal modes as solutions of Fick's second law, Eq. (2.167), with reflecting-boundary conditions at the pore walls. The most elementary (and instructive) example of this sort is one-dimensional diffusion between such barriers [4]. In principle, we have already encountered an application of this category in Sect. 6.8.3: diffusion of structural defects between reflecting barriers [5]. Compare also the discussion of the different potentials considered for polymer confinement in the context of Fig. 5.31.

In three-dimensional pore spaces, the shape of the pores becomes important. The boundary conditions give then rise to characteristic *diffraction-like patterns* [6] of the incoherent dynamic structure factor provided that the root mean-square displacement matches the dimensions of the confining medium. Simple pore geometries such as cubic, spherical, or cylindrical shapes have been evaluated in this sense. In the case of NMR applications, diffusion modes in porous media must be analyzed in combination with surface relaxation, that is, absorbing boundary conditions [7–9]. Note that the root mean-square displacements probed by NMR diffusometry usually exceed mesoscopic pore dimensions by far, so that diffraction-like patterns will not arise in this instance.

On the length scale of the so-called *scaling window*, that is, between the pore dimension and the correlation length, transport is characterized by power laws, provided that the pore space is of a random nature (compare Sects. 2.5.2 and 4.9.3). If fractal or fractal-like properties can be attributed to the geometry, *subdiffusive* mean squared displacement laws

$$\langle r^2 \rangle \propto t^\kappa \quad (7.6)$$

are expected in this regime with $0 < \kappa < 1$. The origin of this anomaly is the tortuosity of the pore space restricting the allowed particle trajectories. The crucial parameter of Eq. (7.6), the exponent κ , in a sense reflects the pore-space structure. Provided that the pore space can be described as a fractal, this exponent can be expressed at least approximately in terms of the fractal dimension d_f according to the *Alexander/Orbach conjecture* $\kappa = 4/(3d_f)$ [10, 11]. The *superdiffusive* counterpart of Eq. (7.6), that is, exponents $\kappa > 1$, arises for *hydrodynamic dispersion* in random pore spaces. This phenomenon has already been discussed in Sect. 4.9.3.

For the sake of completeness, the corset effect described in Sect. 5.4.8 should be mentioned as a further category of restricted-geometry effects. It refers to polymers confined in mesoscopic pores with inert or repulsive walls. Anomalies are attributed in this case to the *finite size* of the system in the sense of statistical physics. The corset effect reveals itself by slowed-down and restricted chain dynamics of macromolecules.

7.1.4 Rotational Versus Translational Diffusion

As frequently exemplified in the previous chapters and discussed in the introduction, Chap. 1, molecular dynamics has two principal forms of appearance: *translational* and *rotational* diffusion. Translational displacements of fluid molecules are affected by obstruction due to any sort of obstacles, trapping in dead ends of the pore space, adsorption at solid surfaces, and exchange between liquid and vapor phases. On the other hand, the rotational counterpart, molecular reorientation by thermal motions, at first sight senses solely fluid/surface interactions, while geometrical restrictions seem to be irrelevant. As will be demonstrated later, this is not entirely true. As soon as anisotropic adsorption at surfaces plays a significant role, there will be an intimate interconnection of translations along surfaces of non-planar topology and reorientations of fluid molecules [12]. The mechanism to which we are alluding is termed *reorientation mediated by translational displacements* (RMTD).¹

¹ A first application of this process was already mentioned at the end of Sect. 6.8.4 as a mechanism competing with shape fluctuations of lipid vesicles.

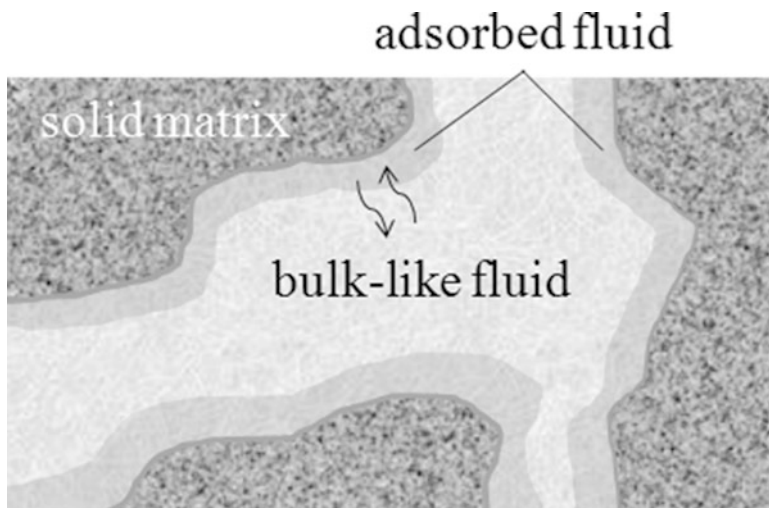


Fig. 7.2 Schematic representation of the two-phase model of fluids confined in a saturated solid matrix. The fluid adsorbed at surfaces is discriminated from the bulk-like phase. Molecular mobilities within and exchange kinetics between these phases determine the dynamics of fluid molecules. In unsaturated pore spaces, vapor as a third phase needs to be taken into account

7.1.5 Fluid Phases and the Intricacy of the Term “Exchange”

In the presence of solid surfaces of saturated pore spaces, one often subdivides the confined liquid crudely in two phases, namely, *adsorbed* and *free* as illustrated in Fig. 7.2. Synonymously, the latter is often referred to as *bulk-like*, a term anticipating practically the same properties as in bulk as concerns molecular dynamics (but not necessarily with respect to thermodynamics). Molecular motions in the adsorbed phase are expected to be slowed down relative to the free phase as a consequence of topological restrictions and (possibly anisotropic) adsorbate/wall interactions. An experiment-based distinction of bulk-like and adsorbed fluid phases is possible with regard to the different freezing temperatures in the two phases: At that level, the bulk-like phase can be defined by a freezing temperature significantly *above* that of the adsorbed phase. Experimentally, this distinction has been demonstrated in numerous reports [13–15], where frozen and unfrozen phases can simply be discriminated by the enormous differences of the NMR linewidths or of the translational diffusivities. The latter criterion will be exemplified in Sect. 7.4.2.

Molecular exchange between the two phases is a matter of thermal activation. This gives rise to interesting *reaction/diffusion phenomena* where the term “reaction” refers to adsorption/desorption processes. A striking example to be described in detail further down is *bulk-mediated surface diffusion* (BMSD) [16–19]: Adsorbate molecules are effectively displaced along solid surfaces by desorption/readsorption cycles with intermittent displacements in the bulk-like phase.

The fact that the present discussion associates terms like *adsorption*, *desorption*, and *reaction* with *diffusion* indicates the intricacy of the designation “exchange”.² In Sect. 3.4 dealing with exchange NMR spectroscopy, we have anticipated that the spin-bearing molecules can populate a discrete number or spectroscopically and/or dynamically differing *sites* among which they can directly jump by thermal activation. Actually, in just this sense, exchange was already examined in the early days of NMR [24]. The more extended *phases* among which exchange is to occur in the scenarios under present consideration, need to be differentiated carefully from the *sites* then in force.

Sites are characterized by well-defined molecular orientations, interactions, activation energies, and positions relative to certain chemical environments. On the other hand, apart from the thermodynamic definition, we specify a *phase* as a more or less *extended* system of molecules homogeneously characterized by certain dynamical features. For example, different phases distinguish themselves by different degrees of reorientation anisotropy, different translational-diffusion properties, different thermal activation energies, etc.

Molecular exchange between phases can only occur at *interfaces of coexistence*. Since phases tend to form extended systems, exchange is intimately related with translational diffusion to and from the interfaces. Instead of the simple exchange kinetics anticipated in Sect. 3.4 for exchange NMR, diffusion modes must be implicated as solutions of Fick’s second law with the corresponding boundary conditions. Fortunately, simplistic but nevertheless successful limits exist where the transport aspect of exchange can globally be modeled by fixed parameters to be specified in the following. It is clear that models on this basis can only work satisfactorily if the extension of the phase regions is *small enough*. On a mesoscopic length scale, there are good prospects, while exchange in macroscopic pore spaces must be left to more demanding concepts.

7.2 Exchange Limits for Two-Phase Systems

In the frame of the *two-phase model* for porous media, exchange between *adsorbed* and *bulk-like* phases is considered as illustrated in Fig. 7.2. Exchange can be classified by defining an *effective* exchange time τ_{ex} characterizing the exchange kinetics between the two phases including transport to and from the interfaces. In

² A short side note: “Exchange” is to refer to *molecular* exchange if not specified otherwise. Selective exchange of atoms such as hydrogen in water or in hydroxyl groups of other compounds, for example, is usually slower and therefore irrelevant in the present context. For example, hydrogen exchange in water of neutral acidity has an exchange time from molecule to molecule in the order of 10^{-3} s [20, 21] compared to exchange times of about 10^{-5} s for molecular exchange between adsorbed and bulk-like water phases. The latter order of magnitude is concluded from the strong frequency dependence of the spin–lattice relaxation time in such systems ranging down to the kHz regime (see Fig. 7.3).

principle, one should distinguish moreover between the mean residence time in the adsorbed phase, $\tau_{\text{ex},a}$, and the mean residence time in the bulk-like phase, $\tau_{\text{ex},b}$. For the sake of simplicity and for discussion purposes, it suffices to take τ_{ex} as the mean of these two residence times.

Whether exchange must be rated as “fast” or “slow” depends on the reference time scale. In this respect, we distinguish the *measuring time scale* – which in turn is determined by the measuring technique – and the *correlation time scale* referring to the decay of correlation functions of molecular motions.

7.2.1 Exchange Limits Relative to Measuring Time Scales

7.2.1.1 Diffusion Time Scale

Let us denote the diffusion time, that is, the interval in which diffusive displacements are probed, by t . In the *slow-exchange* limit, where the exchange time is much longer than the diffusion time, $\tau_{\text{ex}} \gg t$, experimental measurands, that is, primarily the incoherent dynamic structure factor, will be characterized by a superposition of two independent diffusion processes referring to the bulk-like and adsorbed phases. The respective transport properties may be influenced by restricted-geometry effects depending on the pore-space topology and the root-mean-square displacement achieved in t . The diffusion features in the adsorbed phase may moreover be affected by the adsorption effect. The opposite limit, $\tau_{\text{ex}} \ll t$, that is, *fast exchange*, applies for very long diffusion times as they are often relevant under typical measuring conditions. A semiempirical formula for this *two-phase/fast-exchange diffusion scenario* will be given further down.

7.2.1.2 Spin Relaxation Time Scale

In the case of spin relaxation, two different reference time scales must be distinguished, the *relaxation time scale* and the *correlation time scale*. The former is defined by the longitudinal and transverse relaxation times T_1 and T_2 , respectively. The latter characterizes the decay period of the correlation function of the relevant spin interactions. Under favorable conditions, the correlation time scale can be characterized by a single well-defined correlation time.

Relative to the spin-relaxation time scale, the *fast-exchange limit* $\tau_{\text{ex}} \ll T_1, T_2$ manifests itself by *monoexponential* longitudinal or transverse relaxation curves. Molecular exchange rates are then much larger than the relaxation rates in either phase. This is the basis of the *two-phase/fast-exchange relaxation scenario*. To be sure that this limit applies, the monoexponential character should be verified over at least a decade of the decay of the relaxation curves.

The two-phase/fast-exchange relaxation scenario is definitely not suited for macroscopic systems which are too large for the characterization of exchange

kinetics by a fixed exchange time. Instead, the analysis must be based on a system of Bloch equations supplemented by a diffusion term and an *interfacial* exchange term. Spin relaxation, translational diffusion, and molecular exchange must then commonly be assessed [25]. In the opposite limit, *slow exchange on the relaxation time scale*, the two phases do not “communicate” with each other on the relevant time scale. The consequence is that spin-relaxation data represent a superposition of independent systems.

7.2.2 Exchange Limits Relative to the Time Scale of Orientation Correlation Functions

By definition, spin–lattice relaxation times are much longer than the correlation times of the correlation functions on which they are based (see Sect. 3.1.5). The fast-exchange limit *on the relaxation time scale* can therefore be further subdivided in fast- and slow-exchange limits *relative to the time scale on which correlation functions are probed in experiments*. This time scale is related to the Fourier conjugate t_ω of the angular Larmor frequency ω , that is, $\omega \xleftrightarrow{\mathcal{F}} t_\omega$. Exchange limits can be expressed in terms of either variable as $\tau_{\text{ex}} \ll t_\omega, \omega^{-1}$ and $\tau_{\text{ex}} \gg t_\omega, \omega^{-1}$ standing for *fast* and *slow exchange on the correlation time scale*, respectively.

In the following, we will focus in particular on the (normalized) *intramolecular* orientation correlation functions determining homonuclear spin relaxation due to dipolar and/or quadrupolar couplings:

$$G_{\text{or}}(t) = 4\pi(-1)^m \langle Y_{2,m}(0)Y_{2,-m}(t) \rangle_{\text{ensemble}} \quad (m = 0, 1, 2) \quad (7.7)$$

As before, different orders m need not be distinguished explicitly as discussed in Sect. 3.1.5.6. Equation (7.7) correlates the spherical harmonics of second degree, $Y_{2,m} = Y_{2,m}(\vartheta, \varphi)$, at the beginning and at the end of time intervals t (for simplicity, we will omit the subscript ω from now on with the tacit understanding that t is predetermined by the angular frequency ω chosen in the experiment). The time dependence enters via the initial and final polar and azimuthal angles $\vartheta(0), \vartheta(t)$ and $\varphi(0), \varphi(t)$, respectively. These angles specify the molecular orientation relative to the laboratory reference frame.

Four different scenarios can be distinguished for the correlation decay. They are characterized by the following exclusive probabilities: (a) $f_{\text{a,a}}(t)$, fraction of molecules which happen to be initially as well as finally located in the adsorbed phase; (b) $f_{\text{a,b}}(t)$, fraction of molecules which happen to be initially in the adsorbed phase and finally in the bulk-like phase; (c) $f_{\text{b,a}}(t)$, fraction of molecules which happen to be initially in the bulk-like phase and finally in the adsorbed phase; and

(d) $f_{b,b}(t)$, fraction of molecules which happen to be initially and finally in the bulk-like phase. Normalization requires

$$f_{a,a}(t) + f_{a,b}(t) + f_{b,a}(t) + f_{b,b}(t) = 1 \quad (7.8)$$

The subscripts a and b stand for “adsorbed” and “bulk-like”, respectively.

Fast exchange on the relaxation time scale means that spins are subjected to numerous correlation probe intervals t before relaxation becomes perceptible on experimental time scales of the order of T_1 or T_2 . That is, each molecule will consecutively be subject to all four scenarios many times during the measuring process. From the statistical point of view, this permits us to subdivide the correlation function Eq. (7.8) into four partial correlation functions for four subensembles of molecules. The subensembles represent molecules taking part in the diverse scenarios. The correlation function effective for all molecules in both phases is then the weighted average

$$\mathcal{G}_{\text{or}}(t) = f_{a,a}(t)\mathcal{G}_{a,a}(t) + f_{a,b}(t)\mathcal{G}_{a,b}(t) + f_{b,a}(t)\mathcal{G}_{b,a}(t) + f_{b,b}(t)\mathcal{G}_{b,b}(t) \quad (7.9)$$

The partial correlation functions $\mathcal{G}_{i,j}(t)$ for $i = a, b$ and $j = a, b$ refer to subensembles of molecules being initially in phase i and finally in phase j . Their contributions are weighted by the fractions $f_{i,j}$.

Cases (a) and (d) imply that the reference molecule will be still or again in the same phase as initially. That is, cyclic exchange processes in the considered time interval can (but need not) have taken place. This is in contrast to cases (b) and (c) where exchange between the phases is implicated necessarily. Let us now consider the limits of Eq. (7.9) relative to the mean exchange time constant τ_{ex} .

7.2.2.1 Fast Exchange on the Correlation Time Scale

In this limit, the reference molecule will be exchanged frequently on the time scale of the correlation decay, that is, $\tau_{\text{ex}} \ll t$ (recall that t is an experimental parameter predetermined by the adjusted angular frequency, while τ_{ex} is specific for the sample and its temperature). The initial and final probabilities of finding the reference molecule in a certain phase can therefore be established *independently*. The fractions $f_{i,j}$ can be approximated by

$$\begin{aligned} f_{a,a}(t) &\approx f_a^2 \\ f_{a,b}(t) &\approx f_{b,a}(t) \approx (1 - f_a)f_a \\ f_{b,b}(t) &\approx (1 - f_a)^2 \end{aligned} \quad (7.10)$$

where f_a and $(1 - f_a)$ are the (time-independent) populations in the adsorbed and bulk-like phases, respectively. We thus arrive at

$$\begin{aligned} G_{\text{or}}(t \gg \tau_{\text{ex}}) \approx & f_a^2 G_{a,a}(t) + (1 - f_a) f_a G_{a,b}(t) + (1 - f_a) f_a G_{b,a}(t) \\ & + (1 - f_a)^2 G_{b,b}(t) \end{aligned} \quad (7.11)$$

as an approach for the correlation function Eq. (7.9).

Molecular motions in the bulk-like phase of ordinary liquids can be assumed to be isotropic and relatively fast in contrast to the adsorbed phase where reorientations are restricted and slower by tendency. In terms of molecular dynamics, this is just the definition of the difference between the two phases. Let τ_b be the rotational correlation time in the bulk-like phase, so that any orientation correlation vanishes in the limit $t \gg \tau_b$. As a characteristic of the principally fastest process in the scenarios under consideration, the correlation time τ_b can be assumed to be shorter than the effective exchange time τ_{ex} : $\tau_b \ll \tau_{\text{ex}} \ll t$. Provided that the population in the adsorbed phase, f_a , is not too small, the correlation function Eq. (7.11) can then be approached by

$$G_{\text{or}}(t) \approx f_a^2 G_{a,a}(t) \quad (7.12)$$

where $G_{a,a}(t)$ is the only partial correlation function “surviving” on a time scale $t \gg \tau_{\text{ex}} \gg \tau_b$. All other terms in Eq. (7.11), that is, $G_{a,b}(t)$, $G_{b,a}(t)$, $G_{b,b}(t)$, will be subject to extremely fast correlation losses while molecules are in the bulk-like phase. These contributions therefore decay to negligibly small values:

$$(1 - f_a) f_a G_{a,b}(t) + (1 - f_a) f_a G_{b,a}(t) + (1 - f_a)^2 G_{b,b}(t) \ll f_a^2 G_{a,a}(t) \quad (7.13)$$

7.2.2.2 Slow Exchange on the Correlation Time Scale

The effective exchange time is now assumed to be long relative to the time scale of the correlation decay, that is, $\tau_{\text{ex}} \gg t$. Exchange between the adsorbed and bulk-like phases will therefore be unlikely. The molecules will rather stay in their initial phases. The fractions f_{ij} can then be approximated by

$$\begin{aligned} f_{a,a}(t) & \approx f_a \\ f_{a,b}(t) & \approx f_{b,a}(t) \approx 0 \\ f_{b,b}(t) & \approx (1 - f_a) \end{aligned} \quad (7.14)$$

The correlation function Eq. (7.9) thus adopts the form

$$\mathcal{G}_{\text{or}}(t \ll \tau_{\text{ex}}) \approx f_{\text{a}}(t) \mathcal{G}_{\text{a,a}}(t) + (1 - f_{\text{a}}) \mathcal{G}_{\text{b,b}}(t) \quad (7.15)$$

Referring to times longer than the rotational correlation time in the bulk-like phase but shorter than the exchange time, $\tau_{\text{b}} \ll t \ll \tau_{\text{ex}}$, the correlation function Eq. (7.15) can be reduced further to

$$\mathcal{G}_{\text{or}}(t) \approx f_{\text{a}} \mathcal{G}_{\text{a,a}}(t) \quad (7.16)$$

(provided that the population of the adsorbed phase, f_{a} , does not scale down this term too much relative to the second term in Eq. (7.15); that is, $(1 - f_{\text{a}}) \mathcal{G}_{\text{b,b}}(t) \ll f_{\text{a}} \mathcal{G}_{\text{a,a}}(t)$).

The remarkable difference between Eqs. (7.12) and (7.16) is that the former has a *quadratic* and the latter a *linear* dependence on the population of the adsorbed phase. On the other hand, the decay of the effective correlation function of all particles in both phases will be dominated by the subensemble residing initially as well as finally in the adsorbed phase. That is, the function $\mathcal{G}_{\text{a,a}}(t)$ matters in either case.

7.2.3 Combined Limits for Spin Relaxation in “Two-Phase/Fast-Exchange Systems”

Since slow exchange on the relaxation time scale (Sect. 7.2.1.2) is of minor interest in the present context, we restrict ourselves to *two-phase/fast-exchange systems* as a paradigm, where the attribute “fast” refers to the relaxation time scale. As outlined in Sects. 3.1.5.7, 3.1.5.8, and 3.1.5.9, the most important proton spin-relaxation mechanisms are couplings between *like dipoles* on the one hand and interactions with *electron-paramagnetic species* (referred to as *S*-spins) on the other. In the following, we will mainly consider *diamagnetic* systems for which the former case is relevant. Quadrupole interactions of quadrupole nuclei (such as deuterons) can also be assigned to this category because of the formally equivalent spin-relaxation formulas. Later, in Sect. 7.5.8, we will resume the discussion of electron-paramagnetic systems as they may be relevant especially in natural and technical porous media such as rocks and cement, respectively.

According to Eqs. (3.139) and (3.148) for spin–lattice relaxation and Eqs. (3.167) and (3.168) for transverse relaxation, the respective intra-molecular relaxation rates for homonuclear dipolar or quadrupolar spin interactions are given by

$$\begin{aligned}\frac{1}{T_1} &= C_1[I(\omega) + 4I(2\omega)] \\ \frac{1}{T_2} &= C_2[3I(0) + 5I(\omega) + 2I(2\omega)]\end{aligned}\quad (7.17)$$

where C_1 and C_2 are constants specific for the relevant spin couplings. The reduced spectral densities

$$I(\omega) = \int_{-\infty}^{+\infty} G_{\text{or}}(t)e^{-i\omega\tau} dt \quad (7.18)$$

are defined as Fourier transforms of the normalized correlation function. Combining Eq. (7.18) with Eqs. (7.12) and (7.16) gives

$$I_{\text{aa}}(\omega) = f_a^2 \int_{-\infty}^{+\infty} G_{\text{a,a}}(t)e^{-i\omega\tau} dt \quad \text{for } \omega \ll \tau_{\text{ex}}^{-1} \ll \tau_b^{-1} \quad \text{and } f_a \text{ 'finite'} \quad (7.19)$$

(fast exchange on the correlation time scale) and

$$I_{\text{aa}}(\omega) = f_a \int_{-\infty}^{+\infty} G_{\text{a,a}}(t)e^{-i\omega\tau} dt \quad \text{for } \tau_b^{-1} \gg \omega \gg \tau_{\text{ex}}^{-1} \quad \text{and } f_a \text{ 'finite'} \quad (7.20)$$

(slow exchange on the correlation time scale). The attribute “finite” means that the population of the adsorbed phase cannot be neglected relative to that of bulk-like phase. Spin relaxation will therefore be dominated exclusively by processes inside the adsorbed phase in both cases. A typical example is the RMTD process mentioned above. It will be described in more detail further down.

With the aid of spin–lattice relaxation experiments, a distinction of the two limits represented by Eqs. (7.12) and (7.16) or (7.19) and (7.20) is possible via the proportionalities

$$\frac{1}{T_1} \propto f_a^2 \quad \text{for } \omega \ll \tau_{\text{ex}}^{-1} \ll \tau_b^{-1} \quad \text{and } f_a \text{ 'finite'} \quad (7.21)$$

(fast exchange both on the correlation time scale and on the relaxation time scale) and

$$\frac{1}{T_1} \propto f_a \quad \text{for } \tau_b^{-1} \gg \omega \gg \tau_{\text{ex}}^{-1} \quad \text{and } f_a \text{ 'finite'} \quad (7.22)$$

(exchange *slow* on the correlation time scale but *fast* on the relaxation time scale). For transverse relaxation, the situation is a bit more complicated because of the zero-frequency term $I(0)$ conflicting with the limit $\tau_b^{-1} \gg \omega \gg \tau_{ex}^{-1}$ anticipated for Eq. (7.20). In the frame of these limits, contributions of the bulk-like phase to the total spin–lattice relaxation rate are entirely negligible (apart from the correspondingly reduced weighting factor f_a).

The population of the adsorbed phase can be varied by variation of the filling degree of the porous matrix. Small filling degrees correspond to large populations of the adsorbed phase and vice versa. Such experiments have been reported in Ref. [26]. Equivalent Monte Carlo simulations are described in Ref. [27]. The experimental scenarios to be discussed in the following sections can predominantly be attributed to the limit $\tau_b^{-1} \gg \omega \gg \tau_{ex}^{-1}$ (or equivalently $\tau_b \ll t \ll \tau_{ex}$), that is, exchange *slow* on the correlation time scale but *fast* on the relaxation time scale.

7.3 Adsorption Limits

Another category of limiting cases concerns different adsorption properties. Adsorption of liquid molecules on surfaces of colloid particles or pores in porous media can be characterized by the following parameters [1, 16]: The *retention time* t_h indicates how long it takes until the *initial* population of the adsorbed phase is *finally* replaced by exchange with the bulk-like phase. This sort of renewal time is the maximum time scale of the processes of interest in the present context. The retention time is related to a quantity h called *adsorption depth*. It is defined by

$$h = \sqrt{Dt_h} \quad (7.23)$$

where D is the bulk diffusivity of the adsorbate. Adsorption and desorption rates are designated by Q_{ads} and Q , respectively. Specifying furthermore the *capture range* b , that is, the distance over which an adsorbate molecule can directly be adsorbed on the surface in a single displacement step, leads to the relation

$$h = b \frac{Q_{ads}}{Q} \quad (7.24)$$

Equation (7.24) reflects the dynamic equilibrium of the one-dimensional reaction–diffusion problem as which the adsorption process and translational diffusion to and from the surface can be interpreted.

On the basis of the parameters t_h and Q , the *weak-adsorption limit* is specified by

$$t_h Q \ll 1 \quad (7.25)$$

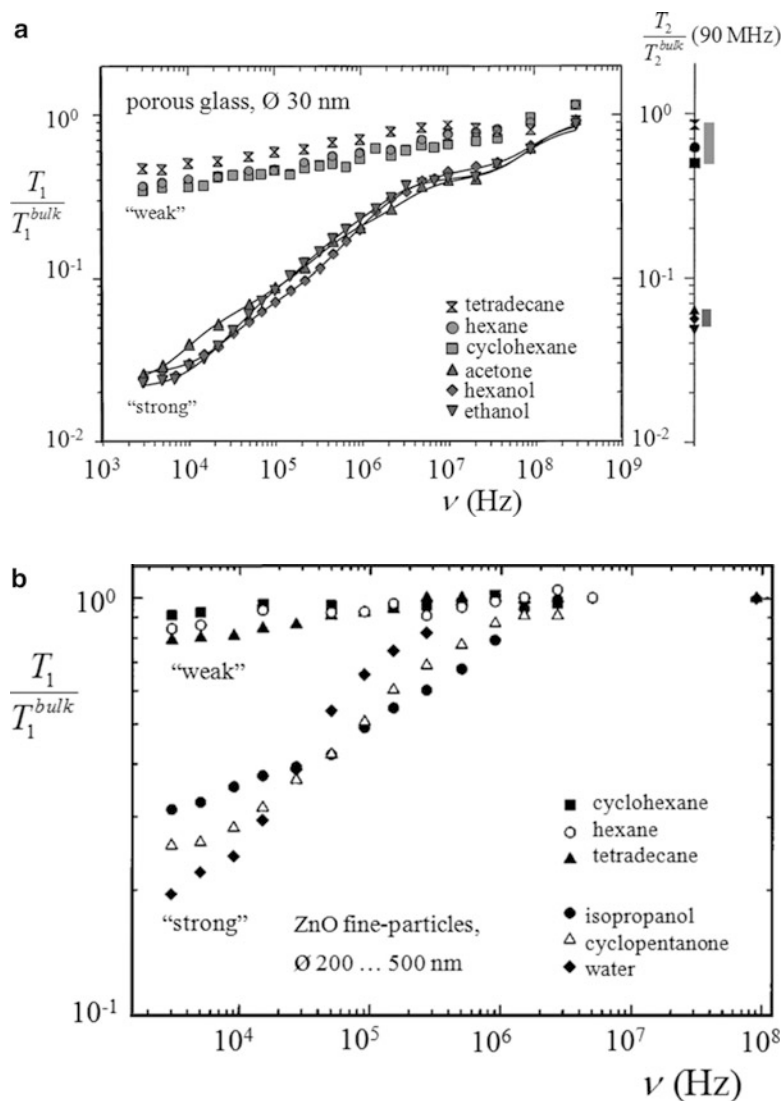


Fig. 7.3 Distinction of weak and strong adsorption in various systems with polar surfaces. The respective limits are relevant for nonpolar and polar adsorbate liquids. This is revealed by weak and strong spin–lattice relaxation dispersions. The different solvents investigated are specified in the insets. (a) Porous silica glass (nominal pore diameter 30 nm). The *solid lines* refer to a tentative analysis reported in Ref. [22] (Reproduced from Ref. [22] with kind permission of © APS 1995); (b) ZnO fine particles (diameters 200–500 nm); (c) TiO₂ fine particles (diameters 200–800 nm) (Reproduced from Ref. [23] with kind permission of © AIP 1998)

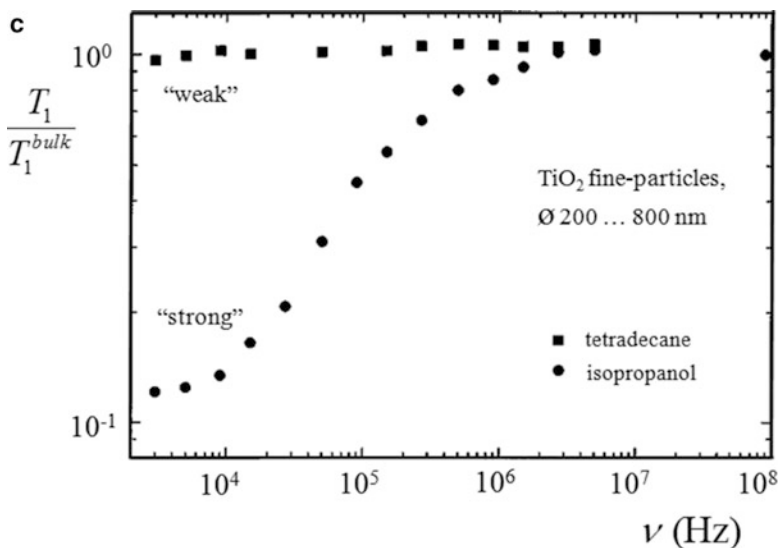


Fig. 7.3 (continued)

Assuming that the bulk-like phase is much larger than the adsorbed phase, there will be little chance that adsorbate molecules return on the experimental time scale after escaping from the surface layer. Rather, they will be dispersed in the large volume of the bulk-like phase. This is in contrast to the opposite condition, the *strong-adsorption limit*

$$t_h Q \gg 1 \quad (7.26)$$

Readsorption is likely after desorption. Numerous intermittent desorption/readsorption cycles may occur in this case before adsorbate molecules finally escape to the vastness of the bulk-like phase on the experimental time scale.

