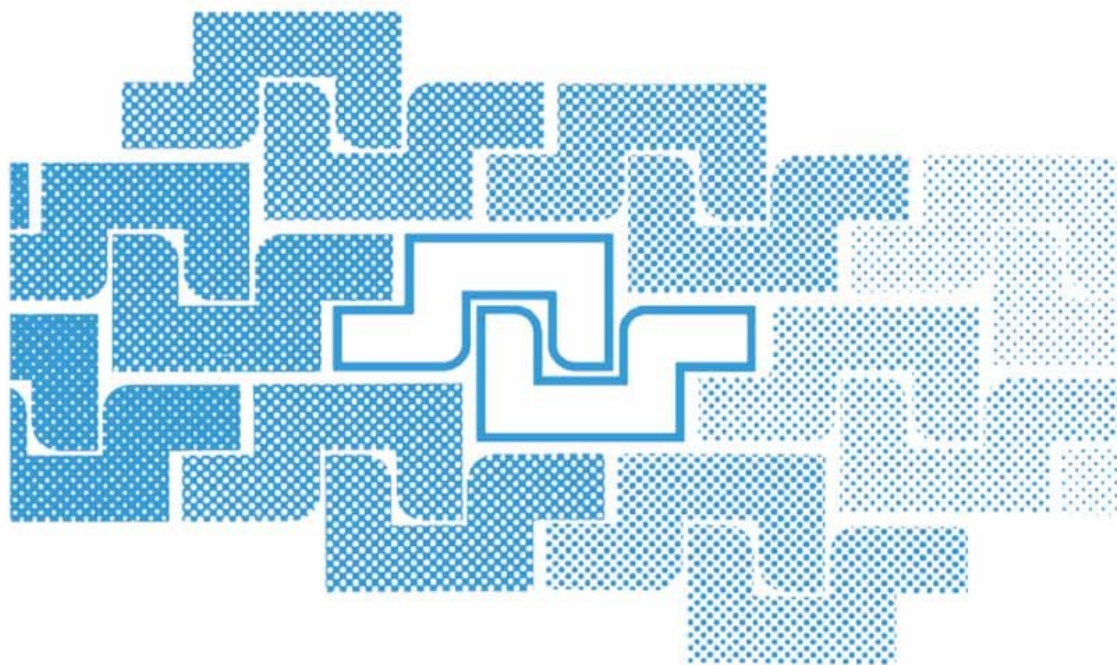




Nonlinear Dielectric Phenomena in Complex Liquids

Edited by

Sylwester J. Rzoska and
Vitaly P. Zhelezny

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Nonlinear Dielectric Phenomena in Complex Liquids

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INTRODUCTION

In the last decade the new physics of complex liquids, associated with the search for universal patterns in such distinct systems as liquid crystals, polymer solutions, critical mixtures, bio-liquids etc, has emerged. Self-assembling, dominant role of mesoscale structures, complex dynamics, unusual phases and enormous sensitivity to perturbations are among the significant features of complex liquids. Extending the definition proposed by F. Yonezawa et al. [*The Physics of Complex Liquids*, World. Sci. Pub., Singapore, 1998], complex liquids may be classified into the following categories:

- 1 *Complex liquids whose complexity originates from specific external conditions, for instance:*
 - a. *“High density liquids”, such as liquids under high pressure or supercooled*
 - b. *“Low density liquids”, such as liquids under negative pressure (stretched liquids), liquids in a random surrounding (pores etc,...) or in the form of scattered clusters.*
 - c. *Liquids under anisotropic external field, such as liquids under strong electric field or under shear flow.*
 - d. *Liquids near a critical point, including spinodal, multicritical, etc. points.*
2. *Complex liquids whose complexity is associated with their structure, such as liquid crystals, polymeric liquids, bio-liquids, micellar solutions, etc..*