How intense or weak adsorbate molecules interact with surfaces, can be demonstrated with field-cycling NMR relaxometry data. Figure 7.3 shows results for different low-molecular solvents embedded in porous silica glass samples and in fine-particle beds. All adsorbent materials employed in these experiments are characterized by *polar* (hydrophilic) surfaces. The polar and nonpolar nature of the solvents manifests itself by dramatically different dispersion slopes of the spin–lattice relaxation times. This finding suggests that *polar* adsorbate liquids are subject to *strong* adsorption on polar surfaces, whereas *nonpolar* liquids are only *weakly* adsorbed on substrates of this sort. The only interpretation is that

reorientational fluctuations of polar adsorbate molecules are slowed down by orders of magnitude relative to non-polar species in the experimental time/frequency window.

7.4 Translational Diffusion of Low-Molecular Fluids Under Confinement

In Chap. 3, a number of techniques suitable for studies of translational diffusion have been described. The function to be probed in experiments and common to most of these methods, the *incoherent dynamic structure factor*, has already been introduced in Eq. (1.10):

$$\mathcal{G}_{\text{inc}}(t) = \langle \exp\{i\mathbf{q} \cdot \mathbf{r}_{\text{self}}\} \rangle \quad (7.27)$$

$\mathbf{r}_{\text{self}} = \mathbf{r}_{\text{self}}(t)$ is the molecular displacement in the diffusion time t . The angle brackets indicate an ensemble average. The definition of the wave vector $\mathbf{q}$ is specific for the technique employed. The diverse versions are listed in Eq. (3.576). With field-gradient NMR diffusometry, the technique we will focus on, it is given by the magnetic field-gradient strength $\mathbf{g}$, the gradient pulse length δ , and the gyromagnetic ratio γ of the resonant nuclei:

$$\mathbf{q} = \gamma \delta \mathbf{g} \quad (7.28)$$

Features of diffusion in porous media will be described preferably on the basis of the diffusion coefficient D which links the mean square displacement with the diffusion time via the Einstein relation

$$\langle \mathbf{r}_{\text{self}}^2 \rangle = 6Dt \quad (7.29)$$

provided that the diffusion process obeys normal conditions (see the discussion in Sect. 2.5.1).

7.4.1 Fluids in Saturated Mesoscopic Pore Spaces

Confinement in saturated porous media affects diffusion in fluids if (1) the root-mean-squared displacement is larger than the mean pore diameter and/or (2) if the population of the adsorbed phase cannot be neglected relative to that of the bulk-like phase. The latter means that the surface-to-volume ratio is accordingly large. The former condition implies that a part of the particle trajectories that would be

possible in bulk are excluded by pore walls and by the pore-space topology. The consequences can be the following: reduced diffusivity, anisotropy of the displacements, trapping, and obstruction effects as already debated in Sect. 2.5.2 in the context of anomalous diffusion. Condition (2) implies that translational degrees of freedom of the particles can intermittently be restricted to the adsorbed phase. In this case, trajectories will only be possible in the interfacial layer if energetically possible at all. The diffusivity effective in the total system is then a matter of exchange between the two phases.

7.4.1.1 Porous Glasses

Porous silica glasses can be taken as a well-studied and well-characterized paradigm for mesoscopic porous media with substantially random pore spaces. A typical electron micrograph is shown in Fig. 7.1. In the following, let us have a closer look at a number of data sets measured with fluids embedded in such systems.

The self-diffusion coefficient in bulk water at room temperature is known to be $D = 2 \times 10^{-9} \text{ m}^2/\text{s}$. The values of other low-molecular solvents are of the same order of magnitude. This is to be compared with data measured in porous silica glasses with nominal pore diameters of 4 and 30 nm. A correlation plot is shown in Fig. 7.4 [28]. Under such confinements, the effective diffusion coefficients were found to be reduced by about 83 and 37%, respectively.

The attribute “effective” means that the measurements represent averages over length scales much longer than the correlation lengths of the pore spaces. In the aforementioned study, the diffusion time was chosen to be about 10 ms or longer so that the root-mean-square displacements are in the order of micrometers. This is three orders of magnitude larger than the pore dimensions not to speak of the width of the surface layers forming the adsorption phase. The correlation lengths of the pore spaces are thus exceeded by far, and anomalous diffusion features can be excluded in this case.³ That is, mean square displacements vary linearly with time.

The following proportionalities for the effective diffusion coefficient suggest themselves for an interpretation: $D_{\text{eff}} \propto \Pi$ (porosity) and $D_{\text{eff}} \propto \tau_{\text{diff}}^{-1}$ (inverse diffusive tortuosity; see Eq. 7.3), and, assuming the two-phase/fast-exchange model for diffusion, $D_{\text{eff}} \propto f_a D_a + (1 - f_a) D_b$, where f_a is the population in the adsorbed phase. D_a and D_b are the local diffusivities in the adsorbed and bulk-like phases, respectively. Taking all three proportionalities together gives

$$D_{\text{eff}} \approx \frac{\Pi}{\tau_{\text{diff}}} [f_a D_a + (1 - f_a) D_b] \quad (7.30)$$

for the effective (i.e., long-range) diffusivity.

³ Anomalies are however expected on shorter time scales below the ms regime as they are accessible with the fringe-field variant of field-gradient diffusometry. In this case, anomalies have been observed indeed (see Ref. [29]).

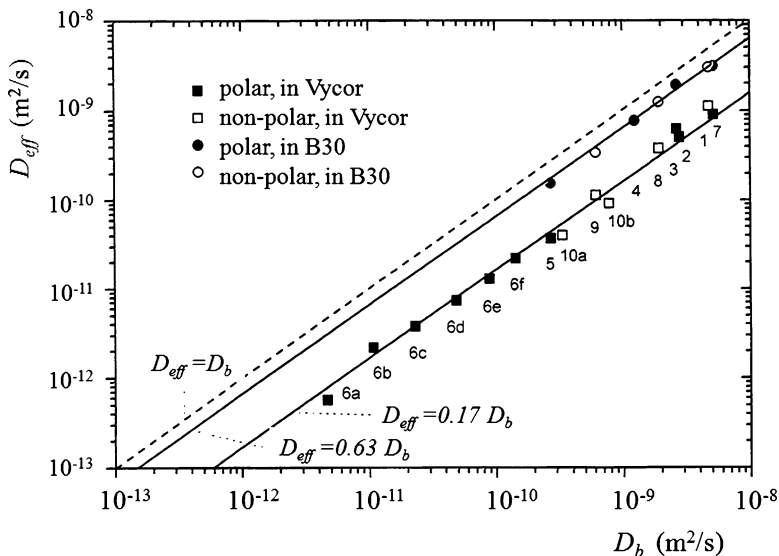


Fig. 7.4 Self-diffusion coefficients of diverse low-molecular liquids in porous silica glasses with trade names Bioran B30 and Vycor. The respective nominal pore diameters are 30 and 4 nm. The effective diffusion coefficients D_{eff} measured under confinement are plotted versus the bulk values D_b . The solvent species and the temperatures are specified in the plot by numbers and letters: (1) acetone at 303 K; (2) toluene at 303 K; (3) water at 303 K; (4) ethanol at 303 K; (5) hexanol at 303 K; (6a-6f) glycerol at temperatures between 305 and 378 K; (7) hexane at 303 K; (8) cyclohexane at 303 K; (9) tetradecane at 303 K; (10a and b) octacosane at 343 and 373 K, respectively. The reduction factors of the diffusion coefficients under confinement relative to the bulk values were found to be 0.63 and 0.17 for Bioran B30 and Vycor, respectively, independent of the solvent species. The *dashed line* represents the expectation in the absence of the confinement effect. All data have been measured with the aid of field-gradient NMR diffusometry. Note that the results are neither affected by internal field gradients nor by the dipolar correlation effect as demonstrated in Ref. [23] (Reprinted from Ref. [28] with kind permission of © Elsevier 1996)

Equation (7.30) can be rewritten in the form

$$\frac{D_{eff}}{\Pi D_b} \approx \frac{1}{\tau_{diff}} \left[f_a \frac{D_a}{D_b} + (1 - f_a) \right] \quad (7.31)$$

All quantities on the left-hand side can be measured separately. For the porous glasses Bioran B30 and Vycor to which the data in Fig. 7.4 refer, the porosities are $\Pi = 0.68$ and 0.28 , respectively. Accordingly, the respective values of the term on the left-hand side of Eq. (7.31) are $D_{eff}/(\Pi D_b) = 0.94 \pm 0.09$ and 0.61 ± 0.05 . The populations of the adsorbed phase can further be estimated as $f_a \approx 0.06$ and 0.4 for minimum surface coverage assuming that the adsorbed phase consists of monomolecular surface layers.

From Vycor to Bioran, the value of the left-hand side of Eq. (7.31) varies by a factor of 1.5, whereas the variation of the populations in the adsorbed phase is only

a factor of 0.15, that is, 10 times less. Since the diffusion coefficient in the adsorbed phase, D_a , and hence the ratio, D_a/D_b , is expected to be practically the same in both silica systems, the conclusion can only be that it is essentially the *tortuosity* that causes the difference in the effective (long-range) diffusion coefficients between the two sample systems. Dynamics within the adsorbed phase are obviously of minor importance in the context of translational diffusion.

This statement is all the more valid for results measured with methods such as quasi-elastic neutron scattering. The displacement length scale probed is then smaller than the pore dimension. In this case, the reduction of the diffusion coefficient under confinement conditions turned out to be minor or even negligible [30–32].

The discussion so far refers to temperatures near room temperature. Below the freezing temperatures of the bulk-like phases, quite interesting diffusion properties arise in so-called nonfreezing surface layers. A discussion follows in Sect. 7.4.2.

7.4.1.2 Aqueous Dispersions and Agglomerates of Fine-Particles

Apart from solid porous matrix materials, suspensions and agglomerates of colloids or fineparticles⁴ in a sense also form mesoscopic pore spaces depending on the particle concentration and diameter. Water diffusion in aqueous particle suspensions is again determined by tortuosity and obstruction effects due to the presence of impenetrable surfaces. Moreover, fractal structure properties of agglomerates have been identified in a wide scaling range [33]. Diffusion anomalies can therefore be expected analogous to those predicted for fractal percolation clusters [10, 11]. Deviations from Fickian diffusion are actually revealed by experimental studies as reported in Ref. [34], for example.

With decreasing water content, the population in the adsorbed phase increases so that the interplay of bulk-like and adsorbed water matters more and more. In cases where the suspension is not too compact, fine particles retain some degree of translational freedom. The fine particles together with their adsorption layers will therefore contribute to water displacements as well and consequently complicate the analysis of the diffusion behavior. In the following, we will focus on another sort of “fine particles” with mesoscopic diameters, namely, large globular proteins which are of considerable interest in life science.

7.4.1.3 Aqueous Solutions of Globular Proteins

Water in aqueous protein solutions and biological tissue is more than just a solvent. Rather, it may even act as a structure-forming and stabilizing element of biopolymers. Modeling of water dynamics by a simple two-phase/fast-exchange concept for diffusion nevertheless turned out to be quite successful despite of its

⁴Trade names of frequently studied, more or less monodisperse silica fine particles are *Alfasil* and *Cab-o-sil* with diameters ranging from a few up to several tens of nanometers.

crudeness. We will therefore restrict ourselves to this approach, keeping in mind that the adsorbed phase may include structure-forming water molecules and exchangeable hydrogen atoms intrinsic to the protein structure. The adsorbed phase is thus considered to represent average properties of the adsorbed water on the one hand and of all subphases possibly contributed by protein constituents on the other.

A typical globular protein of medium size is bovine serum albumin (BSA). It has a molecular mass of about 67,000 Dalton and a prolate ellipsoid shape of dimensions $14 \times 4 \times 4 \text{ nm}^3$. In this sense, the macromolecule can be considered as a mesoscopic colloid particle. Aqueous solutions (or in colloid terminology “dispersions”) can be prepared in the whole concentration range from extreme dilution to practically dry materials.

Figure 7.5 shows the average water diffusion coefficient in aqueous BSA solutions as a function of the BSA concentration at room temperature [35]. There is a continuous decrease of the diffusion coefficients with increasing protein concentration until a sudden cutoff is reached at $c_p \approx 85\%$

This concentration dependence can be interpreted as follows: At relatively low protein concentrations $c_p < 50\%$, the bulk-like water phase dominates. On length scales much larger than the nearest neighbor distance of the (quasi-static) protein molecules, water diffusion will merely be obstructed by macromolecular obstacles according to the empirical relation [36, 37]

$$D_w = D_b(1 - \beta\phi) \quad (7.32)$$

where D_b is the water diffusion coefficient for infinite dilution, ϕ is the volume fraction of the protein, and β is a numerical factor characterizing the shape of the protein molecules. Equation (7.32) is an approximate variant of Eq. (7.30) for $f_a \ll 1$, $\tau_{\text{diff}} \approx 1$, and $\Pi \equiv (1 - \phi) \approx (1 - \beta\phi)$.

Strong tortuosity effects are expected to come into play at protein concentrations around $c_p \approx 50\%$ where the porosity takes similar values as in the case of the porous silica glasses considered in Sect. 7.4.1.1. The full version of Eq. (7.30) is applicable. Finally, beginning with a protein concentration of about 65%, the bulk-like phase vanishes. All water in the system must then be attributed to the adsorbed phase. At this threshold concentration, the overlapping hydration shells form a continuous (i.e., percolating) network as will be shown further down.

At still higher concentrations, $c_p > 65\%$, the adsorbed phase shrinks more and more until the percolating network of the overlap of the hydration shells will be disrupted. The consequence is that hydration shells become unsaturated. Water remains merely in the form of finite clusters on the protein surfaces. The size of the network still accessible for water diffusion falls below a kind of percolation threshold. Water diffusion is then restricted to displacements within isolated clusters and can no longer be measured with ordinary field-gradient NMR diffusometry (see the cutoff in Fig. 7.5). Interestingly, a percolation transition just of that sort was concluded from dielectric studies of the proton conductivity [38].

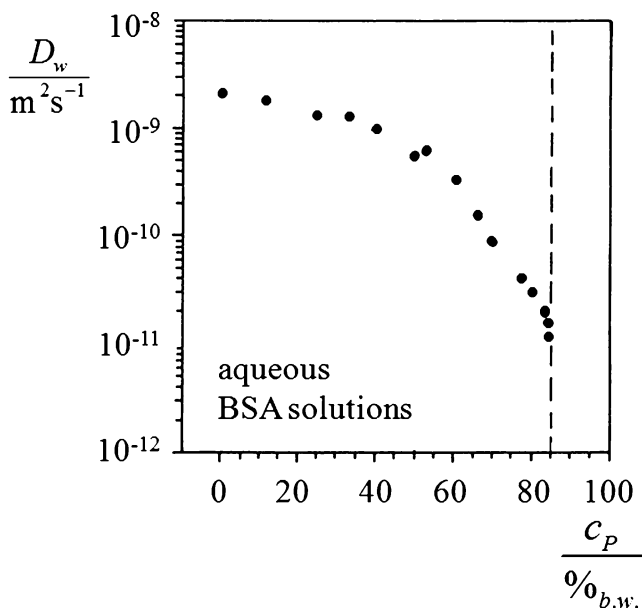


Fig. 7.5 Water diffusion coefficient in aqueous bovine serum albumin (BSA) solutions as a function of the protein concentration by weight, c_p [35]. The proton data were recorded at 20 °C with a field-gradient NMR diffusometry technique. The spin-echo technique practically ensures that the diffusion data refer selectively to the water signal component. The effective diffusion time is 10 ms so that the root-mean-square displacements are in the order of micrometers and exceed the correlation length of the system by far. The data therefore represent *effective* values. At protein concentrations above 87%, the transverse relaxation time drops below 1 ms, so that no diffusive echo attenuation could be measured anymore under the instrumental conditions of that study

7.4.2 Translational Diffusion in the Adsorbed Phase

The findings summarized in the previous section suggest that dispersions of colloid particles compacted to concentrations where no space is left for the bulk-like phase permit diffusion studies selectively in the adsorbed phase provided it is still saturated. The only liquid in the system is then adsorbed.⁵ Another strategy for the examination of diffusion in hydration shells is to take advantage of the different freezing temperatures of the bulk-like and adsorbed phases. It is known that adsorbed phases tend to freeze at a lower temperature than the corresponding bulk-like phases [13–15]. In suitable adsorbate/adsorbent combinations, the experimental temperature can be chosen just between the two freezing temperatures, so that the bulk-like phase will be frozen while the adsorbate phase is still liquid.

⁵ Under such conditions, one must make sure that all remaining pore space is actually filled with liquid. Otherwise, a third phase, namely, the vapor of the liquid, can contribute or even dominate. This phenomenon will be discussed in Sect. 7.4.4.

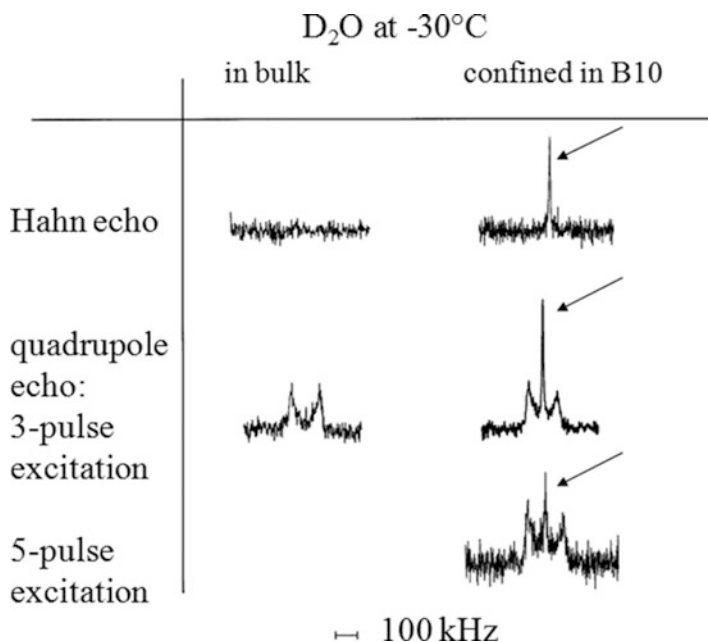


Fig. 7.6 ^2H NMR spectra of heavy water in bulk and confined in a porous silica glass (trade name Bioran B10; nominal pore diameter 10 nm). The deuteron resonance frequency was 46 MHz. At a temperature of -30°C , the bulk-like phase of water is already frozen, whereas the adsorbed phase is still liquid. The so-called *nonfreezing surface layers* are demonstrated in the spectra as *narrow lines* (marked by arrows). Such lines indicate motional narrowing as expected in the liquid state. The spectra acquired on the basis of Hahn spin echoes are selectively sensitive to liquid phases, while signals of solid constituents are suppressed. On the other hand, quadrupole echoes generated in 3 or 5 radio frequency pulse experiments reveal both signals from the solid (i.e., frozen) bulk-like and the liquid adsorbed phases as demonstrated by the superposition of Pake-like spectra due to “solid” signals and Lorentzian-like lines produced by “liquid” signals. The interested reader finds treatments of so-called *solid echoes* in comparison to spin echoes of the Hahn type in Ref. [39], for instance (Reprinted from Ref. [23] with kind permission of © AIP 1998)

The different freezing behaviors of the bulk-like and the adsorbed phases can be demonstrated with the aid of NMR spectroscopy. Figure 7.6 shows deuteron spectra recorded in partially frozen samples with a series of pulse sequences suitable for the distinction of liquid and solid phases.

In such partially frozen samples, all perceptible diffusion takes place in the liquid surface layers forming the adsorbed phase.⁶ This diffusion-sensitive part of

⁶ Immaterial diffusion of spins by flip-flop spin transitions in the frozen material, the so-called *spin diffusion* mentioned several times before, can be excluded for deuterons but might be effective for protons in principle. By all means, the influence on the diffusion behavior in the liquid phase will be entirely negligible, owing to the weak coupling between fluid and solid [23, 40].

the pore space is somewhat imprecisely referred to as *nonfreezing surface layers*.⁷ (See also the illustration in Fig. 7.16 to which we will get back in the context of reorientational dynamics at surfaces.)

7.4.2.1 Aqueous Solutions of Globular Proteins

Let us resume the discussion of aqueous solutions of globular proteins started in Sect. 7.4.1.3. Figure 7.7 represents a diffusion study of water in myoglobin solutions as a function of the inverse temperature for different water contents [35].

Depending on the water content, freezing of bulk-like water results in a more or less abrupt decay of the diffusion coefficient to a concentration independent value below about 270 K. For a water content of 30%, this cross-over is no longer visible. The only liquid phase is then hydration water on either side of the critical crossover temperature.

The fact that translational diffusion with root-mean-square displacements in the order of micrometers can nevertheless be measured in partially frozen samples indicates that the hydration shells form “infinite” percolation clusters permitting displacements from hydration shell to hydration shell over numerous protein molecules as schematically illustrated in Fig. 7.8. Essentially, the character of the cluster of overlapping hydration shells does not change with the water content. The diffusion properties of the adsorbed phase of partially frozen samples should therefore be independent of the water content as long as the hydration shells are saturated. This is demonstrated in Fig. 7.7 and in Fig. 7.9 for data of the partially frozen samples up to protein concentrations of about 65%.

At water contents below saturation, that is, below about 35%, no bulk-like phase exists anymore so that all water remains liquid even if the temperature falls below the bulk freezing temperature. A description is then possible by a simple Arrhenius law for the whole temperature range:

$$D_w = D_\infty \exp\left\{-\frac{E_a}{RT}\right\} \quad (7.33)$$

(compare the data in Fig. 7.7 for a water content of 30% which can be described by a monoexponential decay). The apparent activation energy for translational diffusion, E_a , evaluated on this basis is 20.8 kJ/mol which is about the same as in bulk water. Obviously, water diffusion in the adsorbed phase is strikingly fast, suggesting almost unrestricted translational degrees of freedom on the network of the nonfreezing surface layers. A similar conclusion was drawn for diffusion in the interstitial water inherently incorporated in single crystals (!) of sperm whale

⁷ Incidentally, the peculiar thermodynamic properties of interfacial water at low temperatures have found much attention especially in the biopolymer community. The ongoing discussion of this topic is demonstrated by a recent quasi-elastic neutron scattering study reported in Ref. [41] and other references cited therein.

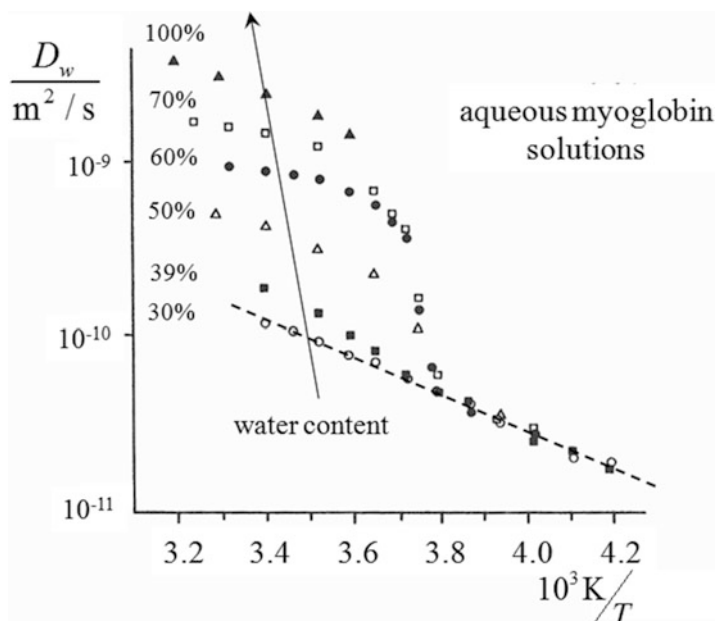


Fig. 7.7 Temperature dependence of the water diffusion coefficient in aqueous myoglobin solutions with different water contents [35]. The proton data were measured with the pulsed field-gradient NMR diffusometry technique for protons. The root-mean-square displacements exceed the correlation length of the system by far, so that the data must be considered as *effective* ones. The *dashed line* represents an Arrhenius law according to Eq. (7.33)

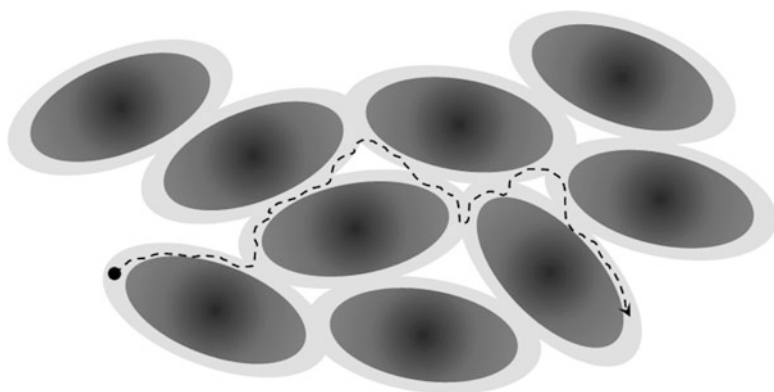


Fig. 7.8 Schematic representation of the overlapping network of the liquid hydration layers in colloidal particle agglomerates. This network permits diffusive displacements of adsorbate molecules exceeding the particle dimension by far and thus makes experimental studies with field-gradient NMR diffusometry feasible in the absence of the bulk-like phase

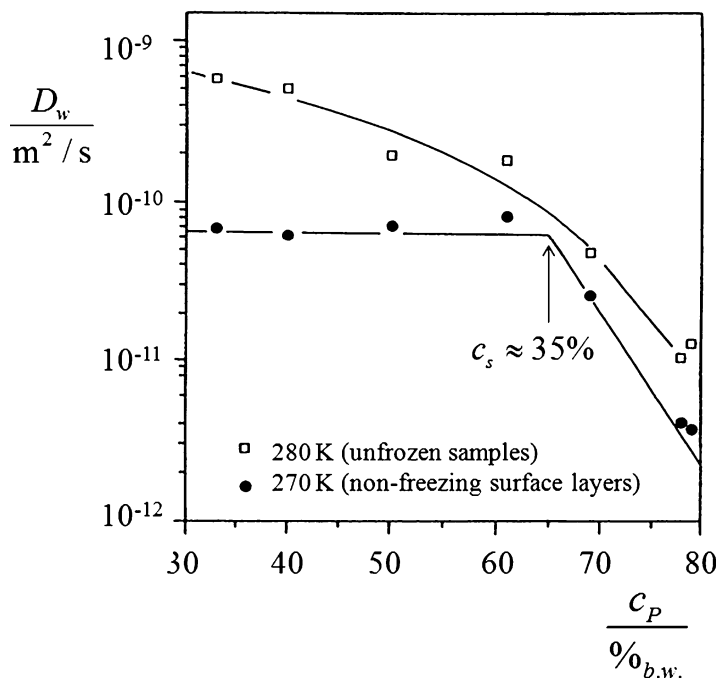


Fig. 7.9 Water diffusion coefficient in aqueous bovine serum albumin (BSA) solutions as a function of the protein concentration by weight [35]. The temperatures were chosen above and just below the freezing temperature of the bulk-like phase. The proton data have been measured with field-gradient NMR diffusometry with a diffusion time of 20 ms. The sharp bend of the curve for the partially frozen sample at 270 K indicates the saturation water concentration of the hydration shells $c_s \approx 35\%$

myoglobin [43]. Findings of this sort are confirmed by molecular-dynamics simulations and neutron scattering data as reported in Ref. [44].

Diffusion in the adsorbed phase can also be determined indirectly via spin relaxation by coupling to electron-paramagnetic centers at the protein surface. In Ref. [45], bovine serum albumin covalently labeled with (electron-paramagnetic) nitroxide radicals has been examined in this way. The analysis of the proton spin-lattice relaxation dispersion generated by dipolar coupling to the paramagnetic relaxation sinks suggests a *local* water diffusion coefficient of about $3 \times 10^{-10} \text{m}^2/\text{s}$ within the first nm from the protein surface. According to Fig. 7.9, this value fits very well to the data measured in the nonfreezing surface layer after correction for the different temperatures at which the experiments were carried out and in view of the fact that the nitroxide label study was performed in the unfrozen, that is, unconstrained system. It should also be kept in mind that the nitroxide-label-based value reflects rather short displacements in the order of nanometers, while the 270-K data in Fig. 7.9 refer to displacements over numerous hydration shells forming a percolation network of nonfreezing surface layers.