A rich set of fluid mesophases associated with continuous or weakly discontinuous phase transitions is also a common feature of complex liquids. Hence, it may be expected that their properties are dominated by critical-like, pretransitional phenomena. Surprisingly, the application of the modern physics of critical phenomena may be puzzling. For instance, in the majority of monographs on the physics of liquid crystals the isotropic–nematic transition is presented as the best example of a simple mean-field description. However, recent studies point to a tricritical, “fluidlike” behavior associated with “glassy” dynamics. It is noteworthy, that the “glassy” dynamics, which is the basic feature of supercooled liquids is one of the most challenging fields in modern materials science. One may expect that the “glassy” dynamics may appear as model description for the whole category of complex liquids. In the last decades, an essentially new insight into the properties of complex liquids was possible due to the technical progress in broadband dielectric spectroscopy (*BDS*). The unique feature of *BDS* is associated with the possibility of testing relaxation processes extending in an extraordinary time-scale range. Nowadays, *BDS* seems to have reached technical maturity. However, understanding properties of complex liquids remains far behind. It remains puzzling even for liquids so extensively studied as the supercooled ones. Hence, the application of novel research methods may be essential for progress in this field. Since mesoscale, bond-ordering structures are an inherent feature of complex liquids, research methods directly coupled to them seem to be of particular importance. One may include here the transient grating Kerr effect, dynamic light scattering, nonlinear dielectric effect, dielectric hole-burning spectroscopy and the novel state-of-the-art analysis of broad band dielectric spectra. An example worth stressing is the nonlinear dielectric effect

(*NDE*), which may be treated as a natural extension of the *BDS*. *NDE* describes changes of dielectric permittivity due to the application of a strong electric field:

$$\varepsilon^E = \varepsilon + \varepsilon_{NDE} E^2 + \dots$$

where $\varepsilon^E, \varepsilon$ are dielectric permittivities in strong and weak electric field E , respectively. ε_{NDE} is the experimental measure of the non-linearity called nonlinear dielectric effect (*NDE*).

The relevant history of *NDE* began 80 years ago when Arkadiusz Piekara, at that time a school teacher in Poland, conducted the first ever measurement of static dielectric permittivity (ε) and *NDE* near the critical point in nitrobenzene - hexane mixture [A. Piekara, 1932, *Phys. Rev.* **42**, 445-447 and A. Piekara, 1936, *C. R. Acad. Sci. Paris*, **203**, pp. 1058-1059]. For *NDE* he noted “a *very strong increase on approaching the critical consolute point*” in the homogeneous phase. The explanation of this phenomenon was not possible until the nineties, when the physics of critical phenomena and the quasi-nematic ordering induced in the mixture by a strong electric field were taken into account [S. J. Rzoska et al.: *Phys. Rev. E* **50** (1993)]. At present there are several experimental techniques applied for *NDE* measurements. They give insight into the properties of critical binary liquids and homogeneous liquid crystals (Polish groups), polymeric films and ferroelectric liquid crystals (Japanese groups) and bio-liquids (UK groups).

The main aim of the ARW NATO “*Nonlinear dielectric phenomena in complex liquids*” 10-14 May 2003, held in Katowice-Jaszowiec (Poland), was the first ever discussion-meeting of researchers interested in nonlinear dielectric phenomena in complex liquids. Particular attention was paid to the nonlinear dielectric spectroscopy (*NDE*). Its limited use so far is related to enormous technical problems encountered. Therefore the workshop was particularly well timed due to just emerging possibilities of constructing the first ever, user-friendly, ***nonlinear dielectric spectrometer***, giving insight into time-scales relevant for complex liquids. Researchers from almost all existing groups associated with the nonlinear dielectric spectroscopy and its related methods took part in the meeting. Discussions were focused on the following items:

1. Basics for nonlinear dielectric and related studies in liquids
2. Nonlinear dielectric and related problems in critical liquids
3. Nonlinear dielectric results for liquid crystalline (mesogenic) materials
4. Nonlinear dielectric and related studies for supercooled/superpressed and polymeric liquids
5. Nonlinear dielectric studies for biologically relevant materials

The workshop was organized in Jaszowiec Valley, in Hotel Jaskółka located in the heart of the Beskidy mountains, 80 km from Katowice, the capital of Upper Silesia, Poland. Lectures started at 9 am and finished at 6 pm, each lasting 35 minutes, with 45 minute coffee-breaks and party-meetings to boost discussions were held every evening. Participants had also the possibility to get acquainted with the still vivid culture of the Beskidy highlanders.

This meeting would not have been such a success without the time devoted to its organization by a number of dedicated people. I would especially like to thank my wife

and the best co-worker Aleksandra Drozd-Rzoska, for her unwavering support and valuable advice. I am also very grateful to PhD students from our lab in Katowice, particularly to Sebastian Pawlus and Monika Sekula for their great organizational skills. I am also indebted to Prof. Vitaly Zhelezny, the co-director, who invited a superb staff of participants from Russia and Ukraine. I would like thank Takeo Furukawa for the photo. Further thanks to the Silesian University for the technical help, particularly to Mrs. Iwona Jarocka from the Financial Dept. of Silesian Univ. I also express the great gratitude to Kluwer for publication of these contributions. Organizers thank all contributing authors and acknowledge the generous and extensive support of the NATO Science Programme. Additional support was given by the Polish Chemical Society Society, branch Katowice.

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Nonlinear Dielectric Phenomena in Complex Liquids
Jaszowiec, Poland 10-14 May 2003

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ANOMALOUS EXPRESSIONS FOR THE NONLINEAR HARMONIC COMPONENTS OF THE ELECTRIC POLARIZATION

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Abstract: In view of having a better interpretation of experimental data of complex liquids which are not well described by usual Debye-like models, we propose to introduce a fractional approach applied to noninertial rotational diffusion of polar molecules. This leads to solve a fractional Smoluchowski equation (in configuration space only) characterized by an anomalous exponent α varying in the interval $]0,1[$ corresponding to a slow relaxation process (subdiffusion). More precisely, we consider the problem of the nonlinear dielectric response due to the application of a strong electric field in the form of either a pure ac field or a strong dc bias field superimposed on a weak ac field. For both cases, we derive in the frequency domain analytical expressions for the electric susceptibilities valid up to the third order in the field strength. This yields harmonic components varying at the fundamental angular frequency ω and in 3ω . To illustrate the results so obtained for the stationary regime, dispersion and absorption spectra are plotted for each harmonic component in order to show the significant departure from the classical Brownian behavior ($\alpha = 1$) as $\alpha \rightarrow 0$. Cole-Cole diagrams are also presented allowing one to see how the arcs become more and more flattened as $\alpha \rightarrow 0$, which corresponds to a broadening of the absorption peaks as effectively observed in most of complex liquids. The theoretical model is in good enough agreement compared (i) with experimental data of the third-order nonlinear susceptibility of a ferroelectric liquid crystal and (ii) data of the third-order nonlinear relative dielectric permittivity of a polymer. The present work represents an extension of previous theories in nonlinear dielectric relaxation by Coffey and Paranjape, here applied to the harmonic dielectric responses in disordered media.

1. Introduction

In the experimental study of complex fluids like liquid crystals, glass forming liquids, polymers, etc., one observes that the time evolution of the dielectric relaxation processes can no longer be described in the form of the exponential function as in the Debye model, but rather by the Kohlrausch-Williams-Watt law corresponding to a stretched exponential function [1-6]. As a consequence, in the frequency domain, when the systems are acted on by ac electric fields, the absorption spectra are characterized by broadened relaxation peaks [7]. For reproducing such typical patterns, three different empirical expressions are generally used for fitting the corresponding experimental data. Expressed in normalized forms, and considering, for instance, the responses provided with the complex electric susceptibilities $\chi(\omega)$, ω being the angular frequency of the applied ac electric field, they are

- the Cole-Cole equation [8]

$$\chi(\omega) = \frac{1}{1 + (i\omega\tau_{cc})^\alpha}, \quad 0 < \alpha \leq 1 \quad (1)$$

- the Davidson-Cole equation [9]

$$\chi(\omega) = \frac{1}{(1 + i\omega\tau_{dc})^\beta}, \quad 0 < \beta \leq 1 \quad (2)$$

- and the combined Havriliak-Negami equation [10]

$$\chi(\omega) = \frac{1}{[1 + (i\omega\tau_{in})^\alpha]^\beta}, \quad \alpha\beta \leq 1 \quad (3)$$

where τ_{cc} , τ_{dc} , and τ_{in} are characteristic relaxation times, and α , β are said stretching exponents. For $\alpha = \beta = 1$, the well-known formulas corresponding to normal diffusion are recovered. As soon as α (or β) becomes different from unity, anomalous diffusion takes place, which is what effectively occurs in disordered media. In order to account for the dielectric relaxation of such systems, it is possible to use a fractional Fokker-Planck equation, based on the continuous-time random walk as shown recently by many authors [11-13]. Moreover, the solution of fractional equations may be accomplished in the same manner as that well developed for usual partial differential equations [12].