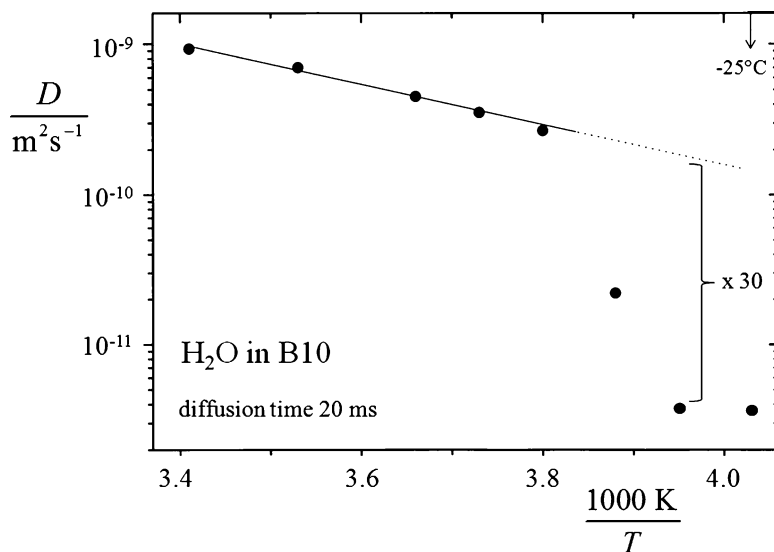


Fig. 7.10 Self-diffusion coefficient of water confined in a sample of porous silica glass (product name Bioran B10, nominal pore size 10 nm) as a function of the reciprocal temperature. The data have been measured with the aid of field-gradient NMR diffusometry with a diffusion time of 20 ms (Reproduced from Ref. [23] with kind permission of © AIP 1998)

7.4.2.2 Porous Silica Glasses

Diffusion in the adsorbed phase in saturated porous glasses can be studied in the same way as with the protein systems discussed above. A typical example revealing the crossover to the partially frozen state of the confined water is demonstrated by the data in Fig. 7.10. At about -25°C , the bulk-like phase is totally frozen.⁸ Merely the interfacial adsorbate layer is still liquid and determines the diffusivity measured in the system. Actually, the fact that we are really dealing with a liquid phase is best demonstrated just by this effect, namely, the long-distance translational diffusion of molecules confined in the interfacial network. The evaluation of the fraction of the resonance line of the liquid material (see Fig. 7.6) suggests a thickness of the nonfreezing surface layer of 0.5 nm at -30°C . This corresponds to one to two molecular monolayers.

According to Fig. 7.10, the water diffusion coefficient measured in the nonfreezing surface layers is a factor of 30 less than the extrapolated value of the unfrozen

⁸ Note that – irrespective of the nonfreezing surface layers – the freezing temperature of the bulk-like phase is reduced slightly according to the *Gibbs/Thomson relation* which predicts a depression proportional to the surface-to-volume ratio of the pores [46]. On this basis, NMR techniques have been suggested for the determination of the pore size and its distribution [47, 48]. With these methods, the freezing temperature is determined by the more or less abrupt change of the NMR linewidth at the phase transition.

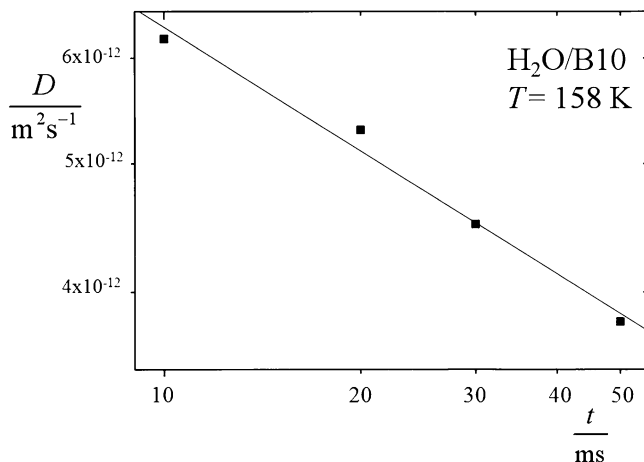


Fig. 7.11 Field-gradient NMR diffusometry data for water in the percolation network formed by the adsorbed phase of a porous silica glass (Bioran B10) at -15°C . The bulk-like water is frozen at this temperature (Reproduced from Ref. [23] with kind permission of © AIP 1998)

liquid. At first sight, this reduction factor appears to be excessive. However, translational diffusion takes place in a network of only one to two molecular diameter thick surface layers. Thus, the porosity is strongly reduced, while the tortuosity is increased (compare Eq. 7.30). In view of these modified conditions, the reduction by a factor of 30 appears to be quite plausible. It is largely due to the topological-confinement effect and not to immobilization at adsorption sites.

A further phenomenon characteristic for diffusion in nonfreezing surface layers is that the self-diffusion coefficient turns out to be time dependent, $D = D(t)$, which indicates anomalous diffusion properties as expected in the scaling window of porous media (see Eq. 7.6). The power law evaluated from the data in Fig. 7.11 is

$$D \propto t^{-0.3} \quad (7.34)$$

in a range from 10 to 50 ms. The percolation network formed by the hydration shells upon freezing of the bulk-like phase appears to approach fractal properties with a particularly long correlation length [10, 11].

7.4.3 Single-File Diffusion

Even in the percolation network formed by the nonfreezing surface layers of porous silica samples, the pore dimensions effective for diffusion are large enough to permit at least topologically two-dimensional displacements of the incorporated fluid molecules. We now turn to systems that allow only for one-dimensional

displacements. Certain zeolites and molecular sieves can have straight pore channels with diameters not much larger than the incorporated fluid molecules. The consequence is that molecules cannot pass each other. Displacement steps can only occur in a single-file manner. As a consequence of this sort of *obstruction effect*, subdiffusive displacement features show up. An illustration is shown in Fig. 2.22.

Single-file diffusion has been demonstrated with the aid of Monte Carlo simulations for the displacement of particles in an elementary one-dimensional system with cyclic boundary conditions [49] or under more advanced conditions with variable channel width [50, 51]. The displacement dynamics of an ensemble of N particles can be described by superimposed equilibration (or “relaxation”) modes with relaxation times increasing with the length scale of the system. The longest relaxation time refers to the total system consisting of N particles. Beyond this time scale, diffusion becomes normal, and a time-independent diffusion coefficient

$$D_{\infty} \propto N^{-1} \quad (7.35)$$

can be defined. In the long-time limit, the particle ensemble is randomly displaced as a whole. At times shorter than needed for complete equilibration, diffusion tends to be subdiffusive, and the time dependence of the mean square particle displacement can be described by

$$\langle z^2 \rangle \propto t^{1/2} \quad (7.36)$$

where z is measured along the one-dimensional pore channel. In this respect, the attentive reader may remember the analogous behavior of polymers reptating in a tube (see Eq. 5.241).

The subdiffusive mean square displacement law Eq. (7.36) was experimentally verified in Refs. [52, 53] using the field-gradient NMR diffusometry technique. The system studied in Ref. [52] consisted of CF_4 molecules (diameter ca. 0.47 nm) confined in pores of zeolite $\text{AlPO}_4\text{-5}$ (pore channel diameter ca. 0.73 nm) at 180 K. The experimental time scale on which Eq. (7.36) was verified was 1–300 ms. It is needless to say that the pore length considerably exceeded the maximum root-mean-square displacement probed in the experiments (ca. 3 μm). End effects owing to exchange with the outside medium did therefore not matter. Furthermore, it was demonstrated that the obstruction effect increases with the CF_4 loading degree of the pores for obvious reasons.

7.4.4 Diffusion Enhanced by a Coexisting Vapor Phase

If the pore space of porous materials or particle agglomerates is not completely filled with liquid, the vapor of the liquid inflating the free space will contribute to diffusion appreciably as a third phase. The diffusivity in the gas phase is four orders of magnitude larger than in the liquid phase whereas the density is three orders of

magnitude smaller. In the case of field-gradient NMR diffusometry, exchange between the diverse phases on the experimental time scale thus leads to the peculiar situation that the measured diffusivity is dominated by the vapor while the liquid phase is responsible for most of the signal. Enhancement factors up to 10 above the value of the bulk liquid were observed in unsaturated pore spaces just contrary to the opposite tendency suggested by the pore-space confinement [54–58].

In Ref. [56], the enhancement of translational diffusion by the vapor phase was directly proven in wet silica fine-particle powders by varying the accessible volume. The adsorbed water phase at the fine-particle surfaces was first saturated by exposing the powdery material to a humid atmosphere. In this initial state, the sample forms a lacunar system containing a considerable volume fraction of free space available to the vapor phase. The initially loosely packed powder was then compacted step by step down to 1/7 of the original volume. As a consequence, the diffusivity initially dominated by the vapor phase was gradually diminished until the bulk water diffusion coefficient was reached at the strongest densification. This is revealed by the data in Fig. 7.12: The initially steep spin-echo attenuation curves indicate a high diffusivity dominated by the vapor phase. The crossover to flat curves after maximum compaction reflects a much lower diffusivity approaching that of bulk water in the absence of the vapor phase.

So far, so plausible. However, the situation is a bit more complicated than expected at first sight. The example described above refers to a polar liquid in a matrix with polar surfaces. This is to be distinguished from a scenario where a nonpolar solvent is filled into a polar matrix (or vice versa). As concerns the effective diffusivity resulting under such circumstances, the tendency can be even opposite [57]. The second question to be clarified is whether the fast-exchange limit one intuitively anticipates is warranted. Actually, this is a matter of the pore size as will be elucidated below [58]. Finally, it must be clarified to what degree diffusion in the vapor phase is of the ordinary *Einstein* type (determined by particle–particle collisions) or of the *Knudsen* type (limited by particle–wall collisions) [59, 60].

7.4.4.1 Exchange Model for Diffusion in Coexisting Liquid and Vapor Phases

In terms of the exchange concept discussed above, one suspects that translational diffusion in unsaturated porous media is determined by all three fluid phases, namely, the adsorbed, bulk-like, and vapor phases. However, as outlined above, the finding for saturated porous media is that the bulk-like phase dominates translational diffusion on the time/length scales of typical field-gradient NMR diffusometry experiments. The decisive factors determining the diffusivity were shown to be the porosity and the tortuosity, whereas adsorption normally plays a

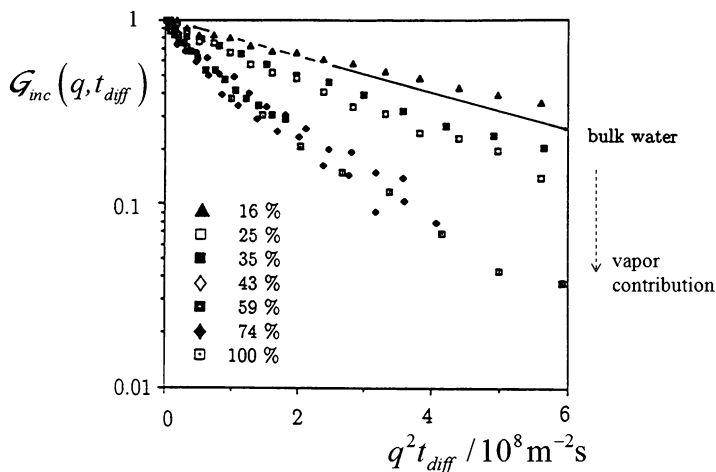


Fig. 7.12 Field-gradient NMR diffusometry data for the incoherent dynamic structure factor $G_{inc}(q, t_{diff})$ of water in a silica fine-particle sample (product name “Alfasil”; particle diameter 7 nm; specific surface area 400 m²/g). These room temperature data are plotted as a function of $q^2 t_{diff}$, where the wave number q is proportional to the amplitude and width of the gradient pulses, and the effective diffusion time $t_{diff} = \Delta - \delta/3$ depends on the timing of the gradient pulses (see Eq. 3.246). The curves refer to different degrees of compaction: 100% corresponds to the uncompressed sample with the fine-particle powder just exposed to a humid atmosphere to reach saturation of the hydration shells. The saturation water content was 38% by weight. The volume of the sample under strongest compaction was reduced to 16% of the volume of the uncompressed sample. Steeper decays mean higher effective diffusivities. The diffusivity is thus reduced upon compaction of the sample (Reproduced from Ref. [56] with kind permission of © Elsevier 1994)

minor role. The treatment of diffusion in unsaturated porous media can therefore be restricted to two phases only, liquid and vapor, forming two interpenetrating systems of different topology and porosity.⁹

In the following, the liquid contribution will be labeled by the subscript ℓ , and the vapor phase will be marked by the subscript v . The mass fractions f_i in the two phases are related with the respective mean residence times τ_i by [61, 62]

$$f_i = \frac{\tau_i}{\tau_\ell + \tau_v} \quad (i = \ell, v) \quad (7.37)$$

In terms of the mass densities ρ_ℓ and ρ_v , the respective mass fractions read

⁹It should be emphasized that this approach is appropriate for *translational* diffusion at typical experimental time and length scales. A totally different situation arises for *rotational* diffusion as probed by spin relaxation to be discussed further down.

$$f_\ell = \frac{1}{1 + [(V_0/V_\ell) - 1](\rho_v/\rho_\ell)} = \frac{F}{F + (1 - F)(\rho_v/\rho_\ell)} \quad \text{and} \quad f_v = 1 - f_\ell \quad (7.38)$$

where V_0 represents the pore-space volume, V_ℓ is the volume of the liquid phase, and

$$F = \frac{V_\ell}{V_0} \quad (7.39)$$

is the filling factor of liquid in the pore space.

In Sect. 7.4.1.1, diffusive transport in saturated pore spaces was shown to depend on geometrical restrictions represented by the matrix parameters *diffusive tortuosity* τ_{diff} and *porosity*

$$\Pi = \frac{V_0}{V_t} \quad (7.40)$$

(see Eq. 7.30). The total sample volume including matrix and pore space is denoted by V_t , while V_0 is the pore-space volume. In order to link these two parameters, one can try a tentative ansatz based on *Archie's law* [1]. This empirical relation was originally proposed for the description of the electrical conductivity in saturated fluid-filled pore spaces. It appears to work satisfactorily with oil well logging applications. It is not so well established with partially saturated porous media where substantial deviations from its predictions have been observed [63]. Moreover, in Sects. 4.9.5 and 4.9.6, the comparison of coherent material and electrical transport properties revealed some intricacies which are not yet entirely understood. The discrepancies in the transport features may however be less severe if material transport is incoherent, that is, a matter of self-diffusion. Let us therefore and nevertheless try the tentative power law

$$\tau_{\text{diff}} \approx \Pi^{-\varepsilon} \quad (7.41)$$

as an approach with an analytical form analogous to Archie's law. ε is an empirical exponent. Referring to Eqs. (4.83) and (7.3), the effective (long-range) diffusion coefficient in the pore space, D_{eff} , is accordingly expected to be reduced by a factor Π^ε relative to its bulk value, D_0 :

$$D_{\text{eff}} = \Pi^\varepsilon D_0 \quad (7.42)$$

In the case of unsaturated porous samples, the situation is more complicated since we are then dealing with two interpenetrating pore systems of different effective porosities

$$\Pi_\ell = \frac{V_\ell}{V_t} \quad \text{and} \quad \Pi_v = \frac{V_0 - V_\ell}{V_t} \quad (7.43)$$

for the liquid and vapor phases, respectively. Employing the ansatz Eq. (7.42) again, the reduced diffusion coefficient in the liquid phase can be written in the form [64, 65]

$$D_\ell = \Pi_\ell^{\varepsilon_\ell} D_{\ell,0} = \Pi^{\varepsilon_\ell} \left(\frac{V_\ell}{V_0} \right)^{\varepsilon_\ell} D_{\ell,0} = \Pi^{\varepsilon_\ell} F^{\varepsilon_\ell} D_{\ell,0} \quad (7.44)$$

where the exponent ε_ℓ is specific for the liquid phase. $D_{\ell,0}$ is the diffusion coefficient in the bulk liquid. Equation (7.44) thus links the porosity effective for the liquid phase, Π_ℓ , to the porosity of the whole sample, $\Pi = \Pi_\ell + \Pi_v$.

The diffusion process in the vapor phase is determined by collisions of molecules on the one hand with each other and with the pore walls on the other. The term “wall” may refer both to liquid–vapor interfaces and to inner surfaces of the solid matrix. The latter mechanism is referred to as *Knudsen diffusion*. As suggested in Ref. [66], the diffusion resistance D_v^{-1} in the vapor phase is composed of the individual diffusion resistances according to a “serial connection”

$$\frac{1}{D_v} = \frac{1}{D_K} + \frac{1}{D_E} \quad (7.45)$$

D_K^{-1} is the Knudsen diffusion resistance relevant if molecule/wall collisions would solely determine the diffusion process. Likewise, D_E^{-1} is the Einstein diffusion resistance which would be pertinent if molecule/molecule collisions would limit the displacement rate.

Anticipating the power-law ansatz Eq. (7.42) again, the quantities D_K and D_E can be represented in terms of diffusive tortuosity factors as before. This permits us to relate the diffusivities under pore constraints with those under bulk conditions:

$$D_K \approx \Pi_v^{\varepsilon_{v,K}} D_{K,0} = \Pi^{\varepsilon_{v,K}} \left(1 - \frac{V_\ell}{V_0} \right)^{\varepsilon_{v,K}} D_{K,0} = \Pi^{\varepsilon_{v,K}} (1 - F)^{\varepsilon_{v,K}} D_{K,0} \quad (7.46)$$

$$D_E \approx \Pi_v^{\varepsilon_{v,E}} D_{v,0} = \Pi^{\varepsilon_{v,E}} \left(1 - \frac{V_\ell}{V_0} \right)^{\varepsilon_{v,E}} D_{v,0} = \Pi^{\varepsilon_{v,E}} (1 - F)^{\varepsilon_{v,E}} D_{v,0} \quad (7.47)$$

The exponents $\varepsilon_{v,K}$ and $\varepsilon_{v,E}$ account for tortuosity effects under Knudsen and Einstein conditions, respectively. These quantities can be determined empirically on the basis of bulk diffusion data [66]. The vapor diffusion coefficient in the Einstein resistance limit $D_E^{-1} \gg D_K^{-1}$, when molecule/molecule collisions are rate limiting, is denoted by $D_{v,0}$. As a matter of course, this quantity equals the vapor diffusion coefficient *in bulk*.

On the other hand, if the diffusion resistance by molecule/wall collisions prevails, one speaks of the Knudsen limit $D_K^{-1} \gg D_E^{-1}$. In this case, the vapor diffusion coefficient will be $D_{K,0}$ which is specified in Ref. [59] as

$$D_{K,0} \approx \frac{2a}{3} \sqrt{\frac{8k_B T}{\pi m}} \quad (7.48)$$

where k_B is the Boltzmann constant, T is the absolute temperature, m is the molecular mass, and a is the mean radius of the vapor-phase domains.

Under wetting conditions, that is, if adhesive forces at the pore walls outbalance the cohesive tendency, the liquid in partially saturated pores will cover the walls in the form of a more or less homogeneous layer. Furthermore, approximating the pore by a hollow cylinder for simplicity, permits us to estimate the diameter of the vapor phase domain as a function of the liquid filling factor F [55, 66]:

$$2a \approx d(1 - F)^{1/2} \quad (7.49)$$

where d represents the mean pore diameter. Combining this with Eq. (7.48) gives the quantity

$$D_{K,0}(F) \approx \frac{d}{3} \sqrt{\frac{8k_B T(1 - F)}{\pi m}} \quad (7.50)$$

needed for the determination of the Knudsen diffusion resistance D_K^{-1} on the basis of Eq. (7.46).

7.4.4.2 Formal Treatment for Field-Gradient NMR Diffusometry

As a standard variant of field-gradient NMR diffusometry, we refer to the stimulated-echo method in the short-gradient pulse limit as described in Sect. 3.2.2.3. The problem is to distinguish partial magnetizations for the two phases under consideration. Coherence evolution during the encoding interval τ_1 (see Fig. 3.25b or d) and the subsequent radio frequency pulse produce longitudinal magnetization components $M_{z,\ell}(z, t)$ and $M_{z,v}(z, t)$ modulated along the field-gradient direction (here arbitrarily assumed along the z -axis of the laboratory frame). In the second radio frequency pulse interval of length τ_2 , these components evolve under the influence of spin–lattice relaxation, diffusion, and interphase exchange.

The combined description of these processes is possible on the basis of the *Hahn/Maxwell/McConnell equations* for exchange and relaxation, Eq. (3.312), suitably supplemented by the right-hand term of *Fick's second law* for diffusion,

Eq. (2.167). We are thus dealing with the following set of equations of motions for the two partial magnetizations:

$$\begin{aligned}\frac{dM_{z,\ell}(z,t)}{dt} &= D_\ell \frac{d^2 M_{z,\ell}(z,t)}{dz^2} - \frac{M_{z,\ell}(z,t) - M_{0,\ell}}{T_{1,\ell}} - \frac{M_{z,\ell}(z,t)}{\tau_\ell} + \frac{M_{z,v}(z,t)}{\tau_v}; \\ \frac{dM_{z,v}(z,t)}{dt} &= D_v \frac{d^2 M_{z,v}(z,t)}{dz^2} - \frac{M_{z,v}(z,t) - M_{0,v}}{T_{1,v}} - \frac{M_{z,v}(z,t)}{\tau_v} + \frac{M_{z,\ell}(z,t)}{\tau_\ell}.\end{aligned}\quad (7.51)$$

The principle of treatments combining relaxation and diffusion was already developed in Ref. [67] in the early days of NMR. The above relations will accordingly be called *Hahn/Maxwell/McConnell/Torrey (HMMT) equations* [58]. $T_{1,\ell}$ and $T_{1,v}$ are the longitudinal relaxation times of nuclear spins in the respective fluid phases in the absence of exchange. $M_{0,\ell}$ and $M_{0,v}$ are the equilibrium magnetizations in the liquid and vapor phases, respectively. The respective mean residence times the adsorbate molecules spend in the liquid and vapor phases are denominated by τ_ℓ and τ_v . Analogously, the self-diffusion coefficients in the two fluid phases are D_ℓ and D_v .

The first term on the right-hand side of either HMMT equation describes self-diffusion inside the individual phases. The second term accounts for longitudinal relaxation in the absence of molecular exchange. The other terms represent exchange rates between the two phases.

As a relatively rough simplification, the HMMT equations anticipate that both phases are spread uniformly in the entire pore space. That is, exchange of molecules between the two phases is assumed to be possible at any position without prior need that the particles diffuse to a liquid/vapor interface. In other words, the time needed for diffusive transport to interfaces is considered to be implied in correspondingly modified exchange rates [58]. Thus, the mean residence times τ_ℓ and τ_v must be taken as *effective* quantities. On the one hand, they are determined by the spatial extensions of the phase regions, and on the molecular mobilities therein on the other. In addition, transport barriers at the interfaces may also play a role.

Neglecting diffusion, relaxation, and exchange during the encoding interval τ_1 of the stimulated-echo RF pulse sequences depicted in Fig. 3.25, the solutions for the longitudinal magnetization components $M_{z,i}(z, 0)$ immediately after the second radio frequency pulse are given by

$$M_{z,i}(z, 0) = -M_{0,i} \cos(qz) \quad (i = \ell, v) \quad (7.52)$$

with the familiar wave number $q = \gamma g \delta$. $M_{0,i}$ is the Curie magnetization of phase i . The field gradient g is assumed to be aligned along the z direction. δ is the width of the gradient pulses, and γ is the gyromagnetic ratio. Equation (7.52) provides the initial conditions for the differential equation system Eq. (7.51).

The diffusion interval τ_2 of the stimulated-echo RF pulse sequence is the proper measuring period in which diffusion and exchange processes are to be probed.

The respective diffusion terms, that is, the first terms on the right-hand sides of the HMMT equations Eq. (7.51), are evaluated as

$$\begin{aligned} D_\ell d^2 M_{z,\ell}(z, t) / dz^2 &= -D_\ell q^2 \\ D_v d^2 M_{z,v}(z, t) / dz^2 &= -D_v q^2 \end{aligned} \quad (7.53)$$

For the ease of calculation, the two partial magnetizations can be combined to the two-dimensional magnetization vectors

$$\mathbf{M}_z(z, t) = \begin{pmatrix} M_{z,\ell}(z, t) \\ M_{z,v}(z, t) \end{pmatrix} \quad \text{and} \quad \mathbf{M}_0 = \begin{pmatrix} M_{0,\ell} \\ M_{0,v} \end{pmatrix} \quad (7.54)$$

In matrix form, the HMMT equation system thus reads (see Sect. 3.4)

$$\frac{d\mathbf{M}_z(z, t)}{dt} = \tilde{L}\mathbf{M}_z(z, t) + \mathbf{R}_0 \quad (7.55)$$

where

$$\tilde{L} = \begin{pmatrix} -\left[q^2 D_\ell + \frac{1}{T_{1,\ell}} + \frac{1}{\tau_\ell}\right] & \frac{1}{\tau_v} \\ \frac{1}{\tau_\ell} & -\left[q^2 D_v + \frac{1}{T_{1,v}} + \frac{1}{\tau_v}\right] \end{pmatrix} \quad \text{and} \quad \mathbf{R}_0 = \begin{pmatrix} \frac{M_{0,\ell}}{T_{1,\ell}} \\ \frac{M_{0,v}}{T_{1,v}} \end{pmatrix} \quad (7.56)$$

The matrix $\tilde{L}$ comprises the rate constants due to diffusion, relaxation, and exchange, while $\mathbf{R}_0$ accounts for longitudinal relaxation. The solution of the linear differential equation given in Eq. (7.55) is

$$\mathbf{M}_z(z, t) = \exp\{\tilde{L}t\}\mathbf{M}_z(z, 0) + \left[\exp\{\tilde{L}t\} - 1\right]\tilde{L}^{-1}\mathbf{R}_0 \quad (7.57)$$

$\tilde{L}^{-1}$ represents the inverse matrix of $\tilde{L}$, and $\mathbf{M}_z(z, 0)$ is the two-dimensional magnetization vector at the beginning of the diffusion interval τ_2 .

The first term on the right-hand side of Eq. (7.57) is spatially modulated via $\mathbf{M}_z(z, 0)$ (see Eq. 7.52). Consequently, it will be this term that is transferred by the third radio frequency pulse into the final signal, the stimulated echo.¹⁰ The second term can be discarded because it does not contribute to the stimulated-echo signal.

The effect of the exponential factor $\exp(\tilde{L}t)$ on the two-dimensional magnetization vector $\mathbf{M}_z(z, 0)$ in Eq. (7.57) can be evaluated by first diagonalizing the matrix and then applying the power series expansion analogous to the treatment outlined in Sect. 3.4.2. The result is

¹⁰ A detailed analysis of echo formation mechanisms can be found in Ref. [39].

$$M_z(t) = M_{z,\ell}(t) + M_{z,v}(t) = A_1 e^{\lambda_{11}t} + A_2 e^{\lambda_{12}t} \quad (7.58)$$

This is the magnetization to which the amplitude of the stimulated echo $a_{\text{st}}(q, t)$, that is, the signal to be measured in this sort of experiment, will finally be proportional. Under the conditions mentioned above, the diffusion time t can be equated with the interval τ_2 . The effective rates $\lambda_{1,2}$ in the exponents are given by

$$\lambda_{1,2} = -\frac{1}{2} \left[q^2(D_\ell + D_v) + \frac{1}{T_{1,\ell}} + \frac{1}{T_{1,v}} + \frac{1}{\tau_\ell} + \frac{1}{\tau_v} \right. \\ \left. \mp \sqrt{\left(q^2(D_\ell - D_v) + \frac{1}{T_{1,\ell}} - \frac{1}{T_{1,v}} + \frac{1}{\tau_\ell} - \frac{1}{\tau_v} \right)^2 + \frac{4}{\tau_\ell \tau_v}} \right] \quad (7.59)$$

The amplitude factors are found to be

$$A_{1,2} = \pm \frac{\tau_v}{\lambda_2 - \lambda_1} \left[\left(\lambda_{1,2} + q^2 D_\ell + \frac{1}{T_{1,\ell}} + \frac{1}{\tau_\ell} + \frac{1}{\tau_v} \right) \right. \\ \left. \left(\lambda_{2,1} + q^2 D_\ell + \frac{1}{T_{1,\ell}} + \frac{1}{\tau_\ell} \right) M_{z,\ell}(0) - \frac{1}{\tau_v} M_{z,v}(0) \right] \quad (7.60)$$

In the limit defined by the conditions $f_v \ll f_\ell \approx 1$, $D_v \gg D_\ell$, and $T_{1,v} \gg T_{1,\ell}$, the attenuation of the relative stimulated-echo amplitude can be approached by [58, 68]

$$\frac{a_{\text{st}}(q, \tau_2)}{a_{\text{st}}(q, 0)} \propto \exp \left\{ -q^2 \left(D_\ell + \frac{f_v D_v}{q^2 \tau_\ell f_v D_v + 1} \right) \tau_2 \right\} = \mathcal{G}_{\text{inc}}(t = \tau_2) \quad (7.61)$$

The proportionality factor refers to attenuation by spin–lattice relaxation which is a constant contribution, provided that the pulse intervals are kept constant in the experiment. In this limit, the right-hand side thus turns out to be equal to the incoherent dynamic structure factor $\mathcal{G}_{\text{inc}}(t)$ for the particular diffusion time $t = \tau_2$ and an effective diffusion coefficient

$$D_{\text{eff}} \approx D_\ell + f_v D_v (q^2 \tau_\ell f_v D_v + 1)^{-1} \quad (7.62)$$

7.4.4.3 Low Wave-Number Limit ($q^2 \tau_\ell f_v D_v \ll 1$)

For small gradient pulses complying with the low wave-number limit $q^2 \tau_\ell f_v D_v \ll 1$, the effective diffusivity will be reduced to $D_{\text{eff}} \approx D_\ell + f_v D_v$ (not to be confused with the fast-exchange case which will be described further down!). Inserting Eqs. (7.44) and (7.45) into this expression gives

$$\begin{aligned}
D_{\text{eff}} &= \Pi^{\ell_\ell} F^{\ell_\ell} D_{\ell,0} + f_v \frac{D_K D_E}{D_K + D_E} \\
&= \Pi^{\ell_\ell} F^{\ell_\ell} D_{\ell,0} \\
&\quad + \frac{(1-F)}{[(\rho_\ell/\rho_v)F + 1 - F]} \frac{\Pi^{\ell_{v,K}} (1-F)^{\ell_{v,K}} \frac{1}{3} d (1-F)^{\frac{1}{2}} \sqrt{\frac{8k_B T}{\pi m}} \Pi^{\ell_{v,E}} (1-F)^{\ell_{v,E}} D_{v,0}}{\left(\Pi^{\ell_{v,K}} (1-F)^{\ell_{v,K}} \frac{1}{3} d (1-F)^{\frac{1}{2}} \sqrt{\frac{8k_B T}{\pi m}} + \Pi^{\ell_{v,E}} (1-F)^{\ell_{v,E}} D_{v,0} \right)}
\end{aligned} \tag{7.63}$$

where the parameters $f_v, D_K, D_E, D_{K,0}$ have been replaced by the relations given in Eqs. (7.38), (7.46), (7.47), and (7.50). The first term on the right-hand side of Eq. (7.63) is the contribution of the liquid phase, while the second term refers to the vapor phase. In the frame of the low-wave-number limit, the effective diffusivity can then be evaluated by fitting the monoexponential decay function

$$a_{\text{st}}(q, \tau_2)/a_{\text{st}}(q, 0) \propto \exp\{-q^2 D_{\text{eff}} \tau_2\} = G_{\text{inc}}(\tau_2) \tag{7.64}$$

to the initial part of the experimental stimulated-echo attenuation curves. Exemplary data are presented in the plots shown in Fig. 7.13a, b.