In this paper, we shall restrict ourselves to the case where the fractal exponent α ranges from 0 to 1, which corresponds to the subdiffusive regime characterized by a much slower decrease of the fractional relaxation function for long times than that observed with the exponential (superslow process) [14]. An attempt to give a demonstration of the Cole-Cole formula has been recently derived by Novikov and Privalko [2] who used a phenomenological relaxation function for describing the electric polarization. The same result has been also obtained by Coffey et al. [15] from the noninertial Fokker-Planck equation. Hence, we shall try to extend the usual theory (normal diffusion) of the nonlinear dielectric response to this context of the fractional dynamics. To accomplish this, we consider a dilute solution consisting of an assembly of noninteracting, rigid, polar, and symmetric-top molecules. With such assumptions, we can consider the rotational motion of a single molecule having a permanent dipole moment μ under the application of an external electric field $E(t)$. In what follows, we shall seek the results obtained for two different electric fields, namely, either a pure alternating field, $E(t) = E_1 \cos(\omega t)$, or a strong dc constant bias field on which is superimposed a weak ac field in the same direction, $E(t) = E_0 + E_1 \cos(\omega t)$ with $E_1/E_0 \ll 1$, and we shall calculate for the stationary process (i.e., when the system has removed all the transient effects so that we consider its behavior a long time after the electric field has been switched on) the harmonic components of the electric susceptibility valid up to the third order in the electric field strength.

2. Theory

For one molecule whose symmetry axis makes the angle ϑ with the electric field, the orientational probability distribution function $W(\vartheta, t)$ in the framework of the fractional dynamics obeys the following partial fractional differential equation written in configuration space only

$$\frac{\partial W(\vartheta, t)}{\partial t} = (2D_R)^\alpha {}_0D_t^{1-\alpha} \frac{1}{2\sin\vartheta} \frac{\partial}{\partial\vartheta} \left[\sin\vartheta \left(\frac{\partial W(\vartheta, t)}{\partial\vartheta} \right) + \frac{W(\vartheta, t)}{kT} \frac{\partial V(\vartheta, t)}{\partial\vartheta} \right], \quad (4)$$

where $V(\vartheta)$ is the orientational potential energy given by

$$V(\vartheta) = -\mu E(t) \cos\vartheta, \quad (5)$$

D_R is the rotational diffusion constant equal to $(2\tau)^{-1}$, τ being the Debye relaxation time, and ${}_0D_t^{1-\alpha}$ is the Riemann-Liouville operator defined by [16]

$${}_0D_t^{1-\alpha} = \frac{\partial}{\partial t} {}_0D_t^{-\alpha}, \quad (6)$$

with

$${}_0D_t^{-\alpha} W(\vartheta, t) = \frac{1}{\Gamma(\alpha)} \int_0^t (t-t')^{-(1-\alpha)} W(\vartheta, t') dt'. \quad (7)$$

We note that Eq. (4) is valid if inertial effects are fully ignored and reduces to the well-known Smoluchowski equation if $\alpha = 1$. From Eq. (7) which has the form of a convolution product, one remarks the presence of a memory kernel indicating the non-Markovian nature of the subdiffusive process. It is also important to note that the Laplace transform of Eq. (7) is simply given by [16,17]

$$\mathcal{L} [{}_0D_t^{-\alpha} W(\vartheta, t)] = p^{-\alpha} \tilde{W}(\vartheta, p), \quad (8)$$

where

$$\tilde{W}(\vartheta, p) = \mathcal{L} [W(\vartheta, t)] = \int_0^\infty e^{-pt} W(\vartheta, t) dt. \quad (9)$$

Since the Riemann-Liouville operator acts only on the time variable and not on the angular (space) variable, we can use the classical methods for solving Eq. (4). By setting $u = \cos\vartheta$, multiplying both sides of Eq. (4) by $P_n(u)$, the n -th Legendre polynomial, and integrating from -1 to $+1$ over the variable u , we arrive at

$$\begin{aligned} \frac{d}{dt} \langle P_n(u) \rangle(t) = (2D_R)^\alpha {}_0D_t^{1-\alpha} \left\{ -[n(n+1)/2] \langle P_n(u) \rangle(t) \right. \\ \left. + (\gamma_0 + \gamma_1 \cos \alpha t) \frac{n(n+1)}{2(2n+1)} [\langle P_{n-1}(u) \rangle(t) - \langle P_{n+1}(u) \rangle(t)] \right\}, \end{aligned} \quad (10)$$

where the angular brackets stand for ensemble averages such that

$$\langle P_n(u) \rangle(t) = \int_{-1}^1 P_n(u) W(u, t) du = \int_0^\pi P_n(\cos \vartheta) W(\vartheta, t) \sin \vartheta d\vartheta, \quad (11)$$

and

$$\gamma_0 = \frac{\mu E_0}{kT}, \quad \gamma_1 = \frac{\mu E_1}{kT} \quad (12)$$

are two dimensionless parameters giving the importance of the orientational potential energy due to the electric field with respect to the thermal energy (k is the Boltzmann constant, and T is the absolute temperature). Now, considering again the Riemann-Liouville operator (fractional derivative) and using the following properties

$$\frac{\partial / \partial t}{{}_0D_t^{1-\alpha}} = \frac{\partial / \partial t}{\frac{\partial}{\partial t} {}_0D_t^{-\alpha}} = {}_0D_t^\alpha, \quad (13)$$

and

$$({}_0D_t^{1-\alpha})^{-1} {}_0D_t^{1-\alpha} = \mathbf{1}, \text{ (identity operator)} \quad (14)$$

Eq. (10) becomes

$$\begin{aligned} {}_0D_t^\alpha \langle P_n(u) \rangle(t) = (2D_R)^\alpha \left\{ -[n(n+1)/2] \langle P_n(u) \rangle(t) \right. \\ \left. + (\gamma_0 + \gamma_1 \cos \alpha t) \frac{n(n+1)}{2(2n+1)} [\langle P_{n-1}(u) \rangle(t) - \langle P_{n+1}(u) \rangle(t)] \right\}. \end{aligned} \quad (15)$$

Since we are solely interested in the determination of the stationary ac response, which is obviously independent of the initial conditions, we can seek the solution of Eq. (15) in the form [18-20]

$$f_n(t) = \langle P_n(u) \rangle(t) = \sum_{k=-\infty}^{+\infty} F_k^n(\omega) e^{ik\alpha t}, \quad (16)$$

where the Fourier amplitudes $F_k^n(\omega)$ satisfy the following condition (the asterisk stands for the complex conjugate)

$$F_{-k}^n(\omega) = [F_k^n(\omega)]^* , \quad (17)$$

because the expectation values of the Legendre polynomials, f_n , are real functions of the time variable t .

The physical quantity which is interesting from an experimental point of view and characteristic of dielectric relaxation is the electric polarization defined by

$$P(t) = N\mu\langle P_1(u) \rangle(t) = N\mu f_1(t) , \quad (18)$$

where N represents the number of molecules per unit volume. It is this quantity that we shall now evaluate for both types of electric fields we have mentioned at the end of the Introduction.

3. Dielectric response in the case of superimposed electric fields

In the situation where a strong dc bias field is superimposed at the same time on a weak ac electric field, the solution for $f_1(t)$ can be presented in the form

$$f_1(t) = F_0^1(\omega) + 2 \sum_{k=1}^{+\infty} \text{Re} [F_k^1(\omega) e^{ik\omega t}] . \quad (19)$$

The first term $F_0^1(\omega)$ in the right-hand side of Eq. (19) is a time-independent but frequency-dependent term due to the presence of the dc field E_0 . In order to calculate the Fourier coefficients of Eq. (19), it suffices to substitute the expression for $f_n(t)$ of Eq. (16) into Eq. (15) which yields

$$\begin{aligned} \left[\left(\frac{i\omega k}{2D_R} \right)^\alpha + \frac{n(n+1)}{2} \right] F_k^n(\omega) &= \gamma_0 \frac{n(n+1)}{2(2n+1)} [F_k^{n-1}(\omega) - F_k^{n+1}(\omega)] \\ &+ \gamma_1 \frac{n(n+1)}{4(2n+1)} [F_{k-1}^{n-1}(\omega) + F_{k+1}^{n-1}(\omega) - F_{k-1}^{n+1}(\omega) - F_{k+1}^{n+1}(\omega)] \end{aligned} \quad (20)$$