In the limit of high liquid filling degrees, $F \rightarrow 1$, Eq. (7.63) approaches

$$D_{\text{eff}}(F \rightarrow 1) \approx \Pi^{\ell_\ell} D_{l,0} F^{\ell_\ell} \propto F^{\ell_\ell} \tag{7.65}$$

Diffusion is then dominated by the contribution of the liquid phase so that the effective diffusion coefficient *increases* with increasing filling degree. The value finally adopted for saturated pore spaces is the bulk value times the factor Π^{ℓ_ℓ} , $D_{\text{eff}}(F = 1) \approx \Pi^{\ell_\ell} D_{l,0}$. In the opposite limit, $F \ll 1$, the effective diffusion follows a reversed tendency

$$D_{\text{eff}}(F \ll 1) \propto \frac{\rho_v}{\rho_\ell} \frac{1}{F} \tag{7.66}$$

where $\rho_\ell/\rho_v \gg 1$ and $F\rho_\ell/\rho_v \gg 1$ (for finite liquid filling degrees). In this case, the effective diffusivity will be dominated by the vapor phase. D_{eff} consequently *decreases* with increasing filling degree. Thus, there are two converse tendencies competing with each other. One therefore expects a minimum at intermediate liquid filling degrees.

7.4.4.4 Slow Liquid/VaporExchange ($\tau_\ell \gg \tau_2$ and $\tau_v \gg \tau_2$)

The exchange dynamics is specified by the respective mean residence times in the liquid and vapor phase, τ_ℓ and τ_v . The experimental time scale is given by the interval τ_2 of the stimulated-echo pulse schemes Figs. 3.25b or d. In the slow-exchange limit, $\tau_\ell \gg \tau_2$ and $\tau_v \gg \tau_2$, molecular exchange can be neglected during τ_2 .

The stimulated-echo signal will then be composed of two independent contributions from the liquid and from the vapor phase. According to Eqs. (7.58) and (7.59), attenuation by diffusive displacements in either phase thus leads to a weighted superposition of two exponentials, one for each phase:

$$\frac{a_{\text{st}}(q, \tau_2)}{a_{\text{st}}(q, 0)} \approx f_{\ell} e^{-(D_{\ell} q^2 + T_{1,\ell})\tau_2} + f_v e^{-(D_v q^2 + T_{1,v})\tau_2} \quad (7.67)$$

Since the number of spins in the vapor phase is usually much smaller than in the liquid phase, $f_v \ll f_{\ell}$, the signal will be governed by the liquid component, that is, by the first term on the right-hand side.

7.4.4.5 Fast Liquid/Vapor Exchange ($\tau_{\ell} \ll \tau_2$ and $\tau_v \ll \tau_2$)

Fast exchange relative to the experimental time scale τ_2 , that is, $\tau_{\ell} \ll \tau_2$ and $\tau_v \ll \tau_2$, means frequent transfers back and forth between the liquid and vapor phases. Molecules experience displacement rates of both phases weighted according to the respective number fractions. The consequence is that diffusion can be described by an effective diffusion coefficient given as the weighted average

$$D_{\text{eff}} \approx f_{\ell} D_{\ell} + f_v D_v \quad (7.68)$$

The coefficients D_{ℓ} and D_v are given in Eqs. (7.44) and (7.45), respectively. Replacing the effective diffusion coefficient in Eq. (7.64) by the expression given in Eq. (7.68) provides the incoherent dynamic structure factor for the fast-exchange limit.

7.4.4.6 Applications to Partially Saturated Porous Silica Glasses

The plots in Fig. 7.13 show typical data for the effective diffusion coefficient D_{eff} as a function of the filling degree F . The data have been measured in cyclohexane and water in unsaturated porous silica glass. These two solvents are taken as representatives for nonpolar and polar adsorbate species, respectively. As a consequence of the different adsorption tendencies to polar surfaces, the distribution of the liquid phases in the pore space varies in a distinguishable way with the imbibing degree [55, 64, 69] as revealed by the effective diffusion behavior. The vapor enhancement effect on diffusion is obvious in both cases.

The respective ratios of the densities in the vapor and liquid phases under normal conditions are $[\rho_v/\rho_{\ell}]_{\text{cyclohexane}} = 5.9 \times 10^{-4}$ and $[\rho_v/\rho_{\ell}]_{\text{water}} = 2.5 \times 10^{-5}$ [70], so that the NMR signal probed in such experiments originates practically entirely from the liquid phase. The diffusivities in the bulk liquids at 298 K are known to be $D_{\ell,0}^{\text{cyclohexane}} = 1.4 \times 10^{-9} \text{ m}^2/\text{s}$ and $D_{\ell,0}^{\text{water}} = 2.3 \times 10^{-9} \text{ m}^2/\text{s}$. These values are to

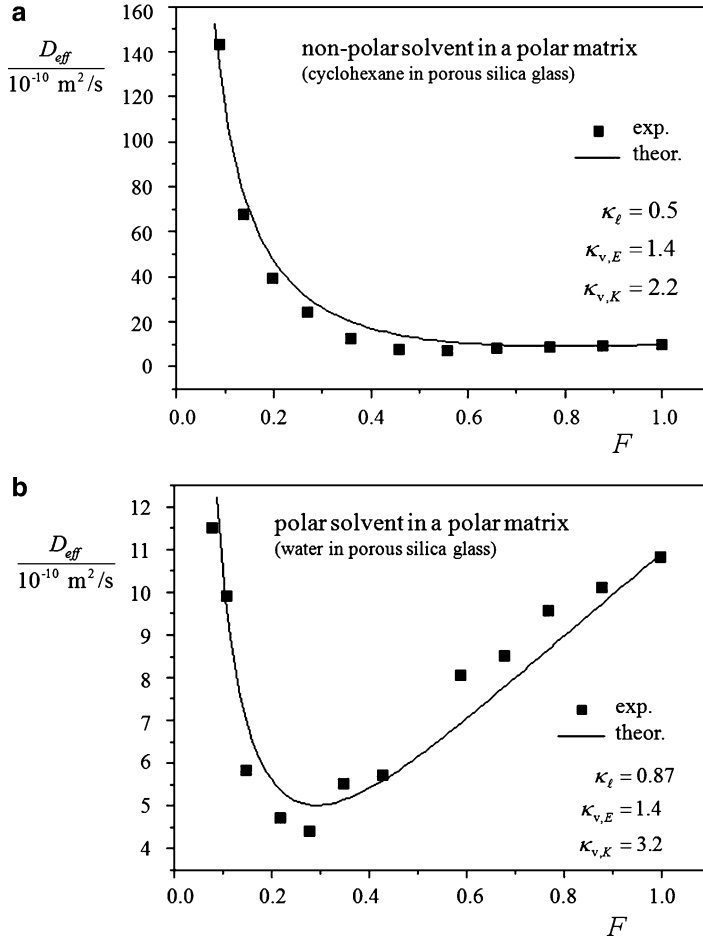


Fig. 7.13 Effective diffusion coefficients D_{eff} in partially saturated porous silica glasses (trade name VitraPor #5, nominal pore diameter 1 μm , porosity 43%) as a function of the filling degree F at room temperature. The data have been measured with the stimulated-echo based field-gradient NMR diffusometry technique with a diffusion time $t \approx \tau_2 = 200 \text{ ms}$. **(a)** Effective diffusion coefficient of cyclohexane as a nonpolar solvent species. **(b)** Effective diffusion coefficient of water as a polar counterpart. The effective diffusion coefficients have been evaluated by fits of Eq. (7.64) to experimental stimulated-echo attenuation curves for low wave numbers. The solid lines represent fits of Eq. (7.63) to the data. The values of characteristic exponents are given in the insets (Reproduced from Ref. [58] with kind permission of © AIP 2004)

be compared with the much larger bulk diffusivities in the vapor under normal conditions [70]: $D_{v,0}^{\text{cyclohexane}} = 8.5 \times 10^{-6} \text{ m}^2/\text{s}$ and $D_{v,0}^{\text{water}} = 2.4 \times 10^{-5} \text{ m}^2/\text{s}$. Apart from the pore confinement effect, that is, Archie's law, the resulting diffusion behavior is then a matter of how far the lower density is compensated by the higher diffusivity in the vapor phase as a function of the filling degree F .

The two data sets in Fig. 7.13 show a number of remarkable features and differences. The data for the nonpolar solvent cyclohexane steadily decrease from high values at low filling degrees to low values approaching the bulk value when saturation of the pore space is reached. That is, $D_{\text{eff}}(F) \geq D_{\ell,0}^{\text{cyclohexane}}$ throughout and contrary to the pore confinement tendency. That is, the vapor phase contributes significantly in almost the entire range of the filling degree. The influence is largely dominated by the limit represented by Eq. (7.66).

This finding is in contrast to the water data. In this case, the effective diffusivities are *below* the bulk value in the whole range, $D_{\text{eff}}(F) < D_{\ell,0}^{\text{water}}$. A pronounced minimum is reached at $F \approx 0.28$ as a result of the competitive actions of the contributions by the vapor and liquid phases. The flanks of the minimum are described by Eq. (7.65) (high liquid filling degrees) and Eq. (7.66) (low liquid filling degrees).

The reason for the different behaviors of the two adsorbate species must mainly be sought in the different density ratios, $[\rho_v/\rho_\ell]_{\text{cyclohexane}} \gg [\rho_v/\rho_\ell]_{\text{water}}$ (see the values given above and Eq. 7.66). In the case of cyclohexane, the large value of this ratio obviously boosts the vapor contribution relative to that of the liquid phase, while the situation is more balanced for water.

The size of the liquid-phase domains in partially saturated porous media is also a matter of the mean pore diameter. At a given filling degree, the domains are expected to increase with the pore size. The mean residence time and hence the exchange limits will vary with the pore size. This was demonstrated in Refs. [57, 71], where it was shown that exchange is *fast* in unsaturated silica glass Vycor (4 nm nominal pore diameter), whereas it is *slow* in the unsaturated VitraPor #4 (10 μm nominal pore size). This is to be compared with the *intermediate* scenario under consideration here for VitraPor #5 (1 μm nominal pore size).

The diffusion time probed in the experiments represented by Fig. 7.13 was 200 ms. On this time scale, the root-mean-square displacement exceeds the correlation length of the medium by far, so that the character of diffusion is normal. However, at diffusion times $\ll 1\text{ms}$, the root-mean-square displacements tend to be in the scaling window mentioned in Sect. 4.9.3.2. Under such conditions, the measured diffusivities are expected to depend on the diffusion time as it was indeed reported in Refs [29, 72].

7.5 Reorientational Dynamics in Surface-Dominated Systems

7.5.1 From Translational to Rotational Diffusion

In the previous sections, we have seen that translational diffusion is substantially affected by mesoscopic confinement. The range of the confinement effects was shown to be within about one order of magnitude. Nevertheless, though pronounced, the *translational* phenomena appear to be moderate if compared with

the much stronger influence of adsorbate/surface interactions on *reorientational* dynamics. Actually, the time constants characterizing rotational diffusion can vary by many orders of magnitude upon mesoscopic confinement.

Several techniques probing reorientational dynamics have been described in Chap. 3. In general, the methods detailed there probe *orientation correlation functions* of the type

$$G_{\text{or}}(t) = 4\pi(-1)^m \langle Y_{l,m}(t) Y_{l,-m}(0) \rangle \quad (7.69)$$

where the spherical harmonics $Y_{l,m}(t)$ are composed of sine and cosine terms of the polar and azimuthal angles $\vartheta(t)$ and $\varphi(t)$ of a molecular axis relative to an external field. As the most versatile measuring principle, let us now focus on spin relaxation, that is, field-cycling and transverse NMR relaxometry. The degree of the relevant spherical harmonics is then $l = 2$, while the order can be $m = 0, 1, 2$. In Sect. 7.2.3, exchange limits of spin relaxation have already been discussed for the two-phase/fast-exchange model which we will employ in the following.

The subject of Sects. 7.5.2, 7.5.3, 7.5.4, 7.5.5, 7.5.6, and 7.5.7 will be *diamagnetic* systems where spin relaxation is dominated by interactions among *like* dipoles. Cases where spin relaxation is affected or even governed by *electron-paramagnetic* impurities on the pore surfaces will be referred to afterward in Sect. 7.5.8.

7.5.2 Spin–Lattice Relaxation in Low-Molecular Solvents Confined in Inorganic Porous Media

7.5.2.1 Polar Liquids at Polar Surfaces (“strong adsorption”)

The consequence of strong adsorption defined in Sect. 7.3 is that adsorbate molecules are effectively displaced along polar surfaces on a time scale $Q^{-1} < t < t_h$ in a series of desorption/bulk-excursion/readsorption cycles. The intermittent excursions to the bulk-like phase can be quite large relative to the displacement steps within the adsorbed phase. The result is *bulk mediated surface diffusion* (BMSD) herein before mentioned [16, 17]. Effectively, this is a step-like diffusion mechanism along surfaces as schematically illustrated in Fig. 7.14. In principle, the displacement steps on the surface are unrestricted. This process therefore reflects features of *Lévy walks* [73] as analytically demonstrated in Ref. [19].

The plots in Figs. 7.3b and 7.15 show typical data of the spin–lattice relaxation time for water under mesoscopic confinement in polar media as a function of the Larmor frequency. Below the megahertz regime, the frequency dispersion $T_1 = T_1(\nu)$ turns out to be remarkably steep while bulk water does not show any frequency dependence in this particular frequency window. In Sect. 7.3, we have associated this strong low-frequency dispersion with the *strong-adsorption limit*. Other polar

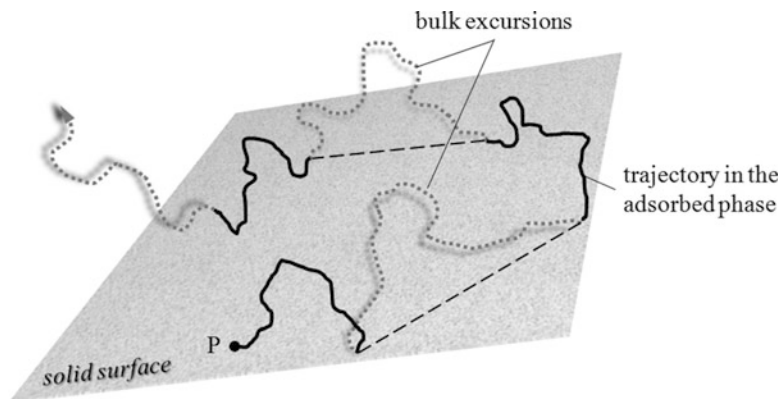


Fig. 7.14 Schematic representation of the *bulk-mediated surface diffusion* (BMSD) mechanism: A particle starting at point P on the surface of a solid matrix is displaced within the adsorbed phase along the surface (trajectories drawn as *black solid lines*). Intermittently, it can be desorbed and perform excursions to the bulk-like phase (trajectories drawn as *gray dotted lines with shades*). After readsorption, it continues to diffuse within the adsorbed phase, and so on until it finally escapes to the vastness of the bulk-like phase (*arrow*). The *black solid* trajectories in combination with the *straight dashed lines* between desorption and readsorption points may be termed “surface diffusion.” The statistics of these effective displacements along surfaces can be described as Lévy walks [16, 19]

adsorbate species in diamagnetic polar matrices show the same behavior as exemplified by the diverse data sets in Fig. 7.3a–c. The pronounced frequency dispersion in polar liquids is in contrast to non-polar adsorbate fluids which will be discussed in the subsequent Section.

We know that the relationship $T_1^{-1} = T_1^{-1}(\nu)$ directly reflects the Fourier transform of the orientation correlation function Eq. (7.69). The experimentally accessible frequency window, $10^2 \text{ Hz} < \nu < 10^9 \text{ Hz}$ corresponding to $2 \times 10^3 \text{ rad/s} < \omega < 2 \times 10^9 \text{ rad/s}$ in terms of angular frequencies, is conjugate to the time range $5 \times 10^{-10} \text{ s} < t < 5 \times 10^{-4} \text{ s}$. This is the time scale to which the following discussion will refer.

The correlation time for molecular reorientations in bulk water at room temperature is of the order $\tau_b \approx 10^{-12} \text{ s}$. That is, all memory to the initial orientation of a molecule will be lost after a few picoseconds. This is to be compared with the reorientation dynamics of water confined in mesoscopic porous media. Since the T_1 dispersion in Fig. 7.15 retains a finite slope even down to the kHz regime, finite orientation correlations must exist on a time scale up to about 10^{-4} s . This is remarkable eight (!) orders of magnitude longer than in bulk.

On the other hand, the confinement effect on translational diffusion was shown in Sect. 7.4.1 to be less than a single order of magnitude in the same sort of systems. How does that fit together? An explanation of this striking (but anyway apparent) “discrepancy” will follow below.

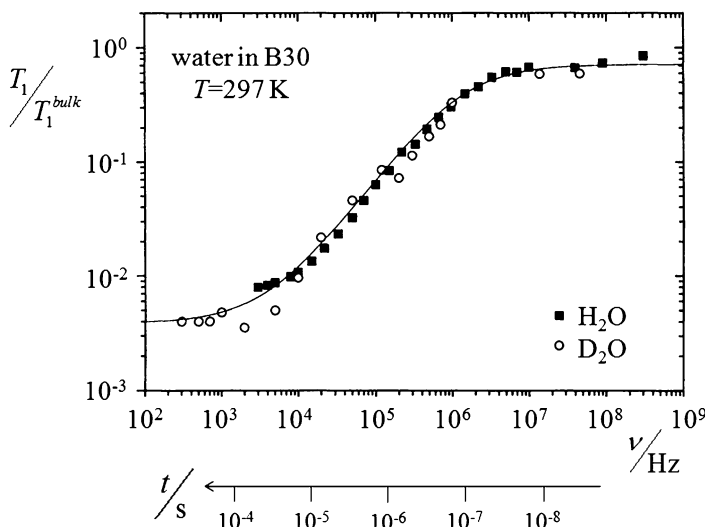


Fig. 7.15 Frequency dispersion of the spin–lattice relaxation time in light and heavy water confined in a porous silica glass (trade name Bioran B30; nominal pore size 30 nm). In order to account for the different spin coupling constants of the respective resonant nuclei, that is, protons and deuterons, the data are presented relative to the corresponding bulk values T_1^{bulk} . The coinciding data for proton and deuteron spin–lattice relaxation suggest that all relevant spin interactions are mainly of an intramolecular nature, so that reorientational dynamics is probed indeed. The time scale conjugate to the frequency scale of the experiments is indicated as a second abscissa axis (Reproduced from Ref. [22] with kind permission of © APS 1995)

An important finding is that the confinement effect on spin–lattice relaxation vanishes when the frequencies approach the upper end of the accessed range, that is, $\nu \rightarrow 3 \times 10^8 \text{ Hz}$ in the case of the experiments represented by Fig. 7.15. Roughly, this corresponds to the conjugate time value $t \rightarrow 5 \times 10^{-10} \text{ s}$. The spin–lattice relaxation times or rates coincide then with the values measured in bulk. The conclusion is that *short-scale* or “*local*” motions remain practically unaffected by mesoscopic confinements as concerns the fluctuation rate.

However, a slight anisotropy of rotational diffusion must nevertheless exist. Being adsorbed means that the molecule has adopted a certain preferential orientation relative to the local site on the pore surface and, hence, relative to external field directions.¹¹ This characteristic anisotropy in the adsorbed phase leaves some slowly decaying residual correlation which is responsible for the low-frequency dispersions revealed by the data in Fig. 7.3 and Fig. 7.15. Actually, this is the system-specific longtime tail of the orientation correlation function mentioned in

¹¹ Provided that motional averaging is still incomplete, the preferential orientation of adsorbate molecules relative to adsorbent surfaces can be demonstrated by dipolar or quadrupolar splitting of NMR resonance lines [74, 75] or, if such splitting is not resolved, by multiple-quantum filtering spectroscopy which is based on residual dipolar or quadrupolar couplings [76, 77].

Sect. 1.1.4 and encountered in analogous form with polymers (see Sect. 5.4.7) and with liquid crystals (see Sect. 6.8.2).

Equivalent results have been obtained with other polar liquids embedded in diverse polar matrix systems. Apart from porous silica glasses, fine-particle agglomerates consisting of ZnO, TiO₂ and SiO₂ fine particles show the same slowdown of reorientational dynamics [22, 23, 78]. This retardation appears to be characteristic for mesoscopic confinement in the strong-adsorption limit.

7.5.2.2 Non-polar Liquids at Polar Surfaces (“Weak Adsorption”)

While the mesoscopic confinement effect on translational diffusion of solvents is the same for polar and nonpolar species (see Fig. 7.4), there is a dramatic difference in the case of reorientational dynamics. As already outlined in Sect. 7.3, nonpolar solvents confined in polar matrices are subject to the *weak-adsorption limit*. That is, the contact to the confining pore walls is much less intense than in the strong-adsorption case relevant for polar species. Nonpolar adsorbate molecules show little affinity to reside at or near the polar surfaces. The adsorbate/wall interactions are therefore only sporadic. The consequence is a comparatively flat spin–lattice relaxation dispersion with little deviations from the behavior in bulk. Several examples of such systems are represented by the data sets plotted in Fig. 7.3a–c.

A different, particularly interesting situation arises if a *nonpolar* solvent in a *polar* host matrix is partially frozen. That is, the adsorbed phase remains liquid and is spread as a layer along the surfaces while the bulk-like phase is solid. All molecular motion relevant for spin-relaxation experiments will then take place in the *nonfreezing surface layers* we are already familiar with from the diffusion studies described in Sect. 7.4.2. Since the solvent molecules populating these layers cannot escape to the bulk-like phase, we have conditions even more constrictive than those in the strong-adsorption limit: The adsorbate molecules are forced to reside *permanently* in the surface layer despite their weak affinity to interact with polar substrates. Spin–lattice relaxation consequently reveals features of strong adsorption rather than of weak adsorption. Investigations of this sort have been reported in Ref. [79]. These experiments thus elucidate the physics behind the strong- versus weak-adsorption distinction.

7.5.3 Surface-Diffusion Formalism for Spin Relaxation in Fluids in the Strong-Adsorption Case

In Sects. 7.2 and 7.3, we have discussed diverse limits with respect to molecular exchange and adsorption properties. A typical scenario for molecular dynamics of polar liquids confined in polar matrices is the following:

1. Adsorption tends to be *strong* (i.e., Eq. 7.26 applies). Molecules initially adsorbed at surfaces will be subject to frequent desorption/readsorption cycles before “finally” escaping to the (by tendency more voluminous) bulk-like phase.
2. Provided the volume ratio of the bulk-like and adsorbed phases is not too large, say, less than 100, all fluid molecules will visit both liquid phases frequently on the relaxation time scale. Empirically, room temperature spin-relaxation times in such systems are limited by $T_1, T_2 > 10^{-3}$ s at all relevant frequencies, whereas molecular exchange times are of the order $\tau_{\text{ex}} \approx 10^{-6} \dots 10^{-5}$ s. Thus, *fast exchange on the relaxation time scale* applies, $\tau_{\text{ex}} \ll T_1, T_2$ (Sect. 7.2.1.2). The *two-phase/fast-exchange relaxation rates*

$$\frac{1}{T_1} = \frac{1-f_a}{T_1^{\text{bulk}}} + \frac{f_a}{T_1^a} \quad \text{and} \quad \frac{1}{T_2} = \frac{1-f_a}{T_2^{\text{bulk}}} + \frac{f_a}{T_2^a} \quad (7.70)$$

are composed of the rates in the bulk-like and adsorbed phases $\left(T_{1,2}^{\text{bulk}}\right)^{-1}$ and $\left(T_{1,2}^a\right)^{-1}$, respectively, weighted by the corresponding phase populations. Equation (7.70) refers both to longitudinal (T_1) and transverse (T_2) relaxation. In the following, we will focus on longitudinal relaxation which is more important in the present context.

3. On the other hand, exchange on the correlation time scale tends to be *slow* since, as a consequence of the strong-adsorption limit, molecular orientation relative to the surface is more or less reestablished many times during the exchange time before the correlation to the initial orientation is finally lost. That is, Eq. (7.16) applies.
4. Even though being restricted to a certain solid angle cone relative to the surface, *local motions* can be considered as an ordinary rotational diffusion process. The respective orientation correlation function is therefore expected to decay exponentially with a correlation time τ_{loc} not much longer than the time constant τ_b in bulk water. A small but anyway *finite residual correlation* $G_{\text{loc}}(t \rightarrow \infty) = 1 - a_1 = \text{const}$ of typically a few percent will be retained in the longtime limit $t \gg \tau_{\text{loc}}$. These features are reflected by the partial correlation function for local motions

$$G_{\text{loc}}(t) = a_1 \exp\left\{-\frac{t}{\tau_{\text{loc}}}\right\} + (1 - a_1) \quad (7.71)$$

in complete analogy to the scenarios treated in the context of polymers (Eq. 5.296) and liquid crystals (Eq. 6.105). The experimental time scale of interest in the following refers to the system-specific *longtime tail* of the orientation correlation function (see Sect. 1.1.4), that is, $t \gg \tau_{\text{loc}}$. In terms of the Fourier conjugate variable, this means $\omega \ll \tau_{\text{loc}}^{-1}$, so that the effective longtime correlation function can be represented as the product

$$\mathcal{G}_{aa}(t \gg \tau_{\text{loc}}) \approx \mathcal{G}_{\text{loc}}(t \rightarrow \infty) \mathcal{G}_{\text{RMTD}}(t) = (1 - a_1) \mathcal{G}_{\text{RMTD}}(t) \quad (7.72)$$

$\mathcal{G}_{aa}(t)$ is the (normalized) orientation correlation function in the adsorbed phase. To be more specific, $\mathcal{G}_{aa}(t)$ refers to the moiety of molecules being *initially as well as finally* in the adsorbed phase irrespective of any intermittent excursions to the bulk-like phase. The mechanism effective for spin–lattice relaxation at angular frequencies $\omega \ll \tau_{\text{loc}}^{-1}$ is represented by the correlation function $\mathcal{G}_{\text{RMTD}}(t)$. Orientation correlation fades away by *reorientation mediated by translational displacements* (RMTD) along the surface topology. Figure 7.16 shows an illustration of this particular process.

In the bulk-like phase, the correlation loss will be complete for $t \gg \tau_{\text{loc}}$, so that the spin-relaxation rate in this phase can be neglected relative to that in the adsorbed phase for populations not too small, say, $f_a > 10^{-2}$. Taking all these limits together – *strong adsorption* (Eq. 7.26), *two-phase/fast-exchange* (Eq. 7.70), *slow exchange on the correlation time scale* (Eq. 7.16), and *longtime/low-frequency limit* $t, \omega^{-1} \gg \tau_{\text{loc}}$ (Eq. 7.72) – and factoring Eqs. (3.139) and (3.148) in, we arrive at the effective proton or deuteron spin–lattice relaxation rate

$$\frac{1}{T_1} \approx \frac{f_a}{T_1^a} = C_1 f_a (1 - a_1) [\mathcal{I}_{\text{RMTD}}(\omega) + 4\mathcal{I}_{\text{RMTD}}(2\omega)] \quad (\omega \ll \tau_{\text{loc}}^{-1}) \quad (7.73)$$

The constant C_1 is specific for the relevant spin interaction (dipolar or quadrupolar). The reduced spectral density is defined by

$$\mathcal{I}_{\text{RMTD}}(\omega) = \int_{-\infty}^{+\infty} \mathcal{G}_{\text{RMTD}}(t) e^{-i\omega t} dt \quad (7.74)$$

It remains to explain the RMTD process more specifically. The idea of the RMTD process is that adsorbate molecules diffuse effectively along the surface and get thus reoriented according to the (nonplanar) surface topology (see Fig. 7.16). At a certain starting site on the surface, the orientation be defined by the polar and azimuthal angles ϑ_0 and φ_0 , respectively. In a curvilinear distance s along the surface, that is, at the readsorption site, these angles will adopt the values ϑ_s and φ_s . Depending on the surface topology, the spherical harmonics formed on the basis of these angles will be more or less correlated according to the *surface orientation correlation function*

$$\mathcal{G}_s(s) = -4\pi \langle Y_{2,1}(\vartheta_s, \varphi_s) Y_{2,-1}(\vartheta_0, \varphi_0) \rangle \quad (7.75)$$

For reasons discussed already in Sects. 3.1.5.6, 3.1.7, and 5.4.3.7, we may restrict ourselves to the degree $l = 2$ and the order $m = 1$. Furthermore, considering the propagator $P(s, t)$ effective for curvilinear displacements s along the surface in a

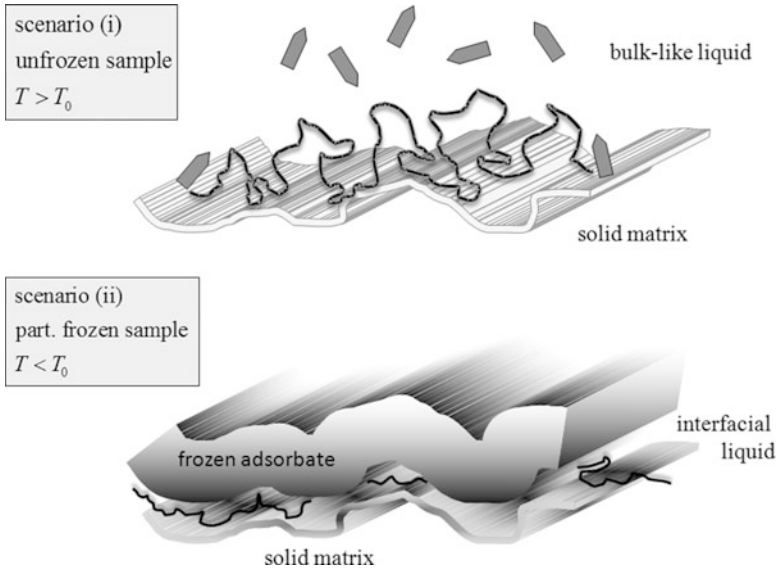


Fig. 7.16 Illustration of the RMTD process (*reorientation mediated by translational displacements*) based on surface diffusion of adsorbate molecules at pore walls of a solid matrix. *Scenario (i)*: Above the bulk freezing temperature T_0 , molecules exchange between the adsorbed phase and the bulk-like phase. In the strong-adsorption limit, many desorption/readorption cycles occur with intermittent bulk excursions until the initial surface population will be completely replaced. Effectively, this results in *bulk-mediated surface diffusion* (BMSD) within the retention time. Since molecules (represented by arrows) adopt a preferential orientation relative to the surface as soon as they become adsorbed, they will be reoriented from adsorption event to adsorption event according to the surface topology. In between, that is, in the bulk-like phase, the orientation will instantaneously be randomized. The propagator effective for surface diffusion effective in the presence of a bulk-like phase is expected to be of the Cauchy type (Eq. 7.84). *Scenario (ii)*: In a certain range below the bulk freezing temperature T_0 , the bulk-like phase is frozen and consequently immobilized, while the adsorbed phase is still liquid. Since BMSD is blocked in this case, surface diffusion within the topologically two-dimensional interfacial liquid layer is expected to be of the normal type, that is, governed by a Gaussian propagator (Eq. 7.82) (Reprinted from Ref. [42] with kind permission of © Elsevier 2002)

time interval t permits one to analyze the time autocorrelation function Eq. (7.7) for $l = 2$ and $m = 1$ as

$$\mathcal{G}_{\text{RMTD}}(t) = -4\pi \langle Y_{2,1}(\vartheta_s, \varphi_s) Y_{2,-1}(\vartheta_0, \varphi_0) \rangle = \int_0^\infty \mathcal{G}_s(s) P(s, t) 2\pi s ds \quad (7.76)$$

Note that the curvilinear displacements s are assumed here to be distributed isotropically in the topologically two-dimensional interfacial space. The propagator $P(s, t)$ is the (two-dimensional) probability density for a curvilinear displacement s in an interval t . $P(s, t) 2\pi s ds$ is consequently the probability that the particle diffuses this distance in any direction.