or in condensed form

$$\begin{aligned} F_k^n(\omega) x_{kn}(\omega) - 2\gamma_0 [F_k^{n-1}(\omega) - F_k^{n+1}(\omega)] \\ - \gamma_1 [F_{k-1}^{n-1}(\omega) + F_{k+1}^{n-1}(\omega) - F_{k-1}^{n+1}(\omega) - F_{k+1}^{n+1}(\omega)] = 0 , \end{aligned} \quad (21)$$

where

$$x_{k,n}(\omega) = 2(2n+1) \left[1 + \frac{2}{n(n+1)} \left(\frac{i\omega k}{2D_R} \right)^n \right]. \quad (22)$$

If we restrict ourselves to the third order in the electric field strength, the time-independent term $F_0^1(\omega)$ will contain quantities proportional to γ_0 , γ_0^3 , and $\gamma_0\gamma_1^2$ only. By using a perturbation procedure on the set of differential recurrence relations Eq. (21), we obtain for $k=0$, $n=1$

$$F_0^1(\omega) = \frac{\gamma_0}{3} \left(1 - \frac{\gamma_0^2}{15} \right) - \frac{\gamma_0\gamma_1^2}{3} \operatorname{Re} \left(\frac{1}{5x_{-1,1}} + \frac{2}{x_{-1,1}x_{-1,2}} + \frac{1}{3x_{-1,2}} \right), \quad (23)$$

where the notation “Re” stands for “real part of”, and setting $\omega' = \omega/(2D_R)$ as reduced variable

$$\begin{aligned} x_{-1,1}(\omega') &= 6[1 + (-i\omega')^\alpha], \\ x_{-1,2}(\omega') &= 10[\bar{1} + (-i\omega')^\alpha/3]. \end{aligned} \quad (24)$$

After some calculation, it is found that the explicit expression for $F_0^1(\omega')$ is

$$\begin{aligned} F_0^1(\omega') &= \frac{\gamma_0}{3} \left(1 - \frac{\gamma_0^2}{15} \right) - \frac{\gamma_0\gamma_1^2}{90} \\ &\times \frac{27 + (23/2)\omega'^{2\alpha} + 4\omega'^\alpha(12 + \omega'^{2\alpha})\cos(\pi\alpha/2) + 9\omega'^{2\alpha}\cos^2(\pi\alpha/2) + (9/2)\omega'^{2\alpha}\cos(\pi\alpha)}{[1 + 2\omega'^\alpha\cos(\pi\alpha/2) + \omega'^{2\alpha}][9 + 6\omega'^\alpha\cos(\pi\alpha/2) + \omega'^{2\alpha}]}. \end{aligned} \quad (25)$$

For $\alpha=1$, this equation yields the result already obtained in [21,22].

We can proceed in the same manner as that used above for determining the first harmonic component of the electric polarization. By keeping again the third-order terms only, this quantity is proportional to γ_1 and $\gamma_0^2\gamma_1$, and so provides the nonlinear response in the ac electric field. Written in complex form, one has for $k=-1$, $n=1$

$$\begin{aligned} F_{-1}^1(\omega') &= -\frac{2\gamma_0}{x_{-1,1}} F_{-1}^2(\omega') + \frac{\gamma_1}{x_{-1,1}} [\bar{1} - F_0^2(\omega')] \\ &= -\frac{2\gamma_0}{x_{-1,1}} \left(\frac{2\gamma_0\gamma_1}{x_{-1,1}x_{-1,2}} + \frac{\gamma_0\gamma_1}{3x_{-1,2}} \right) + \frac{\gamma_1}{x_{-1,1}} \left(1 - \frac{\gamma_0^2}{15} \right). \end{aligned} \quad (26)$$

In Eq. (26), we recognize the linear contribution given by $\gamma_1(x_{-1,1})^{-1}$. Hence, by substituting the expressions given by Eq. (24) in Eq. (26), we have

$$F_{-1}^1(\omega') = \frac{\gamma_1}{6[1+(-i\omega')^\alpha]} - \frac{\gamma_0^2 \gamma_1}{90} \frac{1 + [1+(-i\omega')^\alpha][2+(-i\omega')^\alpha/3]}{[1+(-i\omega')^\alpha][1+(-i\omega')^\alpha/3]}. \quad (27)$$

The second term in Eq. (27) is characteristic of the Langevin saturation with a negative contribution. We can therefore like in normal diffusion define a complex nonlinear dielectric increment such that

$$\begin{aligned} \Delta\epsilon_{NL}(\omega') &= \frac{2F_{-1}^1(\omega')}{\gamma_1} - \frac{1}{3[1+(-i\omega')^\alpha]} \\ &= -\frac{\gamma_0^2}{45} \frac{1 + [1+(-i\omega')^\alpha][2+(-i\omega')^\alpha/3]}{[1+(-i\omega')^\alpha]^2[1+(-i\omega')^\alpha/3]}, \end{aligned} \quad (28)$$

where the subscript “NL” stands for nonlinear, and the factor 2 before $F_{-1}^1(\omega')$ arises from the definition given in Eq. (17). For $\alpha = 1$, Eq. (28) coincides exactly with the results previously obtained by Coffey and Paranjape [23] (see also Ref. [22]). It is interesting to make a partial fraction decomposition of Eq. (28) in view of extending this expression to the time domain, which is also of importance if one refers to some experimental works, namely

$$\Delta\epsilon_{NL}(\omega') = -\frac{\gamma_0^2}{45} \left[\frac{3/2}{[1+(-i\omega')^\alpha]} + \frac{7/4}{1+(-i\omega')^\alpha} - \frac{3/4}{3+(-i\omega')^\alpha} \right]. \quad (29)$$

In order to show the temporal evolution of each term in Eq. (29), it is convenient to introduce the following function

$$g(t) = \frac{t^{\alpha-1}}{\tau} E_{\alpha,\alpha} \left(-\frac{t^\alpha}{\tau} \right), \quad 0 < \alpha \leq 1 \quad (30)$$

whose Laplace transform is

$$G(p) = \int_0^\infty e^{-pt} g(t) dt = \frac{1}{1+tp^\alpha}, \quad (31)$$

where

$$E_{\alpha,\alpha}(-z) = \sum_{k=0}^{+\infty} \frac{(-z)^k}{\Gamma(\alpha k + \alpha)} \quad (32)$$

is the generalized Mittag-Leffler function [24] which reduces to the exponential one for $\alpha=1$, and τ is the relaxation time equal to $(2D_R)^{1/2}$. Applying this definition to Eq. (29), one obtains

$$\begin{aligned} \Delta \varepsilon_{NL}(t) = & -\frac{\gamma_0^2}{45} \left\{ \frac{3}{2} \frac{t^{\alpha-1}}{\tau^\alpha} E_{\alpha,\alpha} \left[-\left(\frac{t}{\tau}\right)^\alpha \right] \otimes \frac{t^{\alpha-1}}{\tau^\alpha} E_{\alpha,\alpha} \left[-\left(\frac{t}{\tau}\right)^\alpha \right] \right. \\ & \left. + \frac{7}{4} \frac{t^{\alpha-1}}{\tau^\alpha} E_{\alpha,\alpha} \left[-\left(\frac{t}{\tau}\right)^\alpha \right] - \frac{3}{4} \frac{t^{\alpha-1}}{\tau^\alpha} E_{\alpha,\alpha} \left[-3\left(\frac{t}{\tau}\right)^\alpha \right] \right\}, \end{aligned} \quad (33)$$

where the symbol $\otimes$ represents a convolution product such as

$$\begin{aligned} h(t) \otimes l(t) &= \int_0^t h(t-t')l(t')dt' \\ &= \int_0^t l(t-t')h(t')dt', \end{aligned} \quad (34)$$

with the important property of the Laplace transform

$$\mathcal{L}[h(t) \otimes l(t)] = \mathcal{L}[h(t)] \mathcal{L}[l(t)]. \quad (35)$$

In view of simplifying the presentation of the above results, we shall use the following reduced quantities

$$X_0(\omega') = \left[F_0^1(\omega') - \frac{\gamma_0}{3} \left(1 - \frac{\gamma_0^2}{45} \right) \right] \frac{90}{\gamma_0 \gamma_1^2}, \quad (36)$$

$$\begin{aligned} \Delta X_1(\omega') &= \Delta X_1'(\omega') - i\Delta X_1''(\omega') \\ &= 45 \frac{\Delta \varepsilon_{NL}(\omega')}{\gamma_0^2} \end{aligned} \quad (37)$$

where $X_0(\omega')$ describes in fact the variations of the second term in the right-hand side of Eq. (25) since only this term is frequency-dependent.