The surface profile on a line between the initial and final adsorption site can be analyzed as a superposition¹² $\tilde{S}(q)$ of surface “modes” with a distribution of “wave” numbers $q = 2\pi/\lambda$ with “wave lengths” λ as counterparts. For practical reasons, it is more favorable to convert Eq. (7.76) to a q -space representation according to

$$\mathcal{G}_{\text{RMTD}}(t) = \frac{1}{(2\pi)^2} \int_0^\infty \tilde{S}(q) \tilde{P}(q, t) 2\pi q dq \quad (7.77)$$

The Hankel transforms in the integrand are defined by

$$\tilde{S}(q) = \int_0^\infty \mathcal{G}_s(s) J_0(qs) 2\pi s ds \quad (7.78)$$

and

$$\tilde{P}(q, t) = \int_0^\infty P(s, t) J_0(qs) 2\pi s ds \quad (7.79)$$

where $J_0(qs)$ is the zeroth-order Bessel function. The conjugate variables for this transform operation are q and s .

The *orientational structure factor*, $\tilde{S}(q)$, is a static function specifying the particular surface topology of the porous medium under consideration. It contains the information of the surface correlation function Eq. (7.75). The *q -space propagator* $\tilde{P}(q, t)$ characterizes the dynamics of translations along the surface. Leaving the character of the surface-diffusion process open for the moment, it can generally be expressed as a *Lévy propagator*

$$\tilde{P}(q, t) = \exp\{-B(t)|q|^\alpha\} \quad (7.80)$$

The exponent α is in the range $0 < \alpha \leq 2$ and implies the whole variety of potential displacement statistics (see below). $B(t)$ is a time function specific for the diffusion properties. Actually, this propagator is a generalization of the ordinary-diffusion case (i.e., for $\alpha = 2$). A more detailed and didactic description of the Lévy walk formalism can be found in Ref. [73].

Let us now compare surface diffusion for two specific scenarios: (i) unfrozen samples where molecules can reside both in the adsorbed and in the bulk-like phase and (ii) partially frozen samples where the nonfreezing surface layers form the only liquid phase relevant for spin–lattice relaxation (i.e. the same scenario that has already been considered in the context of translational diffusion; Sect. 7.4.2).

¹² An analogous (one-dimensional) analysis has been employed above for polymer conformations as illustrated in Fig. 5.22.

As suggested by the illustration in Fig. 7.16, the effective surface propagators will be totally different in these two cases.

In scenario (ii), the interfacial liquid forms a topologically two-dimensional space, in which normal diffusion takes place. With $\alpha = 2$ and $B(t) = Dt$, the q -space propagator Eq. (7.80) reveals itself as the familiar Gaussian function:

$$\tilde{P}(q, t) = \exp\{-Dtq^2\} \quad (7.81)$$

The real-space counterpart is

$$P(s, t) = \frac{1}{4\pi Dt} \exp\left\{-\frac{s^2}{4Dt}\right\} \quad (7.82)$$

(compare Eq. 2.168). D is the effective diffusion constant for topologically two-dimensional displacements along the surfaces.

This is in contrast to scenario (i) where the bulk-like phase is liquid as well. Surface diffusion in the strong-adsorption limit is then a result of frequent desorption – bulk excursion – readsorption cycles during the retention time. As first shown in Ref. [17], the q -space surface propagator $\tilde{P}(q, t)$ effective for this BMSD mechanism is specified by $\alpha = 1$ and $B(t) = ct$. Equation (7.80) thus takes the form

$$\tilde{P}(q, t) = \exp\{-ct|q|\} \quad (7.83)$$

where c is a dynamic constant of dimension [velocity]. The real-space complement is the *Cauchy distribution* characteristic for two-dimensional Lévy walks:

$$P(s, t) = \frac{ct}{\left[(ct)^2 + s^2\right]^{3/2}} \quad (7.84)$$

The q -space surface propagators Eqs. (7.81) and (7.83) can be expressed by the common exponential function

$$\tilde{P}(q, t) = \exp\left\{-\frac{t}{\tau_q}\right\} \quad (7.85)$$

with the time constants $\tau_q = 1/(Dq^2)$ and $\tau_q = 1/(cq)$ for the Gauss and Cauchy cases, respectively. The combination of Eqs. (7.74), (7.77), (7.78), and (7.85) finally leads to the respective spin–lattice relaxation rates Eq. (7.73) for the two scenarios, that is, for the specific propagators Eqs. (7.81) and (7.83). An experimental comparison will be described in the next section.

7.5.4 A First Test Experiment for the Surface-Diffusion Formalism

The orientational surface structure factor $\tilde{S}(q)$ defined in Eq. (7.78) has not yet been specified. The experiment to be described in the following refers to fluids confined in porous silica glass of the type we have already encountered in the context of Figs. 7.3a and 7.15. In this case, the surface topology can be assumed to have a random or even fractal character [80]. As a plausible and tentative ansatz, this suggests that the orientational surface structure factor follows a power law in a certain wave-number range:

$$\tilde{S}(q) = bq^{-\chi-1} \quad (7.86)$$

The exponent χ reflects the surface topology of the matrix. The factor b is a constant.

In combination with Eqs. (7.77) and (7.85), this results in the respective limits for the orientation correlation function and, together with Eqs. (7.74) and (7.73), for the spin–lattice relaxation rate:

$$\left. \begin{aligned} \mathcal{G}_{\text{RMTD}}(t) &= b\Gamma(1-\chi)c^{-(1-\chi)}t^{-(1-\chi)} \\ \frac{1}{T_1^{(i)}} &\propto b\Gamma(1-\chi)c^{-(1-\chi)}\omega^{-\chi} \end{aligned} \right\} \rightarrow \begin{cases} \text{scenario (i)} \\ \text{unfrozen sample} \\ \text{Cauchy propagator} \end{cases} \quad (7.87)$$

and

$$\left. \begin{aligned} \mathcal{G}_{\text{RMTD}}(t) &= \frac{b}{2}\Gamma\left(\frac{1-\chi}{2}\right)D^{-(1-\chi)/2}t^{-(1-\chi)/2} \\ \frac{1}{T_1^{(ii)}} &\propto \frac{b}{2}\Gamma\left(\frac{1-\chi}{2}\right)D^{-(1-\chi)/2}\omega^{-(1+\chi)/2} \end{aligned} \right\} \rightarrow \begin{cases} \text{scenario (ii)} \\ \text{nonfreezing surface layers} \\ \text{Gauss propagator} \end{cases} \quad (7.88)$$

$\Gamma(x)$ is the gamma function (for a definition, see the standard mathematical literature such as Ref. [81]). According to Eqs. (7.87) and (7.88), two *different* spin–lattice relaxation dispersions are predicted for the very *same* surface topology, that is, the *same* exponent χ . This is a direct consequence of the distinct propagators following from Eq. (7.85) for scenario (i), unfrozen sample, and for scenario (ii), partially frozen sample.

In favorable cases where partially frozen and unfrozen samples, that is, scenarios (i) and (ii), can be examined within a small temperature gap, the predicted change in the T_1 dispersion slopes can be verified experimentally as demonstrated by the data plotted in Fig. 7.17. The power-law T_1 dispersions predicted by Eqs. (7.87) and (7.88) on the basis of the orientational surface structure factor Eq. (7.86) were observed indeed. The dispersion slopes can *commonly* be described within the

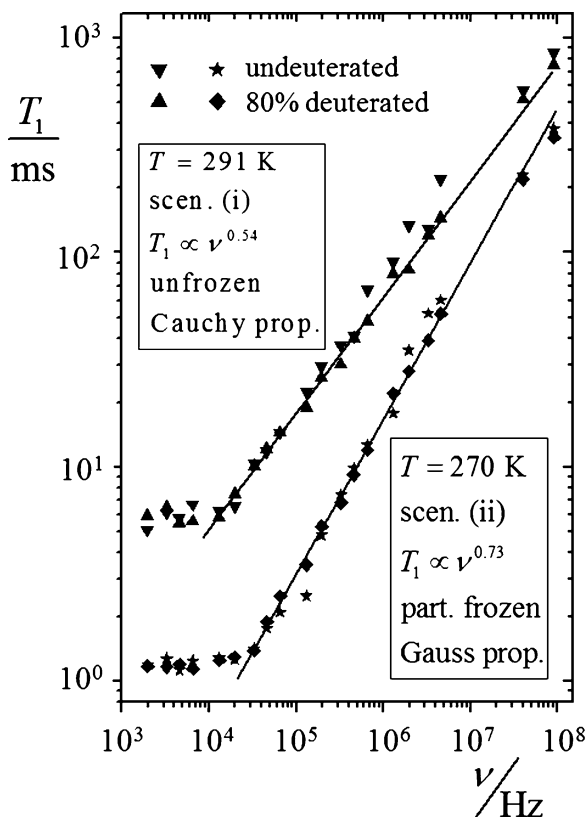


Fig. 7.17 Proton spin–lattice relaxation dispersion of the liquid phases of dimethyl sulfoxide (DMSO) in a porous silica glass (trade name Bioran B10; nominal pore size 10 nm). The coinciding data for undeuterated and isotopically diluted DMSO indicate that *intramolecular* dipolar coupling is the dominating relaxation mechanism as anticipated in the text for the theory of reorientational dynamics. At 291 K, the solvent is totally liquid (*scenario (i)*), while the bulk-like phase is frozen at 270 K (*scenario (ii)*). The data recorded at the latter temperature refer to the signal component selectively originating from the nonfreezing surface layers. The solid lines represent power laws corresponding to Cauchy and Gauss propagators as indicated (see Eqs. 7.88 and 7.87) (Reproduced from Ref. [23] with kind permission of © AIP 1998)

experimental error by the exponent $\chi \approx 0.5 \pm 0.04$ as demanded by the identical surface topologies in both cases.

7.5.5 Spin Relaxation in Aqueous Protein Solutions and Tissue

The category of systems with surface-dominated reorientation dynamics comprises many more examples than the inorganic porous media or particle agglomerates so

far referred to. Practically all complex, that is, heterogeneously structured materials belong to this class if soaked with a fluid. In this sense, biological systems such as aqueous solutions of globular proteins and tissue can be shown to reveal the same sort of surface orientation phenomena as outlined above [74–77]. As before, the focus will be laid on the system-specific long-tail behavior of the orientation correlation function Eq. (7.69).

7.5.5.1 Distinction of Water and Protein Dynamics in Aqueous Protein Solutions

The liquid phases relevant for biological systems are usually of an aqueous nature. However, unlike the inorganic matrices and host materials examined in the previous sections, the problem is now that the solid or solid-like matrices contain hydrogen as well. The “host” material can therefore contribute to proton NMR signals in principle.

Another intricacy inherent to aqueous systems of biopolymers is *exchange* of spins between water and biopolymers while spin relaxation is probed. As mentioned several times before, exchange can be both of a material and of an immaterial nature. The former refers to labile hydrogen atoms of the biopolymers themselves or to water structurally involved in the macromolecular phase. Immaterial spin exchange is mediated by magnetization transfer between the constituents on the basis of flip-flop spin transitions. Such transitions are produced by the operator terms containing products I^+S^- and I^-S^+ (compare the analysis Eq. (3.91) of the Hamiltonian of dipolar coupling for like spins). Numerous studies of this problem have been published in the literature (e.g., see Refs. [82–85]).

Irrespective of how strongly these effects will actually influence spin–lattice relaxation, an experimental distinction of the two principal constituents “water” and “protein” is desirable for the identification and localization of dynamic processes. This can be achieved by using heavy water as solvent, so that the relaxation experiments can be carried out selectively with proton and deuteron resonance. *Deuteron* resonance probes the aqueous phase (including all hydrogens of the biopolymers possibly exchangeable on the time scale of the relaxation experiment), while *proton* resonance registers the biopolymer part. Immaterial spin exchange across the interfaces between these two groups of constituents is negligible because of the strongly deviating gyromagnetic ratios of deuterons and protons.¹³

Typical spin–lattice relaxation data recorded in a protein solution of this sort are shown in Fig. 7.18. This study refers to bovine serum albumin, a medium-sized globular protein mentioned already in Sects. 7.4.1.3 and 7.4.2.1 in the context of translational diffusion. The different types of molecular dynamics in the macromolecules and in the aqueous phase manifest themselves by the deviating

¹³ An analogous strategy has been pursued in the experiments represented by Fig. 5.41 in the context of the corset effect of polymers under mesoscopic confinement.

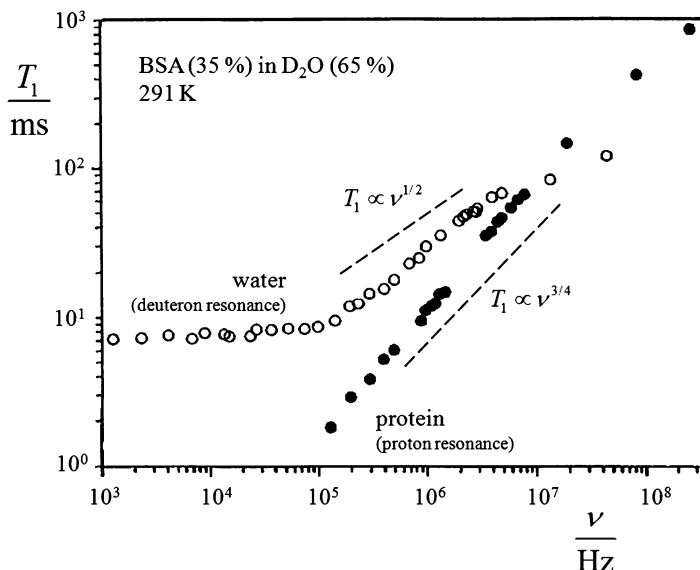


Fig. 7.18 Proton and deuteron spin–lattice relaxation dispersion in a solution of bovine serum albumin (BSA) in D_2O . The proton signal originates predominantly from the non-exchangeable protein hydrogen atoms, whereas the deuteron signal refers to water and exchangeable hydrogen atoms. In this way, the different dynamics of hydrogen atoms inside the protein on the one hand and of the water molecules on the other can be studied selectively in one and the same sample (Reproduced from Ref. [86] with kind permission of © AIP 1990)

dispersion slopes. At intermediate frequencies, the spin–lattice relaxation times empirically approach the power-law proportionalities

$$T_1 \propto \nu^{1/2} \text{ (water); } T_1 \propto \nu^{3/4} \text{ (protein)} \quad (7.89)$$

as indicated in the figure.

7.5.5.2 Spin Relaxation in the Protein Phase of Protein Solutions

The mechanisms governing spin relaxation of macromolecules in solution can in principle be librational fluctuations of the protein backbone, side-group motions, and overall tumbling [87]. The data plotted in Fig. 7.18 have been recorded with a protein concentration of 35% by weight which is high enough to prevent any perceptible contribution by tumbling of the whole macromolecule as will be specified in more detail in Sect. 7.5.5.3. Reorientations of side groups tend to be too fast to matter at frequencies below about 10^7 Hz. Thus, the remaining relaxation mechanism dominating the low-frequency proton data in Fig. 7.18 is backbone fluctuations. According to the laws specified in Eq. (7.89), the spin–lattice relaxation dispersion characteristic for this type of molecular motion appears to be $T_1 \propto \nu^{3/4}$.

An empirical power law $T_1 \propto \nu^{0.75 \pm 0.05}$ has also been found for several other protein species both in concentrated solutions and in almost unhydrated powders [88, 89]. An interpretation is possible on the basis of multiple-trapping diffusion of dilating defects as suggested in Ref. [89]. Another most interesting description is based on the fractal structure of globular proteins in combination with direct spin–phonon coupling as relaxation mechanism [90, 91].

7.5.5.3 Spin Relaxation in the Aqueous Phase of Protein Solutions

Let us now turn to the aqueous phase of protein solutions. In complete analogy to strong-adsorbate fluids in porous glasses, we distinguish the bulk-like phase from the adsorbed phase. The latter consists of hydration shells and to a minor degree of structural water and labile hydrogens of the protein. The contributions to reorientational dynamics in the adsorbed phase can be classified into three *competitive* and *stochastically independent* mechanisms which will be considered separately in the following. The latter attribute alludes again to the familiar different-time-scale limit practically relevant in experiments. Specifying the formalism outlined in Sect. 7.5.3 for protein solutions leads to the following distinctions:

1. *Local motions*: Eq (7.71) can directly be adopted for the present system. In the longtime limit $t \gg \tau_{\text{loc}}$, the residual correlation¹⁴ is $G_{\text{loc}}(t \rightarrow \infty) = 1 - a_1 = \text{const}$ as before.
2. *Reorientation by surface diffusion*: The strong-adsorption limit applies again, so that the long-tail decay of the orientation correlation function will largely be dominated by the RMTD process. The topological basis is the more or less rugged and curved surface of the protein. It turned out that experimental data such as those shown in Fig. 7.19 can be well described under the following assumptions: As the propagator, we use the Gaussian given in Eq. (7.81). That is, we assume that surface diffusion essentially takes place in the topologically two-dimensional space of the hydration layers without excursions to the bulk-like phase. At least for very high protein concentrations leaving no or only very little space for excursions to the bulk-like phase, this appears to be reasonable. In this case, the adsorbed phase consists mainly of overlapping hydration shells as illustrated in Fig. 7.8. As an ansatz for the orientational structure factor, we assume an equipartition of wavenumbers which is to describe the rugged surface topology:

$$2\pi q \tilde{S}(q) = \begin{cases} \frac{\varepsilon}{\Delta q} = \text{const} & \text{if } q_l \leq q \leq q_u \\ 0 & \text{otherwise} \end{cases} \quad (7.90)$$

¹⁴The residual *correlation* of local motions must not be identified with the residual dipolar or quadrupolar *coupling* as revealed in NMR spectroscopy [74–77]. The time scales can be very different. By tendency, these phenomena are however related with each other. The common basis is the anisotropy of local reorientations.

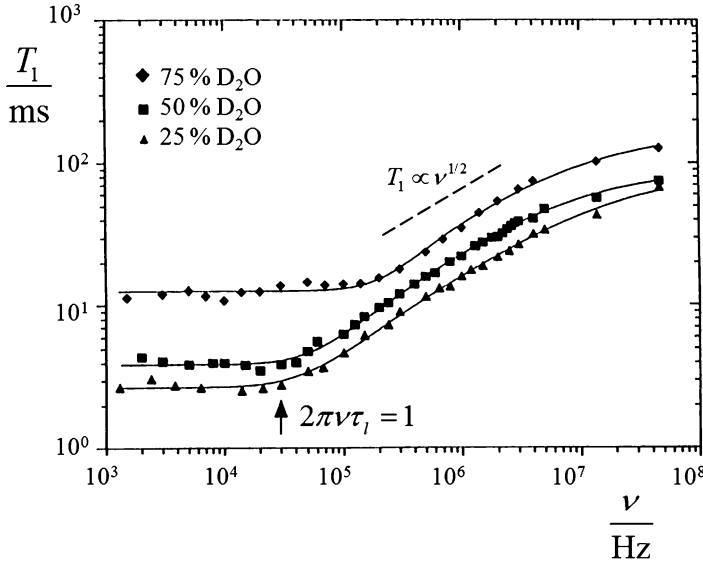


Fig. 7.19 Deuteron spin–lattice relaxation dispersion of solutions of bovine serum albumin in D_2O at 291 K for different water contents c_w . The choice of deuteron resonance in these experiments ensures that there is no contribution from inexchangeable hydrogens of the protein molecules and that there is no contribution by inter-molecular spin interactions so that exclusively reorientational dynamics is probed. The *continuous lines* were calculated using the RMTD formalism in combination with protein tumbling and restricted rotational diffusion of hydration water (Eqs. 7.98 and 7.101). The low-frequency plateau merges into a square-root frequency dependence at a certain inflection frequency depending on the protein concentration. The inflection frequencies for 25% D_2O (no bulk-like water exists) and 50% D_2O (bulk-like water exists) are the same. This indicates that molecular tumbling of the protein molecule is not yet effective, and RMTD dominates the total low-frequency regime. This is in contrast to 75% D_2O where protein tumbling is fast enough to become competitive with RMTD. In this case, protein tumbling determines the crossover to the low-frequency plateau (Reproduced from Ref. [87] with kind permission of © Elsevier 1990)

$\Delta q = q_u - q_l$ is the range of the surface wave vector to which the equipartition refers. q_u and q_l are the upper and the lower cutoff values, respectively. The factor ε is a constant. By combining Eqs. (7.77), (7.81), and (7.90), we arrive at the RMTD correlation function for the adsorbed phase [23]

$$\begin{aligned}
 G_{\text{RMTD}}(t) &= \frac{1}{(2\pi)^2} \int_0^\infty \tilde{S}(q) e^{-Dtq^2} 2\pi q dq \\
 &= \frac{\varepsilon}{8\pi^2 \Delta q} \sqrt{\frac{\pi}{Dt}} \left[\text{erf}\left(q_u \sqrt{Dt}\right) - \text{erf}\left(q_l \sqrt{Dt}\right) \right] \\
 &\approx \frac{\varepsilon}{8\pi^2} \sqrt{\frac{\pi \tau_u}{t}} \left[\text{erf}\left(\sqrt{\frac{t}{\tau_u}}\right) - \text{erf}\left(\sqrt{\frac{t}{\tau_l}}\right) \right] \quad (7.91)
 \end{aligned}$$

$\text{erf}(\cdots)$ is the error function defined by $\text{erf}(x) \equiv 2\pi^{-1/2} \int_0^x e^{-u^2} du$. D is the diffusivity effective along the surfaces. The correlation times characterizing the decay of this correlation function are

$$\tau_u = \frac{1}{Dq_u^2} \approx \frac{1}{D(\Delta q)^2} \quad \text{and} \quad \tau_l = \frac{1}{Dq_l^2} \quad (7.92)$$

Equation (7.91) becomes independent of time in the limit $t \ll \tau_u$ and approaches an exponential decay for $t \gg \tau_l$. In the intermediate range $\tau_u \ll t \ll \tau_l$ between these limits, the decay can be described by the power law

$$G_{\text{RMTD}}(t) \approx \frac{\varepsilon}{8\pi^2} \sqrt{\pi\tau_u} t^{-1/2} \quad (7.93)$$

The conjugate spectral density

$$I_{\text{RMTD}}(\omega) \approx \frac{\varepsilon}{8\pi} \sqrt{2\tau_u} \omega^{-1/2} \quad (7.94)$$

refers to the angular frequency range $1/\tau_l \ll \omega \ll 1/\tau_u$. According to Eq. (7.73), this result predicts the power law

$$T_1(\omega) \propto \tau_u^{-1/2} \omega^{1/2} \quad (7.95)$$

for the spin–lattice relaxation dispersion in good coincidence with the experimental findings (see the deuteron data in Figs. 7.18 and 7.19). Actually, the assumption that the water molecules are more or less permanently residing and diffusing in the hydration shells on the protein surfaces for high enough protein concentrations can be considered to be ratified in this way.

3. *Global tumbling of the protein molecules*: If not obstructed by mutual hindrance, the macromolecules will be able to perform tumbling motions including their hydration shells. As a (for spherical particles isotropic) rotational diffusion process, an exponential orientation correlation function can be assumed (see Eq. 3.204):

$$G_{\text{tumble}}(t) \approx \exp\left\{-\frac{t}{\tau_{\text{tumble}}}\right\} \quad (7.96)$$

It is clear that tumbling must lead to the ultimate loss of any orientation correlation in the limit $t \gg \tau_{\text{tumble}}$. In this sense, there is a competition with the RMTD cutoff mechanism which likewise causes final fading of the orientation correlation for $t \gg \tau_l$.

4. *Combination of all three water relaxation mechanisms:* In the *different-time-scale limit*, the three reorientation components can be considered to be *stochastically independent* of each other. The orientation correlation function effective for molecules being initially as well as finally in the adsorbed phase can therefore be formulated as the product¹⁵

$$\begin{aligned} G_{aa}(t) &= G_{loc}(t) G_{RMTD}(t) G_{tumble}(t) \\ &\approx a_1 \exp(-|t|/\tau_{loc}) + \frac{\varepsilon(1-a_1)}{(2\pi)^2 \Delta q} \int_{q_l}^{q_u} \exp\{-|t|(\tau_{tumble}^{-1} + Dq^2)\} dq \end{aligned} \quad (7.97)$$

In the derivation of this expression, we have combined Eqs. (7.71), (7.90), (7.91), and (7.96). Since the RMTD mechanism and tumbling are comparatively slow, we have furthermore assumed that $G_{RMTD}(t \approx \tau_{loc}) G_{tumble}(t \approx \tau_{loc}) \approx 1$ on the time scale of local motions.

In summary, the water deuteron spin–lattice relaxation rate Eq. (7.70) for (a) *two phase/fast exchange on the relaxation time scale*, (b) *slow exchange on the correlation time scale*, and (c) *strong adsorption* can be formulated as

$$\begin{aligned} \frac{1}{T_1} &= \frac{1-f_a}{T_1^{bulk}} + \frac{f_a}{T_1^a} \\ &\approx_{f_a \rightarrow 1} \frac{f_a}{T_1^a} = C_1 f_a [I_{aa}(\omega) + 4I_{aa}(2\omega)] \end{aligned} \quad (7.98)$$

where the spectral density for the adsorbed phase is given by

$$\begin{aligned} I_{aa}(\omega) &= \int_{-\infty}^{+\infty} G_{aa}(t) e^{-i\omega\tau} d\tau \\ &= a_1 \frac{2\tau_{loc}}{1 + \omega^2 \tau_{loc}^2} + \frac{\varepsilon(1-a_1)}{(2\pi)^2 \Delta q} \int_{q_l}^{q_u} \frac{2(\tau_{tumble}^{-1} + Dq^2)^{-1}}{1 + \omega^2 (\tau_{tumble}^{-1} + Dq^2)^{-2}} dq \end{aligned} \quad (7.99)$$

C_1 is a constant specific for quadrupole coupling (which is known to be of an *intramolecular* nature).

The integral in the resulting expression in Eq. (7.99) covers a range from q_l to q_u . The upper limit corresponds to the shortest correlation time $\tau_u = (Dq_u^2)^{-1}$

¹⁵ Recall the analogous scenarios treated in the context of polymers (Eq. 5.295) and liquid crystals (Eq. 6.104). The analytical form of a product is a consequence of probability theory. The product implies the joint probability that none of the three independent reorientation processes have yet become effective. In other terms, it is the probability that the orientation correlation is still retained at time t .

contributing to the frequency dispersion on the basis of the RMTD mechanism. Spectral densities on this time scale will experimentally be significant if $\omega\tau_u \approx 1$ or less. The angular frequency window typically probed in experiments ranges up to about $\omega \approx 10^9$ rad/s. Thus, correlation times $\tau_u \ll 10^{-9}$ s will not affect the spin–lattice relaxation dispersion under the usual experimental conditions.¹⁶ We can therefore replace the upper limit of the integral in Eq. (7.99) by infinity, $q_u \rightarrow \infty$, without loss of validity:

$$I_{aa}(\omega) \approx a_1 \frac{2\tau_{loc}}{1 + \omega^2\tau_{loc}^2} + \frac{\varepsilon(1 - a_1)}{(2\pi)^2\Delta q} \int_{q_l}^{\infty} \frac{2(\tau_{tumble}^{-1} + Dq^2)^{-1}}{1 + \omega^2(\tau_{tumble}^{-1} + Dq^2)^{-2}} dq \quad (7.100)$$

The integral can be solved in the limits $\tau_{tumble}^{-1} \ll Dq^2$ and $\tau_{tumble}^{-1} \gg Dq^2$ by neglecting the τ_{tumble}^{-1} and the Dq^2 terms, respectively. The crossover between these limits is centered at $q_c = 1/\sqrt{\tau_{tumble}D}$. An approximate solution can thus be composed in closed form by taking the expression for the limit $\tau_{tumble}^{-1} \gg Dq^2$ in the range $q_l \leq q \leq q_c$, and the variant for the limit $\tau_{tumble}^{-1} \ll Dq^2$ otherwise. With the definitions $\tau_l \equiv (Dq_l^2)^{-1}$ and $\tau_c^{-1} \equiv \tau_l^{-1} + \tau_{tumble}^{-1}$, the spectral density Eq. (7.100) is accordingly approached in the whole parameter range by

$$I_{aa}(\omega) \approx a_1 \frac{2\tau_{loc}}{1 + \omega^2\tau_{loc}^2} + \frac{\varepsilon(1 - a_1)\sqrt{\tau_u}}{(2\pi)^2} \left\{ \left(\frac{1}{\sqrt{\tau_c}} - \frac{1}{\sqrt{\tau_l}} \right) \frac{2\tau_c}{1 + \omega^2\tau_c^2} \right. \\ \left. + \frac{1}{\sqrt{2\omega}} \left(\frac{1}{2} \ln \frac{1 + \sqrt{2\omega\tau_c} + \omega\tau_c}{1 - \sqrt{2\omega\tau_c} + \omega\tau_c} + \pi - \arctan \left(\sqrt{\frac{2}{\omega\tau_c}} - 1 \right) \right. \right. \\ \left. \left. - \arctan \left(\sqrt{\frac{2}{\omega\tau_c}} + 1 \right) \right) \right\} \quad (7.101)$$

The combined formalism based on Eq. (7.101) together with Eq. (7.98) describes the deuteron spin–lattice relaxation dispersion very well as demonstrated by the curves fitted to the data in Fig. 7.19 [87]. Note that the fluctuating interaction causing deuteron spin–lattice relaxation is of an entirely *intramolecular* nature. Thus, the reason for the choice of deuteron resonance in this study has not only been to discriminate water signals from those of the macromolecules.

Local (restricted) rotational diffusion matters (and dominates) only above about 10 MHz as indicated by the frequency dispersion getting leveled in this regime. At intermediate frequencies, the T_1 dispersion is governed by the RMTD mechanism of water as indicated by the characteristic square-root frequency dependence. Finally, the crossover to a low-frequency plateau at the *inflection frequency* ν_i is the result of two competing and mutually independent processes, namely, the low-frequency

¹⁶ With the surface diffusion coefficient discussed below, this correlation time limit means root-mean square-surface displacements much less than a few Å. Compare Sect. 7.4.2.1, where translational diffusion in the adsorbed phase has been examined.

cutoff of the RMTD mechanism on the one hand and macromolecular tumbling on the other¹⁷:

$$v_i \approx \frac{1}{2\pi\tau_c} = \frac{1}{2\pi} \left(\frac{1}{\tau_{\text{tumble}}} + \frac{1}{\tau_1} \right) \quad (7.102)$$

It is then the question which of the two cutoff mechanisms is the faster one. At low water contents in the range $c_w \leq 50\%$, global tumbling will be hindered by steric interactions of the tightly packed (nonspherical) protein molecules (compare Fig. 7.8). The consequence is $\tau_{\text{tumble}} \gg \tau_1$, so that the inflection frequency will be determined by $v_i \approx (2\pi\tau_1)^{-1}$. The protein molecules are then more or less immobilized, and the whole low-frequency dispersion is dominated by the RMTD process and its cutoff.

High water contents enable protein molecules to tumble globally, so that the opposite limit $\tau_{\text{tumble}} \ll \tau_1$ will be relevant. Under such circumstances, the inflection frequency is given by $v_i \approx (2\pi\tau_{\text{tumble}})^{-1}$. The inflection of the spin–lattice relaxation dispersion is shifted toward higher frequencies with increasing dilution of the solution as demonstrated by the data set for $c_w = 75\%$ in Fig. 7.19.

The description of the data in Fig. 7.19 with the model outlined above refers to a certain *time* (or *frequency*) scale. The plausibility of this analysis can be tested with regard to another scale, namely, the *length* scale of the system. Let us elucidate this point by the following compatibility consideration: The value of the correlation time τ_1 , Eq. (7.92), fitted to the experimental data is¹⁸ $\tau_1 = 1.6 \times 10^{-5}$ s. For an estimation of the surface diffusion-coefficient, we can take the lowest value that could be measured in aqueous BSA solutions according to Fig. 7.5:

$$D(T = 294 \text{ K}, c_p = 85\%) \approx 1.3 \times 10^{-11} \text{ m}^2/\text{s} \quad (7.103)$$

This value is associated with the water content just at the percolation threshold where hydration shells start to overlap and, hence, where continuous long-distance diffusion from protein to protein molecule is enabled. Inserting the values for τ_1 and D into Eq. (7.92) provides the *longest* surface “wave length”

$$\lambda_1 = \frac{2\pi}{q_1} = 2\pi\sqrt{\tau_1 D} \approx 91 \text{ nm} \quad (7.104)$$

¹⁷ The analytical structure of Eq. (7.102) can be rationalized as follows: The correlation function effective in the crossover regime is composed of the statistically *independent* partial correlation functions for tumbling on the one hand and for the longest RMTD mode on the other. That is $\exp\{-t/\tau_c\} = \exp\{-t/\tau_{\text{tumble}}\} \exp\{-t/\tau_1\}$ with $\tau_c = (\tau_{\text{tumble}}^{-1} + \tau_1^{-1})^{-1}$.

¹⁸ Note that this value must simultaneously be taken as the upper limit of the exchange time between the adsorbed and bulk-like phases. That is, $\tau_1 < \tau_{\text{ex}}$ as anticipated for slow exchange on the correlation time scale.

The diameter of a BSA molecule along its long axis is about 14 nm. That is, this value of the cutoff surface wavelength λ_l corresponds to 6–7 protein diameters. In other words, this is the distance over which a water molecule must diffuse in the average until its orientation correlation has entirely faded away via the RMTD mechanism. In view of the hydration-shell network formed by the densely packed protein molecules (see Fig. 7.8), this is certainly a plausible value.

7.5.5.4 Concentration Dependence of Spin Relaxation in the Aqueous Phase

In the following, mass proportions relative to the total weight (water plus protein) will be denoted by the symbol c and those relative to the water content by the symbol f with the respective subscripts. In this notation, the respective contents of water in total, water in the bulk-like phase, water in the adsorbed phase, and protein in aqueous protein solutions are given by

$$c_w = \frac{m_w}{m_w + m_p}; \quad c_b = \frac{m_b}{m_w + m_p}; \quad c_a = \frac{m_a}{m_w + m_p}; \quad c_p = \frac{m_p}{m_w + m_p} \quad (7.105)$$

where m_w , m_b , m_a , and m_p are the masses of total water, bulk-like water, adsorbed water, and protein in the sample. The water content indicating saturation of the hydration shells is likewise specified by

$$c_s = \frac{m_s}{m_s + m_p} \quad (7.106)$$

where m_s is the maximum mass of hydration water in the sample. The respective populations of the adsorbed and bulk-like phases are defined as

$$f_a = \frac{m_a}{m_w}; \quad f_b = 1 - f_a \quad (7.107)$$

Bulk-like water can exist in protein solutions for two reasons. First, it is the excess water beyond saturation of the hydration shells. Since the Gibbs free energy in the adsorbed phase tends to be lower than in the bulk-like phase, water molecules can additionally be released from the bound state to the bulk-like phase by thermal activation. Below saturation of the hydration shells, that is, for $c_w < c_s$, thermal activation will be the only reason for the existence of a bulk-like phase. The fraction of nuclei in the bulk-like water phase can thus be expressed by

$$f_b = 1 - f_a = \frac{m_b}{m_b + m_a} = \left(1 + \frac{m_a}{m_b}\right)^{-1} = \frac{1}{1 + \exp\{A_G/RT\}} \quad (7.108)$$

A_G is the difference of the molar Gibbs free energies in the bulk-like and the adsorbed water. In the opposite case, $c_w > c_s$, this fraction is given by

$$f_b = 1 - f_a = \frac{m_w - m_s}{m_w} + \frac{m_s}{m_w} \frac{1}{1 + \exp\{A_G/RT\}} \quad (7.109)$$

or

$$f_b = \frac{1}{1 - c_s} \left[\frac{c_w - c_s}{c_w} + \frac{c_s}{c_w} (1 - c_w) \frac{1}{1 + \exp\{A_G/RT\}} \right] \quad (7.110)$$

As suggested by the illustration in Fig. 7.20, the onset of unrestricted macromolecular tumbling is characterized by a certain critical water content c_0 to be further specified below. At this particular concentration, protein tumbling and the RMTD process become comparably effective for spin–lattice relaxation as discussed in the context of Eq. (7.102) for the inflection frequency.

The critical water content enabling protein tumbling can be treated with the aid of a kind of free-volume formalism as it was originally developed for translational-diffusion problems in condensed matter physics. According to the *Cohen/Turnbull theory* [92–94], a translational jump of a molecule in condensed matter is only possible if a void with a minimum volume V^* is formed in the vicinity of the molecule, where V^* is comparable to the volume excluded by the molecule to be displaced. Let us now apply the principle of this model to macromolecular tumbling. In the present context, *free volume* is interpreted as *volume of “free” (i.e., bulk-like) water*, and *translational diffusion* is replaced by *rotational diffusion*. One thus arrives at an analogous picture for molecular tumbling rates limited by the available access to unobstructed space.

The shape of globular protein molecules can often be approached by oblate or prolate ellipsoids. A spherical contour would be an extreme exception. Rotational jumps consequently require a sufficient volume V^* of bulk-like water in the surrounding medium. It is clear that V^* will be the larger the stronger the hydrated protein complex deviates from a spherical shape (see Fig. 7.20). The probability, that a molecule finds an amount of adjacent free water exceeding the minimum volume V^* is

$$P(V^*) = \exp\left\{-\frac{\gamma^* V^*}{V_b}\right\} \quad (7.111)$$

where V_b is the volume of bulk-like water per protein molecule in the average. The numerical coefficient γ^* accounts for the fact that protein molecules in this sense share bulk-like water to some degree. The value of γ^* is expected somewhere between 1/2 and 1.

The volume of a hydrated protein molecule is $V_p + V_s$, where V_p and V_s are the volumes of the bare protein and its saturated hydration shell, respectively. The shape of a hydrated protein molecule is approached by an ellipsoid of volume $V_{\text{ell}} = 4\pi\hat{a}\hat{b}\hat{c}/3$, where $\hat{c} > \hat{a}, \hat{b}$ are the semiaxes, and $\hat{c}$ is longer than $\hat{a}$ and $\hat{b}$. The minimum volume for unrestricted rotational diffusion of the hydrated protein complex is then that of a sphere of radius $\hat{c}$ circumscribing the protein ellipsoid

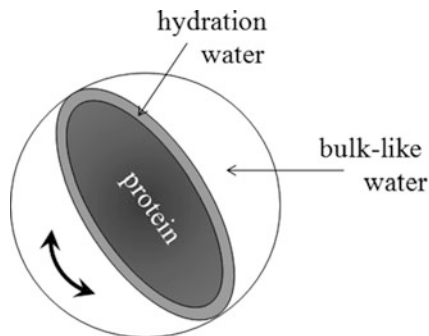


Fig. 7.20 Schematic illustration of the *free-water volume model* of macromolecular tumbling. A protein molecule (represented by an ellipse in *dark gray*) is surrounded by a hydration shell (*light gray*). The complex can only tumble if sufficient free water is available in the vicinity. The minimum free-water volume for free tumbling corresponds to the circumscribing sphere which defines the critical water content c_0

as illustrated in Fig. 7.20. The volume of such a sphere is $V_{\text{sph}} = 4\pi\hat{c}^3/3$. The ratio of the volumes is

$$\hat{r} = \frac{V_{\text{sph}}}{V_{\text{ell}}} = \frac{\hat{c}^2}{\hat{a}\hat{b}} \geq 1 \quad (7.112)$$

On this basis, the minimum volume of bulk-like water enabling a hydrated protein complex to tumble can be expressed by

$$V^* = V_{\text{sph}} - V_{\text{ell}} = (\hat{r} - 1)(V_p + V_s) \quad (7.113)$$

Inserting this into the probability, Eq. (7.111), suggests a tumbling rate

$$\tau_{\text{tumble}}^{-1} = \tau_{i0}^{-1} P(V^*) = \tau_{i0}^{-1} \exp\{-\gamma^*(\hat{r} - 1)(V_p + V_s)/V_b\} \quad (7.114)$$

where τ_{i0} refers to infinite dilution, that is, to the limit $V_b \rightarrow \infty$.

According to Eqs. (2.189) and (3.205), the rotational correlation time of a particle in a viscous medium is given by

$$\tau_{i0} = (6D_r)^{-1} \quad (7.115)$$

for the degree $l = 2$ of spherical harmonics as they are relevant for spin relaxation. The rotational diffusion coefficient D_r is assumed to obey the *Stokes/Einstein/Debye law* Eq. 2.204¹⁹:

$$D_r = \frac{k_B T}{8\pi\eta_b a_h^3} \quad (7.116)$$

¹⁹ In Ref. [95], some modification of this law is suggested based on a pulsed photoexcitation study of labeled proteins. For the present treatment, this is however of little relevance.

where η_b is the dynamic viscosity of bulk water, and a_h is the hydrodynamic radius of the hydrated protein complex of volume $V_p + V_s$. The hydrodynamic radius is defined by that of a sphere of the same volume as the protein complex:

$$V_p + V_s = \frac{4\pi a_h^3}{3} \quad (7.117)$$

Combining Eqs. (7.115), (7.114), (7.115), (7.116), and (7.117) results in the time constant for unobstructed tumbling

$$\tau_{t0} = \frac{\eta_b(V_p + V_s)}{k_B T} \quad (7.118)$$

The volumes V_p and V_s are proportional to the corresponding masses and, hence, to the respective concentrations c_p and c_s , where we anticipate the same proportionality factor. According to Eq. (7.114), the tumbling correlation time is thus approached by

$$\tau_{\text{tumble}} \approx \tau_{t0} \exp \left\{ \frac{\gamma^*(\hat{r} - 1)(c_p + c_s)}{c_b} \right\} \quad (7.119)$$

It diverges in the absence of bulk-like water, that is, for $c_b \rightarrow 0$, as it must be. With

$$c_b \approx c_w - c_s \quad \text{and} \quad c_p = 1 - c_w \quad (7.120)$$

τ_{tumble} can be further specified as

$$\tau_{\text{tumble}} = \tau_{t0} \exp \left\{ \gamma^*(\hat{r} - 1) \frac{1 - c_w + c_s}{c_w - c_s} \right\} \quad (7.121)$$

Tumbling sets on if the water content exceeds a critical value $c_w = c_0$. At lower contents, $c_w < c_0$, the tumbling time diverges, so that the inflection frequency Eq. (7.102) will be dominated by the (*concentration independent*) time constant τ_1 of the RMTD-controlled relaxation mechanism. The critical water content thus reveals itself as a crossover of the inflection frequency from a plateau to a steep concentration dependence as demonstrated by the data in Fig. 7.21a. The value is $c_0 \approx 60\%$. For water contents $c_w \ll c_0$, the tumbling time diverges, $\tau_{\text{tumble}} \rightarrow \infty$, so that the inflection frequency will solely be determined by τ_1 . With respect to the water content, the corresponding limits of Eq. (7.102) are

$$v_i \approx \begin{cases} (2\pi\tau_1)^{-1} \approx \text{const} & \text{for } c_w \ll c_0 \\ [2\pi\tau_{\text{tumble}}(c_w)]^{-1} & \text{for } c_w \gg c_0 \end{cases} \quad (7.122)$$

For $c_w \approx c_0$, Eq. (7.122) suggests $\tau_1 \approx \tau_{\text{tumble}}$. In combination with Eq. (7.121), we thus arrive at

$$\tau_1 = \tau_{t0} \exp \left\{ \gamma^* (\hat{r} - 1) \frac{1 - c_0 + c_s}{c_0 - c_s} \right\} \quad (7.123)$$

Solving this relation for c_0 results in

$$c_0 = c_s + \frac{\bar{\gamma}}{1 + \bar{\gamma}} \quad (7.124)$$

where

$$\bar{\gamma} = \frac{(\hat{r} - 1)\gamma^*}{\ln(\tau_1/\tau_{t0})} \quad (7.125)$$

With the empirical values $c_0 \approx 60\%$ and $c_s \approx 35\%$ suggested by the data in Fig. 7.21, the parameter $\bar{\gamma}$ adopts the value $\bar{\gamma} \approx 0.33$. All theoretical curves shown in the plots in Fig. 7.19 (deuteron T_1 dispersion), Fig. 7.21a (concentration dependence of the inflection frequency of the deuteron spin–lattice relaxation dispersion), and Fig. 7.21b (concentration dependence of the deuteron transverse relaxation time) have been calculated commonly on the basis of the above concept with a single parameter set (see Refs. [87, 96]).

7.5.5.5 Remarks on Spin Relaxation in Biological Tissue

Biological tissue consists predominantly of biopolymers embedded in aqueous environments. Polar surfaces of proteins and other microstructural components such as lipid membranes form the confining interfaces where low-frequency spin relaxation of water nuclei essentially takes place. It is therefore not too surprising that the relatively elementary relaxation model for protein solutions outlined in the previous sections can also be applied with some success to biological tissue. Of course, preparation of such systems with heavy water will hardly be possible. Apart from potentially broad parameter distributions, studies based on proton magnetic resonance nevertheless evince the same relaxation principles as outlined above. From the experimental point of view, it may be favorable to suppress direct contributions from solid-like macromolecules or membranes by spin-echo signal detection (see Sect. 3.1.4.4) and/or to use narrowband excitation RF pulses.

Examples of field-cycling NMR relaxometry studies of biological tissue can be found in Refs. [87, 97–99], for example. Remarkably, a quantitative description of spin–lattice relaxation dispersion data recorded in intact frog muscles, liver tissue, and living leeches is possible on the basis of the above model [87]. In this way, decisive mechanisms and relaxation factors needed for interpretations of

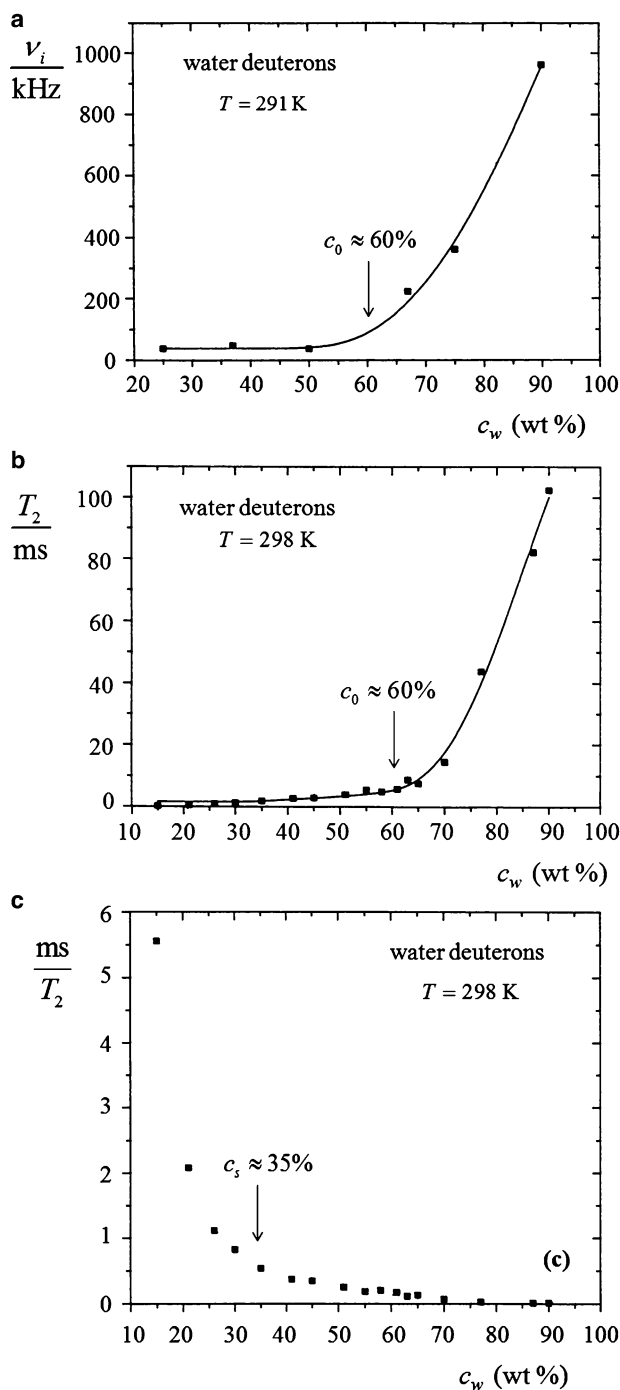


Fig. 7.21 Dependences of various quantities on the water content c_w of aqueous bovine serum albumin solutions in D_2O . The *solid lines* have been calculated on the basis of the formalism described in the text. (a) Inflection frequency $v_i = v_i(c_w)$ of the deuteron spin-lattice relaxation

experimental data can be revealed. This is of particular interest for biomedical magnetic resonance imaging (MRI), since the contrasts of MRI images essentially reflect nuclear magnetic relaxation properties.

7.5.6 Special Surface Topologies

One of the striking consequences of the RMTD relaxation mechanism is that it is not only thermal activation that determines the reorientation rates of adsorbate molecules. An equally important factor is the (static) surface topology the adsorbed phase is subjected to. That is, molecular reorientation dynamics depends on micro *structural* properties. For an analytical description of the surface topology, we have introduced the orientational structure factor $\tilde{S}(q)$ in Eq. (7.78). The variable is the wave number q representing topological surface “modes” (in the static sense). The second (independent) element of the RMTD model is the propagator $\tilde{P}(q, t)$, Eq. (7.79), characterizing the distribution of curvilinear displacements along the surface. The RMTD concept thus intertwines structural and dynamical features.

The surface topologies of the porous media and macromolecular solutions considered so far have been assumed to have a more or less random shape. In the case of protein solutions, this assumption is reflected by the equipartition of wave numbers proposed in Eq. (7.90). The spin-relaxation data of fluids confined in porous silica glasses on the other hand suggested an orientational structure factor in the form of a fixed power law, Eq. (7.86), alluding to potentially fractal surface topologies [80, 100].

Let us now add two more application examples concerning peculiar, well-specified surface structures. “Well specified” means that the surface topology should be known a priori from microscopy techniques such as electron microscopy, atomic force microscopy, and tunneling microscopy. The question is whether distinct features of surface topologies revealed by microscopy can likewise be rendered by conjugate characteristics of spin relaxation.

Fig. 7.21 (continued) dispersion. Below the critical water content $c_0 \approx 60\%$, macromolecular tumbling is sterically blocked, so that the inflection frequency is determined by RMTD. By contrast, above c_0 , the dominating mechanism is tumbling of the macromolecules. The experimental data were evaluated directly from T_1 frequency dispersion curves such as those shown in Fig. 7.19. **(b)** Transverse relaxation time $T_2 = T_2(c_w)$ of the water deuterons. The data indicate a value $c_0 \approx 60\%$ for the critical water content in accordance with that estimated from plot **(a)**. **(c)** Transverse relaxation rate $T_2^{-1} = T_2^{-1}(c_w)$ of water deuterons. This type of plot emphasizes the behavior at *small* T_2 values. The bend of the concentration dependence suggests a saturation water content of $c_s \approx 35\%$ for the hydration shells as already indicated by the diffusion data in Fig. 7.9 (Reproduced from Ref. [96] with kind permission of © Wiley 1990)

7.5.6.1 Hydration Water of Lipid Bilayers in the Ripple Phase

The Three Phases of Lipid Bilayers

Lipid bilayers, well known as model systems for biological membranes, can adopt a number of different phases (compare Sect. 6.8.3). Between the liquid-crystalline phase (LC) at high temperatures and the gel phase at low temperatures, there is a narrow temperature interval of a few degrees in which the so-called *ripple phase* appears [101, 102]. The phase transition temperatures depend on the length of the fatty acid residues and on the type of the polar headgroups forming the interfaces to the aqueous environment. The term “ripple” reminds of the corrugated shape of the water/lipid interfaces as illustrated in Fig. 7.22, right-hand side, and in Fig. 7.23.

This particular ripple topology has been assessed in great detail with the aid of freeze-etching electron microscopy [101] and electron tunneling microscopy [105]. Indirectly, the surface undulation is confirmed by the collapse of the quadrupole splitting in deuteron spectra of deuterated hydration water as demonstrated in Fig. 7.22. The coalescence of spectral splittings can indeed be treated as a consequence of the RMDT process as will be shown further down. Figure 7.23 visualizes how fluctuations of the orientation of hydration water follow from translations on the ripple-phase topology.

The Corrugated-Sheet Model for Deuteron Spin–Lattice Relaxation in Adsorbed Water of Ripple-Phase Bilayers

Let us first examine how the ripple structure affects spin–lattice relaxation in the hydration layers. In analogy to the scenario described in the context of Eq. (7.98), the water (deuteron) spin–lattice relaxation rate is governed by (a) *intramolecular couplings*, (b) *two-phase/fast exchange on the relaxation time scale*, (c) *slow exchange on the correlation time scale*, and (d) *strong adsorption*. Spin-lattice relaxation can therefore be treated by means of the formalism employed in Sects. 7.5.4 and 7.5.5.3. Tying on Eq. (7.98) and the definitions declared in this context, the water (deuteron) spin–lattice relaxation rate can be represented by

$$\begin{aligned} \frac{1}{T_1} &\equiv R_1 = \frac{1-f_a}{T_1^{\text{bulk}}} + \frac{f_a}{T_1^a} \\ &\approx_{f_a \rightarrow 1} \frac{f_a}{T_1^a} = C_1 f_a \left[I_{aa}^{(1)}(\omega) + 4I_{aa}^{(2)}(2\omega) \right] \end{aligned} \quad (7.126)$$

Analogous to Eq. (7.97), three different types of motion contributing to molecular dynamics in the adsorbed phase need to be distinguished:

$$\mathcal{G}_{aa}^{(m)}(t) = \mathcal{G}_{\text{loc}}^{(m)}(t) \mathcal{G}_{\text{RMTD}}^{(m)}(t) \mathcal{G}_{\text{tumble}}^{(m)}(t) \quad (7.127)$$

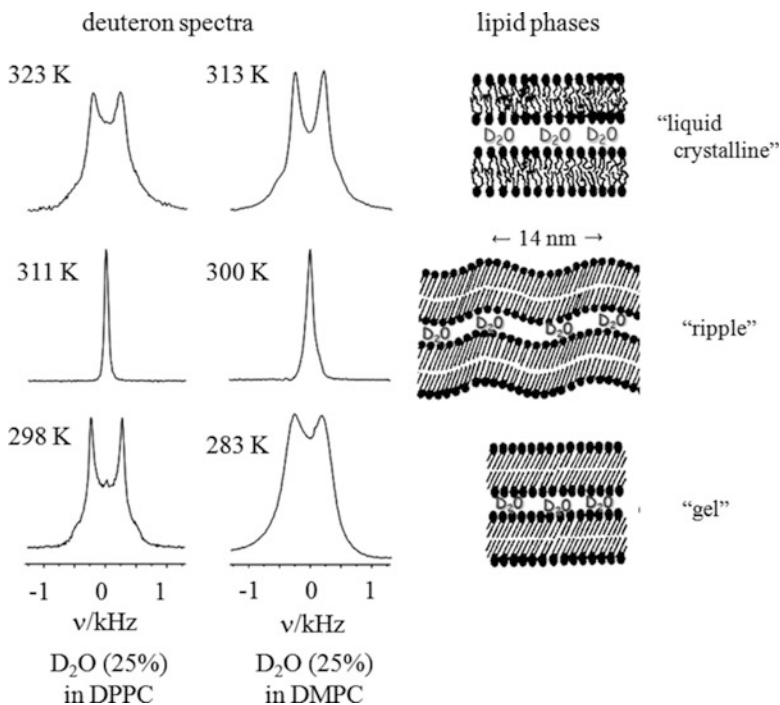


Fig. 7.22 Deuteron magnetic resonance spectra of (*heavy*) hydration water in the three phases of lamellar lipid bilayers (*left*) and schematic representation of the bilayer structures (*right*). The ripple “wave length” is concluded from an X-ray analysis [102]. The lipids under investigation are DPPC (= 1,2-di-palmitoyl-*sn*-3-phosphatidylcholine) and DMPC (= 1,2-di-myristoyl-*sn*-3-phosphatidylcholine). The finite quadrupole splitting in the water spectra indicates a certain degree of order in the gel and liquid-crystalline phases. In these cases, the preferential orientation of water molecules relative to the bilayer surfaces forms fixed angles with the external magnetic field. This is in contrast to the ripple phase where the quadrupole splitting collapses due to the leveling effect by fast translational diffusion along the undulated surface. “Fast” means that the molecular reorientation rate exceeds the spectral splitting (Reproduced from Ref. [103] with kind permission of © AIP 2000)

As detailed in Sects. 3.1.7.1 and 5.4.3.7, different orders $m = 1, 2$ of spherical harmonics need normally not be treated separately, provided that all molecular orientations in space can be reached on the correlation time scale with more or less the same probability. It is then sufficient to weight the contributions of the corresponding spectral densities by numerical prefactors as specified in Eq. 3.127 and as represented by the factor of 4 in the brackets in Eq. (7.126). However, the present case is different: The peculiar topology of ripple-phase bilayers entails that reorientations on the correlation time scale are strongly restricted. Contrary to the practice in the previous sections, we have therefore specified the orders $m = 1, 2$ in Eqs. (7.126) and (7.127) for the sake of generality. This will be relevant specifically for $G_{\text{RTD}}^{(m)}(t)$, but not for the other partial correlation functions.

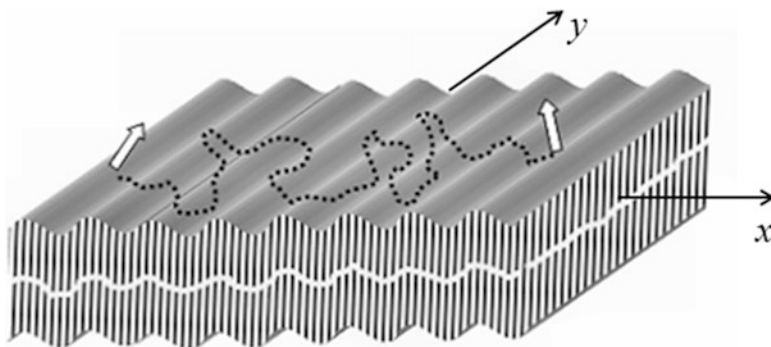


Fig. 7.23 Schematic representation of RMTD at the surfaces of lipid bilayers in the ripple phase (compare Fig. 7.22). This is the basis of the corrugated-sheet model for spin relaxation at undulated surfaces (Reproduced from Ref. [104] with kind permission of © Elsevier 2004)

Following Eq. (7.71), restricted local rotational diffusion of adsorbed water molecules is characterized by the partial correlation function

$$G_{\text{loc}}^{(m)}(t) = G_{\text{loc}}(t) = a_1 \exp\left\{-\frac{t}{\tau_{\text{loc}}}\right\} + (1 - a_1) \quad (7.128)$$

which is independent of the order m and which decays to a plateau $G_{\text{loc}}(t \gg \tau_{\text{loc}}) = 1 - a_1 = \text{const}$ at long times $t \gg \tau_{\text{loc}}$. In the high-field limit, deuteron spins are relaxed by fluctuations of the electric-field-gradient tensor relative to the external magnetic field B_0 . On a time scale $t \gg \tau_{\text{loc}}$, the electric-field-gradient tensor in the molecules effectively becomes *rotationally symmetric* about the mean rotation axis, that is the unit normal vector $\mathbf{u}_s$ on the local bilayer surface.

RMTD on a corrugated sheet causes fluctuations of the polar angle $\vartheta \equiv (\mathbf{B}_0, \mathbf{u}_s)$ spanned by $\mathbf{B}_0$ and $\mathbf{u}_s$. For an illustration, see Fig. 7.24. Since the undulation is assumed to be uniform, the correlation functions $G_{\text{RMTD}}^{(m)}(t)$ depend solely on the polar angle ϑ according to

$$G_{\text{RMTD}}^{(m)}(t) = \frac{\langle \Phi_{2,m}(0) \Phi_{2,m}(t) \rangle}{\langle |\Phi_{2,m}|^2 \rangle} \quad (7.129)$$

The functions $\Phi_{2,m}$ are the relevant spherical harmonics (Eq. 1.8) deprived of the azimuthal-angle terms:

$$\begin{aligned} \Phi_{2,1} &= \sin \vartheta \cos \vartheta \\ \Phi_{2,2} &= \sin^2 \vartheta. \end{aligned} \quad (7.130)$$

The need to distinguish the orders $m = 1, 2$ will become obvious further down.

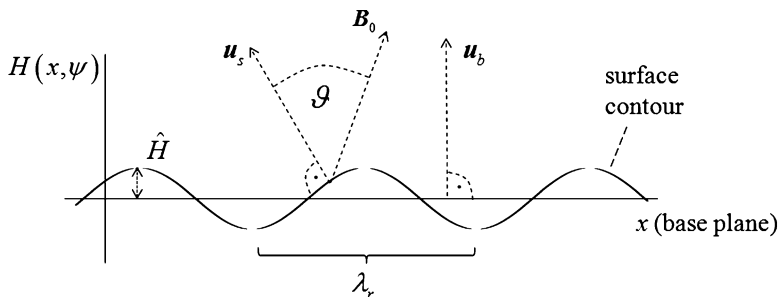


Fig. 7.24 The surface contour function $H(x, \psi)$ describing the corrugated sheet as a model for ripple-phase bilayers. $\mathbf{u}_s$ is the unit normal vector on the surface assumed to coincide with the orientation of the effective principal axis of the field-gradient tensor of the hydration water molecules. $\mathbf{B}_0$ is the magnetic flux density relevant for NMR experiments. $\mathbf{u}_b$ is the unit normal vector on the base plane of the bilayer

The third component factor in Eq. (7.127) accounts for global motions of the whole liposomes composed of the bilayers. This process will certainly be relatively slow but, in principle, competes with the longest modes of the RMTD process in the sense that the faster process prevails (see Eq. 7.102). As before, an exponential decay independent of m can be assumed:

$$\mathcal{G}_{\text{tumble}}^{(m)}(t) = \mathcal{G}_{\text{tumble}}(t) \approx \exp\left\{-\frac{t}{\tau_{\text{tumble}}}\right\} \quad (7.131)$$

In typical field-cycling NMR relaxometry experiments, the components $\mathcal{G}_{\text{loc}}(t)$ and $\mathcal{G}_{\text{tumble}}(t)$ are expected to reveal themselves merely as limiting high- and low-frequency plateaus. They are therefore of subordinate interest. By contrast, $\mathcal{G}_{\text{RMTD}}^{(m)}(t)$ is the function determining the T_1 dispersion in most of the experimental frequency window.

Assuming a sine function along the x direction, the bilayer surface can be described by a height function

$$H(x, y, \psi) = \hat{H} \sin(q_r x + \psi) \quad (7.132)$$

as graphically represented by Fig. 7.24. The x and y axes are defined in Fig. 7.23. The angle ψ is the phase angle at $x = 0$, and q_r is related to the “wave length” λ_r by $q_r = 2\pi/\lambda_r$. The amplitude of the function $H(x, \psi)$ is denoted by $\hat{H}$. For generalizations, it may be worthwhile to note that this sine function can be considered as a Fourier component of any periodic non-sinusoidal function. Judged from the structural X-ray and microscopy studies reported in Refs. [101, 102, 105], the corrugation function Eq. (7.132) can be considered to be stationary on the time scale of NMR experiments. That is, the only fluctuation relevant in the hydration

water will be due to molecular motion of the water molecules relative to a static surface.

Displacements in the topologically two-dimensional interfacial layer are measured in *curvilinear* distances r

$$r = \sqrt{s^2 + y^2} \quad (7.133)$$

The quantity s is the contour length of the corrugated surface along the x -coordinate. The propagator be $P(r, t)$. The correlation functions (Eq. 7.129) can then be written in integral form as

$$\mathcal{G}_{\text{RMTD}}^{(m)}(t) = \int_0^{2\pi} d\psi \int_{-\infty}^{\infty} ds \int_{-\infty}^{\infty} dy P(r, t) \Phi_{2,m}(0) \Phi_{2,m}(t) \quad (7.134)$$

The curvilinear displacement element ds is related to its projection on the x -axis, dx , by

$$ds = \sqrt{1 + [H'(x, \psi)]^2} dx \quad (7.135)$$

where $H'(x, \psi) \equiv dH/dx$. Assuming for the moment that the external magnetic field $\mathbf{B}_0$ is oriented perpendicular to the base plane of the bilayer, the polar angle $\vartheta = \vartheta_{s,b}$ can be expressed in terms of the height function $H(x, \psi)$ by

$$\vartheta_{s,b}(t) = \arctan[\hat{H}q_r \cos\{q_r x(t) + \psi\}] \quad (7.136)$$

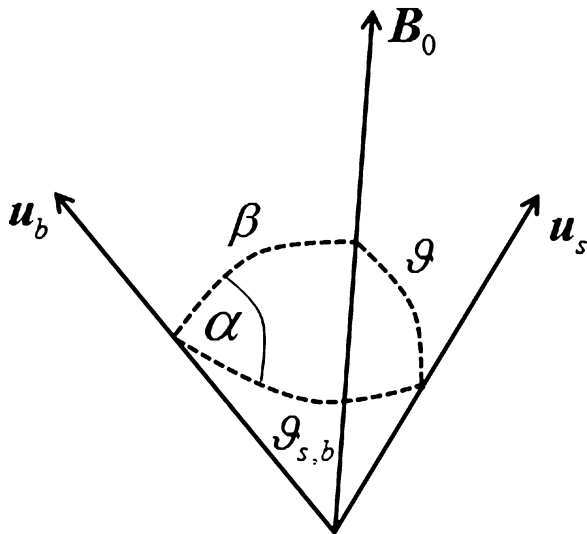
where $x(0) = 0$. In reality, the orientation of the magnetic flux density relative to the base plane will be arbitrarily distributed in a powdery sample. That is, the correlation function finally of interest will be a powder average of $\mathcal{G}_{\text{RMTD}}^{(m)}(t)$. Note that carrying out the powder average already on the level of correlation functions (rather than on the basis of relaxation rates) generally anticipates that the spin ensemble experiences all available surface orientations during the spin–lattice relaxation time by fast water diffusion across an extended part of the sample.

For the calculation of the powder average, we introduce the angle $\beta \equiv (\mathbf{B}_0, \mathbf{u}_b)$ = $0 \cdots \pi$ between the magnetic flux density $\mathbf{B}_0$ and the unit normal vector $\mathbf{u}_b$ on the base plane of the bilayer. Furthermore, the plane spanned by the vectors $\mathbf{B}_0$ and $\mathbf{u}_b$ forms the angle $\alpha = 0 \cdots \pi$ with the plane spanned by the vectors $\mathbf{u}_s$ and $\mathbf{u}_b$. Using the cosine theorem of spherical trigonometry, the cosine of the polar angle $\vartheta \equiv (\mathbf{B}_0, \mathbf{u}_s)$ can be written as a function of the angles $\alpha, \beta, \vartheta_{s,b}$ as

$$\cos \vartheta = \cos \beta \cos \vartheta_{s,b} + \sin \beta \sin \vartheta_{s,b} \cos \alpha \quad (7.137)$$

(see Fig. 7.25). Inserting Eq. (7.136) results in

Fig. 7.25 Definition of the angles $\alpha, \beta, \vartheta, \vartheta_{s,b}$ relating the orientations of the vectors u_b, u_s, B_0



$$\vartheta(t) = \arccos \left[\cos \beta \cos \left(\arctan \left[\hat{H} q_r \cos \{q_r x(t) + \psi\} \right] \right) + \sin \beta \sin \left(\arctan \left[\hat{H} q_r \cos \{q_r x(t) + \psi\} \right] \right) \cos \alpha \right] \quad (7.138)$$

The powder average of the correlation function Eq. (7.129) can then be evaluated according to

$$\overline{G_{\text{RMTD}}^{(m)}(t)} = \frac{1}{2\pi} \int_0^\pi d\alpha \int_0^\pi d\beta G_{\text{RMTD}}^{(m)}(t) \sin \beta \quad (7.139)$$

where $G_{\text{RMTD}}^{(m)}(t)$ is obtained by inserting the polar angles $\vartheta(0)$ and $\vartheta(t)$ into Eqs. (7.129) and (7.130).

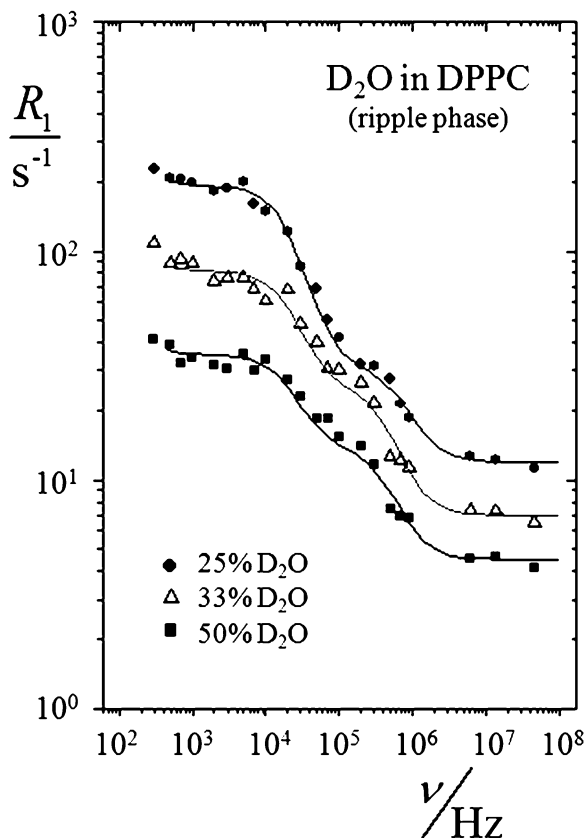
As discussed in Sect. 7.4.2, diffusion in the interfacial layer can be described by a Gaussian propagator for topologically two-dimensional (and in this sense curvilinear) displacements r in a time t :

$$P(r, t) = \frac{1}{4\pi} \frac{\exp\{-r^2/(4Dt)\}}{Dt} \quad (7.140)$$

The ordinary variant of diffusion appears to be justified at least for water contents below about 30% where practically all water is in the adsorbed phase. In this case, no bulk-like phase exists, so that an influence of the BMSD mechanism can be excluded.

In summary, the corrugated-sheet model for deuteron spin-lattice relaxation can be formulated by combining Eqs. (7.126), (7.127), (7.128), (7.129), (7.130), and (7.131) and expressing the RMTD correlation function by the combination of Eqs. (7.134), (7.135), (7.136), (7.137), (7.138), (7.139), and (7.140). The numerical evaluation of the resulting relaxation rates can then be used for parameter fits to

Fig. 7.26 Frequency dependence of the deuteron spin–lattice relaxation rate in the hydration water of DPPC bilayers at three different contents of (*heavy*) water. The temperature was 311 K corresponding to the ripple phase of the bilayers (compare Fig. 7.22). The solid lines represent fits of the corrugated-sheet model (Reproduced from Ref. [103] with kind permission of © AIP 2000)



experimental data. Figure 7.26 shows the frequency dependence of the deuteron spin–lattice relaxation rate R_1 in aqueous 1,2-di-palmitoyl-*sn*-3-phosphatidylcholine (DPPC) systems in the ripple phase at three different water contents [103]. The solid lines have been calculated with ripple wavelengths in the range $\lambda_r = 12 - 14.8$ nm and a ripple amplitude of $\hat{H} = 3.8$ nm in accordance with the structural parameters directly evaluated from electron tunneling microscopy experiments [105]. Based on deuteron field-gradient NMR diffusometry data, the water diffusion coefficient in the adsorbed phase was determined as $D \approx 5 \times 10^{-11}$ m²/s which closely corresponds to the values measured in hydration shells of aqueous protein systems (see Figs. 7.5, 7.7, and 7.9).

Collapse of the Splitting of Deuteron Quadrupole Spectra

The splitting of the water deuteron spectra in the liquid-crystalline and gel phases coalesces in the ripple phase as demonstrated in Fig. 7.22. This finding can readily be explained in the following way. Water molecules on the lipid bilayer surface are

oriented along a preferential orientation relative to the local surface. As long as the bilayer has a quasiplanar topology, translational diffusion along the surface scarcely affects the water orientation relative to the external magnetic field on the NMR time scale for motional averaging, that is, $10^{-5} \dots 10^{-4}$ s. Under these circumstances, deuteron spectra adopt the shape of partially averaged Pake powder patterns characterized by a finite quadrupole splitting.²⁰ The quadrupole splitting simultaneously indicates that the adsorbate molecules are in fact ordered relative to the surface as anticipated for the RMTD mechanism. In the ripple phase, things are different: The RMTD process along the corrugated surface levels the local fields causing the quadrupole splitting. The splitting therefore coalesces to a single Lorentzian-like line.

The spacing of the singularities of a Pake powder pattern is given by [39]

$$\Delta\nu_Q = \frac{3}{4} \frac{e^2 q Q}{h} \frac{1}{2} \langle 3\cos^2\vartheta - 1 \rangle_{\tau, \text{powder}} \quad (7.141)$$

The electric-field-gradient tensor can be taken to be effectively rotationally symmetric, owing to rapid rotation of the water molecules about an axis perpendicular to the surface. e is the elementary charge, Q is the deuteron quadrupole moment, h is Planck's constant, and $\bar{q}$ is the principal-axis value of the electric-field-gradient tensor along the effective symmetry axis. As before, the polar angle of the effective field gradient relative to the external magnetic field is denoted by ϑ . The angle brackets indicate both motional averaging by diffusion on the bilayer surface and a powder average. The effective quadrupole splitting common to the gel and liquid-crystalline phases was found to be $\Delta\nu_Q \approx 500$ Hz (see Fig. 7.22). The time scale conjugate to this spectral splitting is of the order

$$\tau \approx \frac{1}{2\pi \cdot 500 \text{ Hz}} \approx 3 \times 10^{-4} \text{ s} \quad (7.142)$$

In the ripple phase, the second-order Legendre polynomial on the right-hand side of Eq. (7.141) will be averaged over all orientations on the corrugated surface reached within τ . On the basis of the above model considerations, the quadrupole splitting can be expressed by

$$\Delta\nu_Q \approx \frac{3}{8\pi} \frac{e^2 q Q}{h} \left\langle \int_0^{2\pi} d\psi \int_{-\infty}^{\infty} ds \int_{-\infty}^{\infty} dy P(r, \tau) (3\cos^2\vartheta - 1) \right\rangle_{\text{powder}} \quad (7.143)$$

where $r = \sqrt{s^2 + y^2}$. The powder average can be calculated analogous to Eq. (7.139).

The deuteron spectra in Fig. 7.22 suggest a ratio of the quadrupole splitting in the gel and LC phases relative to the linewidth (= full linewidth at half height) in the

²⁰ For an explanation of this sort of powder spectrum, see Ref. [39], for instance.

ripple phase of about $\Delta v_Q^{\text{gel,LC}} : \Delta v_Q^{\text{ripple}} = 500 \text{ Hz} : 80 \text{ Hz} = 6.25$. Based on the water diffusion coefficient $D = 5 \times 10^{-11} \text{ m}^2/\text{s}$ measured in the adsorbed phase, the root-mean-squared displacement along the surface is of the order 10^{-6} m in the interval τ specified in Eq. (7.142). This is the equivalent of about six ripple periods. On the one hand, this length scale is long enough to probe all possible orientations on the corrugated surface, but, on the other hand, short enough to neglect the overall curvature of the liposome shape. The linewidth $\Delta v_Q^{\text{ripple}}$ for the ripple phase can thus be calculated on the basis of Eq. (7.143). This results in the ratio $\Delta v_Q^{\text{gel,LC}} : \Delta v_Q^{\text{ripple}} = 6.37$ reproducing the empirical value very well. The coalescence of quadrupole splitting as an independent information source can thus be described consistently with spin–lattice relaxation dispersion.

7.5.6.2 Hydration Water in Aqueous Suspensions of Saponite Clay Platelets

Mesoscopic objects with planar surfaces are formed by so-called platelets of synthetic saponite clays [106, 107]. The diameters of these disklike structures are in the order of 50 nm. In an aqueous suspension, the platelets form a quasi-static matrix of surfaces with a hydration layer in the strong-adsorption limit. In diluted suspensions, the BMSD mechanism is again expected to be responsible for displacements on the surfaces. The orientation correlation will be recovered completely as long as initially adsorbed water molecules return to the platelet surface after intermittent excursions to the bulk-like phase. On the other hand, complete loss of correlation must be expected if the effective displacements along the surface exceed the extension of the platelet. A schematic illustration of the scenario is shown in Fig. 7.27. Figuratively, it may be referred to as “pancake model” [108, 109].

Intramolecular spin–lattice relaxation of water in the vicinity of such a polyhedral ensemble of planar surfaces can be treated analogously to the formalisms outlined above. The platelet structure of the saponites is modeled by a set of circular disks of radius r . The orientation correlation function is given by the probability that the particle will be found still or again on the original disk after a time t .

Relative to the original platelet, the particle position is specified in polar coordinates ρ, β as indicated in Fig. 7.27. The initial and final positions are ρ_0, β_0 and ρ_1, β_1 , respectively. If both positions are on the same disk, the distance traveled by the particle is

$$s = \sqrt{\rho_0^2 + \rho_1^2 - 2\rho_0\rho_1 \cos(\beta_1 - \beta_0)} \quad (7.144)$$

The probability that a particle starting at a position ρ_0, β_0 will finally be adsorbed on the same disk as initially can be calculated as

$$w(\rho_0, \beta_0, s, t) = \int_0^r \int_0^{2\pi} \rho_1 P(s, t) d\beta d\rho_1 \quad (7.145)$$

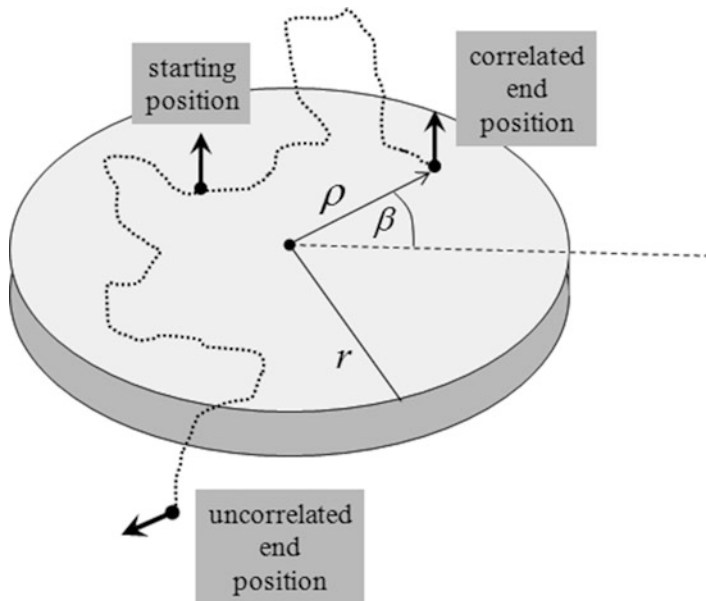


Fig. 7.27 Schematic representation of the “pancake model” for nuclear magnetic relaxation on clay surfaces. The matrix forms planar platelets. Assisted by the BMSD process, adsorbate molecules can diffuse along the platelet surfaces without loss of correlation to the initial orientation. As soon as the effective displacement along the surface exceeds the platelet dimension and if the particles do not return to the original platelet, the orientation correlation will be lost entirely (Reproduced from Ref. [104] with kind permission of © Elsevier 2004)

where $P(s, t)$ is the propagator effective for surface diffusion. Depending on the existence of a bulk-like water phase, either a Gaussian or a Cauchy distribution will be relevant as discussed in Sects. 7.5.3 and 7.5.4.

The orientation correlation function can be expressed as the ensemble average of $w(\rho_0, \beta_0, s, t)$ over all initial positions. That is,

$$\mathcal{G}_{\text{RMTD}}(t) = \frac{1}{\pi r^2} \int_0^r \int_0^{2\pi} \rho_0 w(\rho_0, \beta_0, s, t) d\beta_0 d\rho_0 \quad (7.146)$$

The substitution $\alpha = \beta_1 - \beta_0$ leads to

$$\mathcal{G}_{\text{RMTD}}(t) = \frac{1}{r^2} \int_0^r \int_0^r \int_0^{2\pi} \rho_0 \rho_1 P(s, t) d\alpha d\rho_0 d\rho_1 \quad (7.147)$$

If a Gaussian propagator applies for surface diffusion, we have

$$\mathcal{G}_{\text{RMTD}}(t) = \frac{1}{2\pi D t r^2} \int_0^r \int_0^r \int_0^{2\pi} \rho_0 \rho_1 \exp\left\{-\frac{\rho_0^2 + \rho_1^2 - 2\rho_0 \rho_1 \cos \alpha}{4Dt}\right\} d\alpha d\rho_0 d\rho_1 \quad (7.148)$$

In the case of a Cauchy distribution, Eq. (7.84), the integral to be solved is²¹

$$\mathcal{G}_{\text{RMTD}}(t) = \frac{ct}{\pi r^2} \int_0^r \int_0^r \int_0^{2\pi} \frac{\rho_0 \rho_1}{\left[\rho_0^2 + \rho_1^2 - 2\rho_0 \rho_1 \cos \alpha + (ct)^2\right]^{3/2}} d\alpha d\rho_0 d\rho_1 \quad (7.149)$$

The factors before the integrals in Eqs. (7.148) and (7.149) define the characteristic time constants $\tau_{\text{Gauss}} = r^2/D$ and $\tau_{\text{Cauchy}} = r/c$, respectively. A point of major interest is that these quantities imply information on the geometrical extension r of the planar surfaces.

The numerical evaluation of Eqs. (7.148) and (7.149) suggests power laws in the limit of long times relative to τ_{Gauss} or τ_{Cauchy} . For $t \gg \tau_{\text{Cauchy}} = r/c$, Cauchy distributions lead to $\mathcal{G}_{\text{RMTD}}(t) \propto t^{-2}$, whereas Gaussian propagators suggest $\mathcal{G}_{\text{RMTD}}(t) \propto t^{-1}$ in the limit $t \gg \tau_{\text{Gauss}} = r^2/D$. On a time scale $t \approx (0.1 \dots 1) \times \tau_{\text{Cauchy}}$ or $t \approx (0.1 \dots 1) \times \tau_{\text{Gauss}}$, the correlation functions approach logarithmic decays within about a decade.

As with all other surface-related model scenarios, the correlation function for the RMTD process must be supplemented by a term representing *local motions* and a term taking into account potential *tumbling* fluctuations of the platelets (compare Eqs. (7.97) for proteins and (7.127) for liposomes). Practically, these phenomena give rise to high- and low-frequency plateaus of the spin–lattice relaxation rate in the experimental frequency window. At medium frequencies, say, $10^4 \dots 10^6$ Hz, the dispersion of the spin–lattice relaxation rates $T_1^{-1}(\nu)$ will however be dominated by the RMTD process described above.

In the experiments reported in Ref. [108], it turned out that the formalism for the Cauchy propagator describes the experimental data significantly better than that for the Gaussian propagator. This finding is not unexpected in view of the large bulk-like water phase in the samples. The platelet radii evaluated on this basis lie in the range $r = 28 - 91$ nm in accordance with literature values based on X-ray studies.

²¹ A complete expression for the BMSD propagator on planar surfaces has recently been derived in Ref. [19]. This implies the prevalence of a Cauchy distribution at short displacements (as they are relevant in the present case) and a terminating Gaussian decay in the limit of long distances.

7.5.7 The NMR Flow-Relaxation Effect

7.5.7.1 Qualitative Description

In the previous sections, RMTD was identified as mechanism often dominating the long-tail decay of the orientation correlation function in the vicinity of strongly adsorbing surfaces. Apart from thermal activation processes, it was demonstrated that mesoscopic surface topologies can have a strong effect on spin–lattice relaxation at low frequencies. Let us now examine the potential consequences of superimposed *hydrodynamic flow*.

A dynamic scenario of this sort is of particular interest for the following reasons. (1) The essence of the RMTD relaxation process is that adsorbate molecules are subject to frequent adsorption–desorption–readsorption cycles at the pore walls effectively leading to surface diffusion. Hydrodynamic flow superimposed to surface diffusion is expected to *accelerate* transport along surfaces and, hence, the RMTD process as schematically illustrated in Fig. 7.28. As a consequence, the orientation correlation function will decay on a shorter time scale than in the static case. This phenomenon should manifest itself by a reduction of the low-frequency spin–lattice relaxation rate. (2) Another aspect is *hydrodynamic* (or Taylor/Aris) *dispersion* [111, 112], that is, the superposition of *incoherent* Brownian particle motions and *coherent* flow. We have encountered this sort of phenomena already in Sect. 4.9.3. The present discussion refers however to spin relaxometry, that is, to extremely short length scales inaccessible to field-gradient NMR techniques. The time scale probed by field-cycling NMR relaxometry is less than 10^{-4} s. Therefore, the relevant root-mean-square displacements by Brownian motions are less than 100 nm for water at room temperature. Flow/spin-relaxation experiments thus concern surface layers thinner than 100 nm, a length scale that is attributed to nanofluidics. We are dealing with a sort of *rotational analogue* of Taylor/Aris dispersion [111, 112]. Such studies may elucidate a question frequently raised in fluid dynamics, namely, whether *interfacial slip* exists or whether a *stick boundary* condition is appropriate at confining surfaces. An important parameter in this context is the *Péclet number*

$$P_e = \frac{\Phi \xi}{d_p D} \quad (7.150)$$

where ξ is the correlation length of the pore space, Φ is the hydrodynamic flux, D is the molecular diffusion constant in the bulk, and d_p is the pore width (compare Eq. 4.94).

7.5.7.2 Analytical Treatment

According to Eq. (7.73), the surface-related spin–lattice relaxation rate of an ensemble of two-spin-1/2 systems of like nuclei subject to intramolecular dipolar coupling is given by

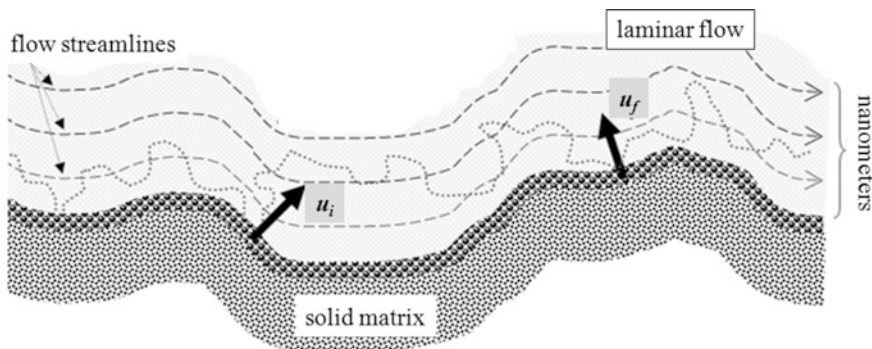


Fig. 7.28 Illustration of the flow-relaxation effect on adsorbate reorientation by hydrodynamic dispersion. The *dotted line* is to represent a trajectory of a molecule by Brownian motion in the presence of laminar flow along the surface. Flow streamlines are drawn as *broken lines*. The adsorption layer on the solid matrix is indicated by the interface area shaded in *light gray*. The *arrows* refer to the local preferential orientations at the initial and final surface sites. The thickness of the fluid layer along the surface in which flow-enhanced RMTD is expected ranges from molecular diameters up to several nanometers (Reproduced from Ref. [110] with kind permission of © APS 2005)

$$\frac{1}{T_1} \approx C_1 f_a [\mathcal{I}_{aa}(\omega) + 4\mathcal{I}_{aa}(2\omega)] \quad (7.151)$$

The relevant conditions are (1) *strong adsorption* (Eq. 7.26), (2) *significant populations of the adsorbed phase* f_a , (3) *two-phase/fast-exchange* (Eq. 7.70), (4) *slow exchange on the correlation time scale* (Eq. 7.16), and (5) *longtime/low-frequency limit* $t, \omega^{-1} \gg \tau_{\text{loc}}$. Taking these conditions for granted, the problem will be to generalize the RMTD formalism to the case of superimposed hydrodynamic flow, that is, hydrodynamic dispersion.

The curvilinear coordinate along a streamline is denoted by s (see Fig. 7.28). The basis of the following formalism is the *convective-diffusion equation* we have encountered already in Sect. 4.9.3.3. Assuming coarse-grained homogeneity and isotropy in the medium, local dispersion coefficients $D_{\perp}$ and $D_{\parallel}$ perpendicular (“transverse”) and parallel (“longitudinal”) to the flow velocity $\mathbf{v}$ can be distinguished. In terms of these quantities, the convective-diffusion equation for the propagator $P(s, t)$ reads

$$\frac{\partial P}{\partial t} + \mathbf{v} \cdot \nabla P = D_{\perp} \nabla_{\perp}^2 P + D_{\parallel} \frac{\partial^2 P}{\partial s^2} \quad (7.152)$$

where $\nabla_{\perp}^2$ is the Laplace operator acting in a direction transverse to flow and $\mathbf{v}$ is the local flow velocity.

In the present context, merely the longitudinal version of hydrodynamic transport is of interest. Longitudinal displacements by flow and Brownian diffusion are

collinear, and $D_{\parallel}$ can be identified with the self-diffusion coefficient D . After Fourier transformation, the solution of Eq. (7.152) is

$$\tilde{P}(q, t) = \tilde{P}(q, 0) e^{-D t q^2} e^{-i q v t} \quad (7.153)$$

where v is taken as the local flow velocity component in longitudinal direction. The wave number q is the reciprocal space variable conjugate to the real-space curvilinear displacement variable s .

Note that the Gaussian term in the propagator Eq. (7.153) anticipates ordinary diffusion. The arguments outlined in Sect. 7.5.3 for the strong-adsorption limit suggest that features of Lévy walks along the surface should be relevant if a significant bulk-like phase exists. A Cauchy propagator would therefore be more appropriate in principle. For the sake of simplicity, we will nevertheless restrict the treatment to the ordinary-diffusion case. The numerical Monte Carlo simulations referred to further down in Sect. 7.5.7.3 will imply the true character of the propagator anyway [113].

With the initial condition $P(s, 0) = c_0 \delta(s)$, the (one-dimensional) Fourier expression conjugate to $\tilde{P}(q, t)$ reads

$$P(s, t) = \frac{c_0}{2\pi} \int_{-\infty}^{+\infty} e^{-(D t q^2 + i q v t)} e^{i s q} dq \quad (7.154)$$

where c_0 is a constant and $\delta(s)$ is Dirac's delta function. In analogy to Eq. (3.192), the autocorrelation function describing orientational fluctuations of molecules with fixed intramolecular interdipole distances can be expressed by

$$\begin{aligned} G_{\text{or}}(t) &= 4\pi (-1)^m \langle Y_{2,m}(\mathbf{u}_i) Y_{2,-m}(\mathbf{u}_f) \rangle_{\mathbf{u}_i, \mathbf{u}_f} \\ &= 4\pi (-1)^m \int \langle P_c(\mathbf{u}_i, \mathbf{u}_f, t) Y_{2,m}(\mathbf{u}_i) \rangle_{\mathbf{u}_i} Y_{2,-m}(\mathbf{u}_f) d\Omega_f \end{aligned} \quad (7.155)$$

where the angle brackets indicate ensemble averages. $\mathbf{u}_i$ and $\mathbf{u}_f$ are unit vectors normal to the surface indicating the initial and the final orientations of the molecule under consideration (see Fig. 7.28). $d\Omega_f$ is the differential solid angle into which $\mathbf{u}_f$ points. As in several previous cases, we will not distinguish different orders m of the spherical harmonics $Y_{2,m}$ since this is not expected to affect the results significantly.

The conditional probability density $P_c(\mathbf{u}_i, \mathbf{u}_f, t)$ for a final orientation $\mathbf{u}_f$ if the initial orientation was $\mathbf{u}_i$ can be expressed by

$$P_c(\mathbf{u}_i, \mathbf{u}_f, t) = \int_{-\infty}^{\infty} \Theta(\mathbf{u}_i, \mathbf{u}_f, s) P(s, t) ds \quad (7.156)$$

where $\Theta(\mathbf{u}_i, \mathbf{u}_f, s)$ is the probability that the surface orientation changes from $\mathbf{u}_i$ to $\mathbf{u}_f$ in a curvilinear distance s . The initial condition is $\Theta(\mathbf{u}_i, \mathbf{u}_f, 0) = \delta(\mathbf{u}_f - \mathbf{u}_i)$ in terms of Dirac's delta function. $\Theta(\mathbf{u}_i, \mathbf{u}_f, s)$ can be expanded according to

$$\Theta(\mathbf{u}_i, \mathbf{u}_f, s) = \sum_{l', m'} Y_{l', -m'}(\mathbf{u}_i) Y_{l', m'}(\mathbf{u}_f) G_s(s) \quad (7.157)$$

where $G_s(s)$ is the normalized surface orientation correlation function between surface sites separated by a curvilinear distance s (see Eq. 7.75). The combination of Eqs. (7.155), (7.156), and (7.157), and making use of the orthonormal properties of spherical harmonics, leads to

$$G_{\text{or}}(t) = \int_{-\infty}^{+\infty} G_s(s) P(s, t) ds \quad (7.158)$$

in a certain analogy to Eq. (7.76). In contradistinction to the formalism in Sect. 7.5.3, Eq. (7.158) now refers to curvilinear transport directed along a stream-line. The displacements s in the interfacial layer are therefore no longer distributed isotropically in the quasi-two-dimensional space.

Inserting the propagator Eqs. (7.154) into (7.158) gives

$$G_{\text{or}}(t) = \int_{-\infty}^{+\infty} G_s(s) \left(\frac{c_0}{2\pi} \int_{-\infty}^{+\infty} e^{-(Dtq^2 + iqv t)} e^{iqs} dq \right) ds \quad (7.159)$$

After regrouping the factors exclusively depending on the space variable s , we arrive at the *orientational structure factor* for one dimension along the flow direction:

$$\tilde{S}(q) = \frac{c_0}{2\pi} \int_{-\infty}^{+\infty} G_s(s) e^{iqs} ds \quad (7.160)$$

The autocorrelation function Eq. (7.155) can thus be rewritten as

$$G_{\text{or}}(t) = \int_{-\infty}^{+\infty} \tilde{S}(q) e^{-(Dtq^2 + iqv t)} dq \quad (7.161)$$

The corresponding spectral density, that is, the real part of the Fourier transform of Eq. (7.161), is

$$I_{\text{aa}}(\omega) = \int_{-\infty}^{+\infty} \tilde{S}(q) \frac{2Dq^2}{(Dq^2)^2 + (qv + \omega)^2} dq \quad (7.162)$$

Up to now, a well-defined flow velocity v was assumed. In reality, a distribution of flow velocities $W(v)$ varying with the pore width and the distance from the surfaces will be more appropriate. Averaging the above expression in this respect leads to

$$I_{\text{aa}}(\omega) = \int_{v_{\min}}^{v_{\max}} W(v) \int_{q_{\min}}^{q_{\max}} \tilde{S}(q) \frac{2Dq^2}{(Dq^2)^2 + (qv + \omega)^2} dq dv \quad (7.163)$$

where $v_{\min}$ and $v_{\max}$ define the range over which the velocities are distributed. Likewise, the orientational structure factor $\tilde{S}(q)$ is assumed to have finite values only in the range between $q_{\min}$ and $q_{\max}$.

Combining this expression for the spectral density with Eq. (7.151) gives the velocity-dependent spin–lattice rate

$$\begin{aligned} \frac{1}{T_1} &= C_1 f_a [I_{aa}(\omega) + 4I_{aa}(2\omega)] \\ &\approx C I_{aa}(\omega) = C \int_{v_{\min}}^{v_{\max}} W(v) \int_{q_{\min}}^{q_{\max}} \tilde{S}(q) \frac{2Dq^2}{(Dq^2)^2 + (qv + \omega)^2} dq dv \end{aligned} \quad (7.164)$$

where C is an effective constant. In case of equipartitions of the flow velocity in the range $0 \dots v_{\max}$ and of the orientational structure factor in the range $q_{\min} \dots q_{\max}$ (see Eq. 7.90), the spin–lattice relaxation rate takes the form

$$\frac{1}{T_1} \approx C \frac{2}{v_{\max}(q_{\max} - q_{\min})} \int_0^{v_{\max}} \int_{q_{\min}}^{q_{\max}} \frac{Dq^2}{(Dq^2)^2 + (qv + \omega)^2} dq dv \quad (7.165)$$

The influence of flow velocity suggested by the above expressions for the spin–lattice relaxation rate is called the *flow-relaxation effect* [110, 113].

7.5.7.3 Verification

The conditions under which the flow-relaxation effect can be verified in experiments can tentatively be tested with the aid of (two-dimensional) Monte Carlo simulations [113]. A pack of ellipsoidal grains may serve as a test structure mimicking the surface topology to be expected in a real porous medium. A model picture is shown in the inset of Fig. 7.29. Grains of ellipsoidal shape are randomly distributed in a flow conduit. The porosity of this model pore space is $\Pi \approx 0.415$ with a mean pore size around $1.1 \mu\text{m}$. The correlation length ξ is taken as half the semimajor axis of the ellipses. The velocity field can be imported from computational fluid dynamics simulations for different Péclet numbers for this particular system. The orientation correlation function can then be evaluated numerically. The spin–lattice relaxation dispersion calculated on this basis is shown in Fig. 7.29 for different Péclet numbers.

Assuming a Gaussian orientational structure factor $\tilde{S}(q)$ and fitting the analytical formalism, that is, Eq. (7.161), for this particular structure factor to the simulated correlation decay provides the dynamic parameters v and D . Setting the computer unit length 10^{-6}m and the computer recycle time 10^{-7}s suggests the experimental window shown in the inset box of Fig. 7.29. Judged from these results, the flow-relaxation

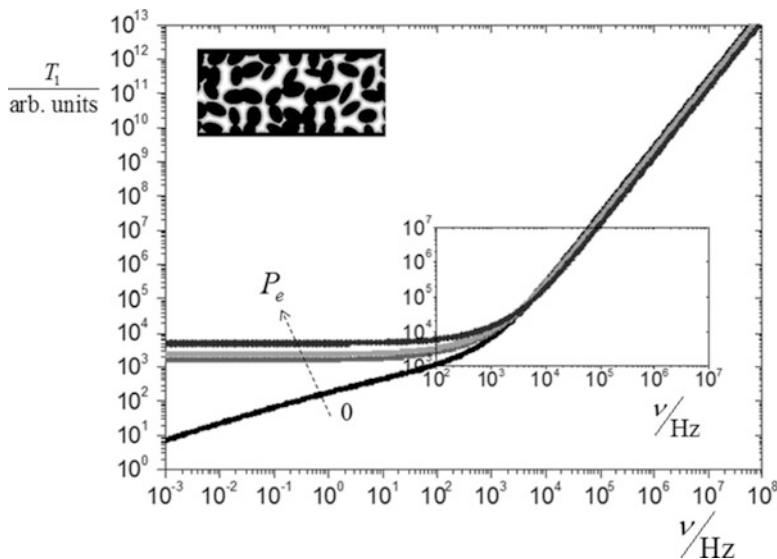


Fig. 7.29 Spin–lattice relaxation times versus frequency for different Péclet numbers P_e for a fluid flowing through the ellipsoidal grain model structure illustrated in the *inset*. The data represent the numerical Fourier transform of the simulated orientation autocorrelation function. The Péclet numbers are 0; 1.92; 4.73; 9.35 from the *bottom to the top* following the arrow. The frequency window accessible in typical field-cycling NMR relaxometry experiments is marked by the *box* (Reproduced from Ref. [113] with kind permission of © APS 2005)

effect can be expected to be measurable with the aid of the field-cycling technique at resonance frequencies below 100 kHz.

The main difficulty one will face with flow-relaxation experiments is that hydrodynamic flow is not homogeneously distributed in the whole pore space. It rather tends to occur along certain percolation pathways as demonstrated by the computational fluid dynamics simulation shown in Fig. 4.11. The consequence is that most of the sample volume will not be affected by flow of sufficient velocity or will even consist of stagnant zones. The effectively measured flow effect on spin–lattice relaxation may therefore be reduced appreciably.

Other factors challenging the experimental detectability are the weak longtime stability of the flow field and the potential heating of the sample due to energy dissipation upon forced flow through porous media. Despite all these impediments, an experimental demonstration of a small but anyway finite effect of about 20% has indeed been possible as reported in the field-cycling NMR relaxometry study Ref. [110]. This experiment has been set up with a chromolith column as it is in use in high-pressure liquid chromatography.

A problem frequently discussed in literature (see, e.g., Ref. [114]) is the question what *interfacial boundary condition* is relevant for flow. Judged from these results, a modified interfacial slip boundary condition should be appropriate in the sense that molecules move in a sort of hopping process along the surfaces as illustrated in Fig. 7.28.

7.5.8 *Electron-Paramagnetic Surface Relaxation Sinks*

The interpretation of the spin–lattice relaxation data discussed so far in this chapter anticipates that paramagnetic impurities such as transition metal ions are absent or negligible. Suspects, where this condition might be violated, are not so much the synthetic porous media addressed above, but materials of natural origin such as porous rocks or technical products such as building materials and cement [115–117]. In such cases, the relaxation formalism outlined in Sect. 3.1.5.8 will be relevant.

Samples can be checked in this respect by using electron spin resonance for the direct detection of unpaired electrons [115]. Another strategy is to employ isotopic dilution of the fluid in test experiments. In the case of proton resonance, the nonresonant isotope of the choice is ^2H . The gyromagnetic ratio of deuterons is roughly seven times smaller than that of protons. Proton spin relaxation by proton–proton dipolar coupling is therefore about 50 times more efficient than by dipolar interaction between protons and deuterons. That is, the presence of deuterons is largely negligible in proton relaxation studies. On the other hand, chemical exchange, if present, ensures homogeneous mixing of the two isotopes, so that dilution by deuterons causes a corresponding reduction of the proton spin–lattice relaxation rate or, equivalently, a prolongation of the spin–lattice relaxation time.

A typical isotopic-dilution experiment of this sort is represented by the plot in Fig. 7.30. In this case, water confined in a porous silica glass has been studied. The spin–lattice relaxation times are prolonged in accordance with the isotopic-dilution ratio. This finding proves that there is no significant relaxation mechanism other than by dipolar coupling from proton to proton. The influence of paramagnetic impurities can thus be excluded. By the way, this conclusion is also confirmed by the fact that the deuteron and proton spin–lattice relaxation dispersions are identical as demonstrated in Fig. 7.15: The fluctuations of the dominant spin interactions are the same so that (intermolecular) couplings to any electron-paramagnetic species are ruled out in this case.

On the other hand, in case electron-paramagnetic species have been identified as constituents of the surfaces exposed to the adsorbate fluid, the interpretation of spin relaxation must be adapted according to the *S*-spin equilibrium limit treated in Sect. 3.1.5.8. Such paramagnetic impurities immobilized on surfaces of porous media will be efficient relaxation sinks. Spin relaxation of the nuclei in the fluid may even be dominated by interactions with these centers. The relaxation scenario is then reduced to a translational-diffusion problem: The relaxation rate is determined by the rate with which the nuclei get into contact with the paramagnetic impurities. This in turn is mediated by diffusive normal modes in the pore space (see Sect. 7.2.1). The interested reader finds a pertinent formalism specific for surfaces of macroporous media in Ref. [25]. Other diffusion-mode theories have been reported in Refs. [7, 9] including applications to biological materials.

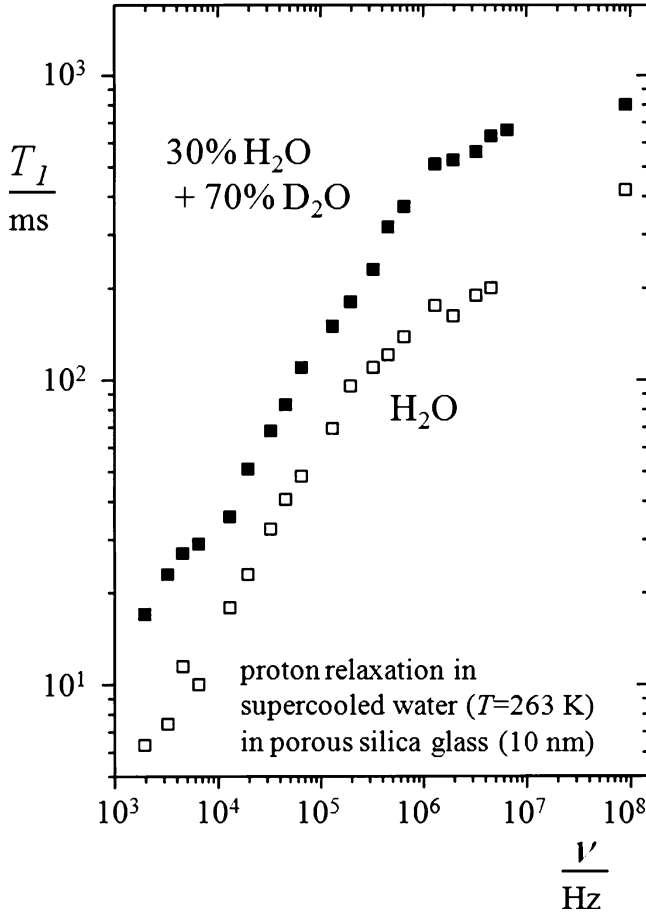


Fig. 7.30 Proton T_1 dispersion of supercooled (i.e., still liquid) water in porous silica glass (trade name Bioran 10; nominal pore diameter 10 nm). Isotopic dilution by D_2O reduces dipolar couplings from proton to proton. The proton spin-lattice relaxation times are correspondingly prolonged. This finding proves that there is no significant relaxation mechanism due to paramagnetic impurities (Reproduced from Ref. [23] with kind permission of © AIP 1998)

Likewise, the different exchange scenarios mentioned above can be relevant for paramagnetic relaxation centers as well. This is of particular interest, if the impurities are distributed in different sub-pore spaces as expected in heterogeneous materials. According to Ref. [118], two-dimensional NMR relaxation-correlation plots (see Sect. 3.4.5) of cement pastes reveal potential exchange processes between different pore species.

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Glossary of Frequent Symbols, Units, Constants and Abbreviations

(if not specified otherwise in the text)

Vectors are denoted in bold letters. (Quadratic) *matrices* and *tensors* are signified by a tilde underneath such as $\underline{\chi}$. Fourier, Laplace or Hankel transformed quantities are marked by an overhead tilde such as $\tilde{E}(\mathbf{q}, t)$. *Operators* are preferably (but not exclusively) represented by special symbols and calligraphic letters such as $\mathcal{O}$. Conjugate complex quantities are marked by an asterisk.

a	Radius, attenuation factor, acceleration, signal amplitude
a_h	Hydrodynamic radius
A	Area, amplitude, scalar coupling constant
A_G	Gibbs free energy
A_H	Helmholtz free energy
AC	Alternating current
AQ	Acquisition (interval)
AW	Anderson/Weiss (theory)
α	Polarizability, thermal diffusivity
α_{exp}	Thermal expansion coefficient
b	Capture range, scattering length, Kuhn length, Rouse segment length
$\mathbf{B}$, B_0 , B_1	Magnetic-flux density vectors
BMSD	Bulk mediated surface diffusion
BPP	Bloembergen/Purcell/Pound (theory)
BSA	Bovine serum albumin
BWR	Bloch/Wangsness/Redfield (theory)
c	Concentration, correlation function
c_0	Vacuum velocity of light
c_V	Specific heat at constant volume
cc	Conjugate complex
C_∞	Characteristic ratio of polymers
CFD	Computational fluid dynamics (simulations)
CPMG	Carr/Purcell/Meiboom/Gill (RF pulse sequence)
CSA	Chemical shift anisotropy

χ	Exponent
χ_e	Electric susceptibility
χ_m	Magnetic susceptibility
d	Spacing, diameter, dimensionality
D	(Translational) Self-diffusion coefficient
D_{cm}	Center-of-mass diffusion coefficient
D_r	Rotational diffusion coefficient
DC	Direct current
DLS	Dynamic light scattering
δ	Time interval, (gradient) pulse width, Dirac's delta function, loss angle, differential
δ_{lm}	Kronecker symbol
Δ	Diffusion time, gradient pulse interval (in field-gradient NMR diffusometry)
e	(Positive) Elementary charge (occasionally also represented by e_0), Euler's number
$\text{erf}\{\dots\}$	Error function $\text{erf}\{\xi\} \equiv 2\pi^{-1/2} \int_0^\xi \exp\{-u^2\} du$
$\text{erfc}\{\dots\}$	Complementary error function $\text{erfc}\{\xi\} \equiv 1 - \text{erf}\{\xi\} = 2\pi^{-1/2} \int_\xi^\infty \exp\{-u^2\} du$
E	Young's modulus, magnitude of the electric field strength, energy eigen-value
$\mathbf{E}$	Vector of the electric field strength
$\tilde{E}$	Elasticity tensor
E_a	Activation energy
EOF	Electro-osmotic flow
ε	Binding or dissociation energy (per bond), unit operator, exponent
$\tilde{\varepsilon}$	Strain tensor
ε_0	Electric field constant
ε_{int}	Internal energy per unit mass
ε_r	Relative dielectric permittivity
f	Fraction, population, line-shape function
$\mathbf{f}$	Stochastic (random) force vector, force per unit mass
F	Force, quantum number of total spin, filling factor
$\mathbf{F}$	Force vector, total spin vector operator
$\mathcal{F}\{\dots\}$	Fourier transform
FID	Free-induction decay
FT	Fourier transformation
φ, ϕ	Azimuthal angle, phase angle, dihedral angle
$ \varphi\rangle$	Ket for the wave-function φ
Φ	Electrostatic potential, velocity potential, flux (transported quantity per unit time and unit area)
η	(Dynamic) Viscosity (SI unit: $\text{kg m}^{-1} \text{s}^{-1}$)
η_0	Zero-shear viscosity

$\mathbf{g}$	Magnetic-field gradient vector, gravity acceleration vector
G	Shear modulus
$G(t)$	(Original) Temporal correlation function, shear relaxation modulus
G'	Storage modulus
G''	Loss modulus
$\mathcal{G}(t)$	Normalized (or synonymously: reduced) temporal autocorrelation function ($\mathcal{G}(0) = 1$)
$\mathcal{G}_{\text{inc}}(t)$	Incoherent dynamic structure factor ($\mathcal{G}_{\text{inc}}(0) = 1$)
$G_{\text{coh}}(t)$	Dynamic structure factor for relative pair diffusion ($G_{\text{coh}}(0) = S(\mathbf{q})$)
γ	Gyromagnetic ratio, shear angle
$\Gamma(x)$	Gamma function
$\tilde{\Gamma}$	Electric-field gradient tensor
h	Planck's constant (quantum of action)
$\hbar$	Planck's constant divided by 2π
H	Height
$\mathcal{H}$	Hamilton operator (in energy units)
HMM	Hahn/Maxwell/McConnell (equations)
HMMT	Hahn/Maxwell/McConnell/Torrey (equations)
i	Imaginary unit
I	Spin quantum number, moment of inertia
$\mathbf{I}$	Spin vector operator (in units $\hbar$)
I_d	Particle detection rate
$\mathcal{I}(\omega)$	Reduced spectral density (intensity function) = Fourier transform of $\mathcal{G}(t)$
$\Im\{\dots\}$	Imaginary part of ...
I_x, I_y, I_z	Cartesian components of the spin vector operator (in units $\hbar$)
I^+, I^-	Raising and lowering spin operators (in units $\hbar$)
ICD	Ionic current density
$\mathbf{j}$	Current density vector
J	Compliance, mass flux
J	Joule ($1 \text{ J} = 2.388 \times 10^{-4} \text{ kcal}$)
J_k	Bessel function of order k
$J^{(m)}(\omega)$	(Original) Spectral density (intensity function) = Fourier transform of $G_m(t)$
k	Wave number, rate constant
$\mathbf{k}$	Wave vector
k_B	Boltzmann constant ($= 1.381 \times 10^{-23} \text{ J K}^{-1} = 3.298 \times 10^{-27} \text{ kcal K}^{-1}$)
kcal	Kilo calorie ($1 \text{ kcal} = 4,186.8 \text{ J}$)
K	Spring (or elastic) constant (SI unit: kg s^{-2})
$\hat{K}$	Curvature-elastic or Frank/Oseen constant (SI unit: $\text{kg s}^{-2} \text{ m}$)
K_c	Compression (or bulk) modulus
κ	Thermal conductivity
l	Degree of spherical harmonics
ℓ	Length

<i>l</i>	Bond vector
<i>ℓ</i>	Distance vector
<i>l_p</i>	Persistence length
<i>L</i>	Length, contour length
LC	Liquid crystal
<i>λ</i>	Wave-length, eigen-value, elongation, affine deformation factor, length
<i>m</i>	Mass, molecular mass, magnetic quantum number, order of spherical harmonics, complex transverse magnetization ($m = M_x + iM_y$)
<i>M</i>	Molecular mass
<i>M</i>	Magnetization vector (expectation value)
<i>M_c</i>	Critical molecular mass
<i>M_e</i>	Entanglement molecular mass
<i>M_K</i>	Molecular mass of a Kuhn segment
MRI	Magnetic resonance imaging
<i>μ</i>	(Electrical) Mobility, magnitude of dipole moment
<i>μ</i>	Magnetic dipole vector (operator), electric dipole vector
<i>μ₀</i>	Magnetic field constant
<i>μ_r</i>	Relative magnetic permeability
<i>n</i>	Number density of objects, refractive index, Rouse-segment number variable
<i>n</i>	Order director
<i>N</i>	Number of objects
<i>N_A</i>	Avogadro number ($= 6.022 \times 10^{23} \text{ mol}^{-1}$)
<i>N_K</i>	Number of Kuhn segments per polymer chain
NMR	Nuclear magnetic resonance
<i>ν</i>	Frequency, lateral contraction number (Poisson's ratio), number (not to be confused with the Roman letter <i>ν</i> in italics used as symbol for 'velocity')
∇	Nabla differential vector operator (del)
ODF	Order director fluctuations
ℳ	Operator in general
<i>ω</i>	Angular frequency
<i>Ω</i>	Offset of angular frequencies, solid angle, number of conformations
<i>p</i>	Momentum, population, pressure, a priori probability, statistical weight, normal-mode number, normal-coordinate number
<i>P</i>	Probability, probability density, distribution function, propagator
<i>P</i>	Electric polarization vector
<i>P₂</i>	Second-order Legendre polynomial
<i>P_e</i>	Péclet number
<i>P</i>	Operator
PGSE	Pulsed gradient spin echo (method)
PIF	Pressure-induced flow
<i>π</i>	pi

Π	Porosity
ψ, Ψ	Wave function, response function
q	Charge, heat, wave number
$\mathbf{q}$	Scattering vector, wave vector
Q	Heat, nuclear quadrupole moment, quotient
$\hat{Q}$	Operator of an observable
Q_{dc}	Dipolar-correlation quotient
r	Radius
$\mathbf{r}_{\text{ee}}$	End-to-end vector
$\mathbf{r}$	Position vector, distance vector, displacement vector (in the context of diffusion and hydrodynamic dispersion)
$\langle r^2 \rangle$	Mean-square displacement, second moment of the propagator
R	Gas constant ($R = k_{\text{B}}N_{\text{A}} = 8.315 \text{ J K}^{-1} \text{ mol}^{-1} = 1.986 \times 10^{-3} \text{ kcal K}^{-1} \text{ mol}^{-1}$), Ohm resistance, flow resistance, relaxation rate
$\mathbf{R}$	Position vector (especially in the context of diffusion and hydrodynamic dispersion)
$\tilde{R}$	Relaxation rate matrix
$\Re\{\dots\}$	Real part of ...
R_1	Spin-lattice relaxation rate
R_{a}	Rayleigh number
R_{e}	Reynolds number
R_{g}	Polymer radius of gyration
RF	Radio frequency
RMTD	Reorientation mediated by translational displacements
ρ	Mass density, spin density, density operator
$\rho_{\text{c}}, \rho_{\text{q}}$	Charge density
ρ_{W}	Energy density
s	Curvilinear coordinate, signal voltage per unit volume
$\mathbf{s}$	Displacement vector
S	Spin quantum number, signal voltage, entropy, static structure factor
$\hat{S}$	Spin vector operator (in units $\hbar$)
S_{or}	Order parameter
$\tilde{S}(q)$	Orientational structure factor
S^+, S^-	Raising and lowering spin operators (in units $\hbar$)
SGSE	Steady gradient spin echo (method)
σ	Reduced density operator, scattering cross-section, force per unit area, (electrical) conductivity
$\tilde{\sigma}$	Stress tensor, chemical shielding tensor
$\boldsymbol{\sigma}$	Stress vector
t	Time, time interval
t_{E}	Echo time
t_{R}	Repetition time
T	Absolute temperature

$\mathbf{T}$	Torque vector
T_1	Spin-lattice (or longitudinal) relaxation time
$T_{1\rho}$	Rotating-frame spin-lattice relaxation time
T_2	Transverse relaxation time
$\text{Tr}\{\dots\}$	Trace operation
τ	Time interval, tortuosity (in the geometrical sense)
$\boldsymbol{\tau}$	Shear stress
$\tilde{\tau}$	Deviatoric stress tensor
τ_{shear}	Shear stress tensor
τ_{diff}	Diffusive tortuosity
ϑ, θ	Polar angle, valence angle
θ	Polar angle
$\mathbf{u}$	Unit tensor
$\mathbf{u}$	Unit vector, (flow) velocity
U	Potential, internal energy, voltage
$\mathbf{v}$	Velocity vector (not to be confused with the Greek letter ν)
V	Volume
$\mathcal{V}$	Operator of interaction potentials
w	Probability, probability per unit time, energy density
W	(Interaction) Potential, work, energy, probability per unit time, probability density, distribution function
WLF	William/Landel/Ferry formalism
X	Normal coordinate
ξ	Correlation length
$Y_{l,m}$	Spherical harmonics of degree l and order m
ζ	Zeta potential, friction coefficient, displacement
ζ_{rot}	Vorticity

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