The dc component $X_0(\omega')$ of the electric polarization is presented in Fig. 1 for α values ranging from 0 to 1 (subdiffusive process). One can remark that the asymptotic value $X_0(\infty) = 0$ is more rapidly attained when $\alpha \rightarrow 1$. Everywhere else, $X_0(\omega')$ takes on negative values. In Figs. 2 and 3 are pictured the real $\Delta X_1'$ and imaginary $\Delta X_1''$ parts of the complex nonlinear dielectric increment $\Delta X_1(\omega')$ as a function of ω' and α ($0 < \alpha \leq 1$) corresponding to the contribution of the first harmonic component to the linear response in the ac electric field. The higher α is, the steeper is the slope in the increase of the dispersion plot [$\Delta X_1'(\omega')$]. Regarding the absorption curves $\Delta X_1''(\omega')$, the height of the peaks augments in proportion with α while their maxima shift to the lowest

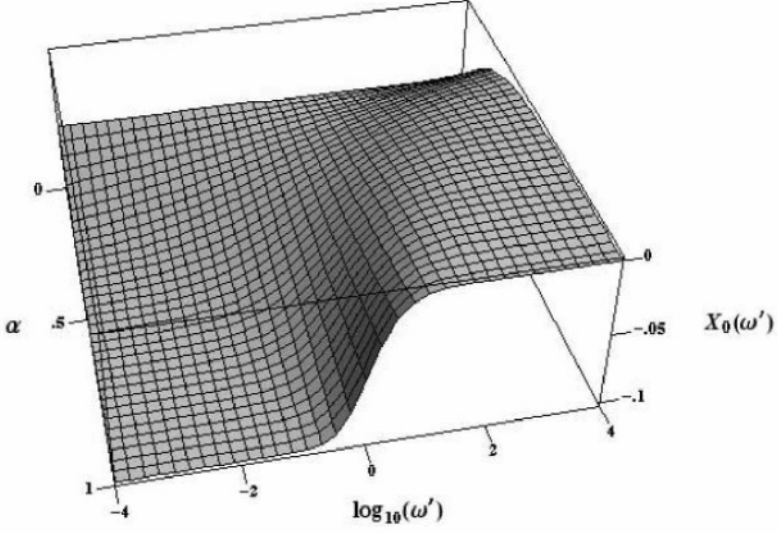


Figure 1. 3D plot of the steady-state component X_0 as a function of the reduced angular

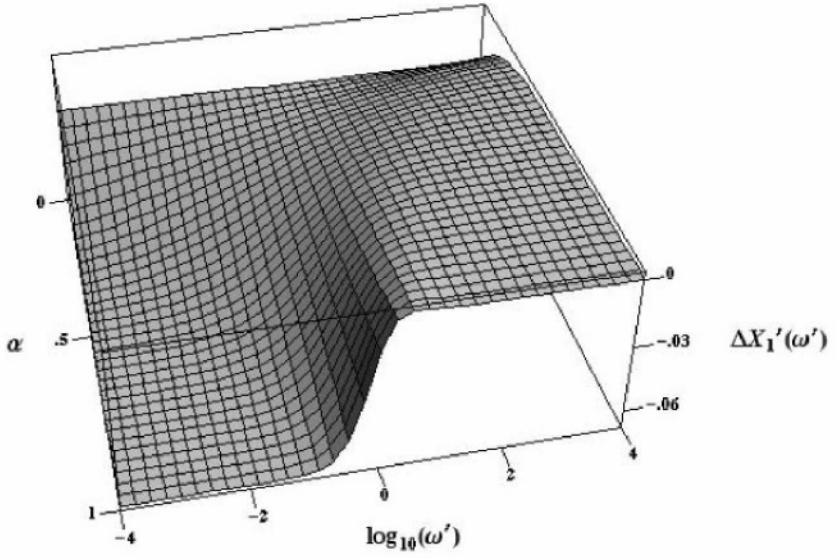


Figure 2. 3D plot of the real part of the nonlinear dielectric increment $\Delta X_1'$ (first harmonic component of the electric polarization) as a function of ω' and α .

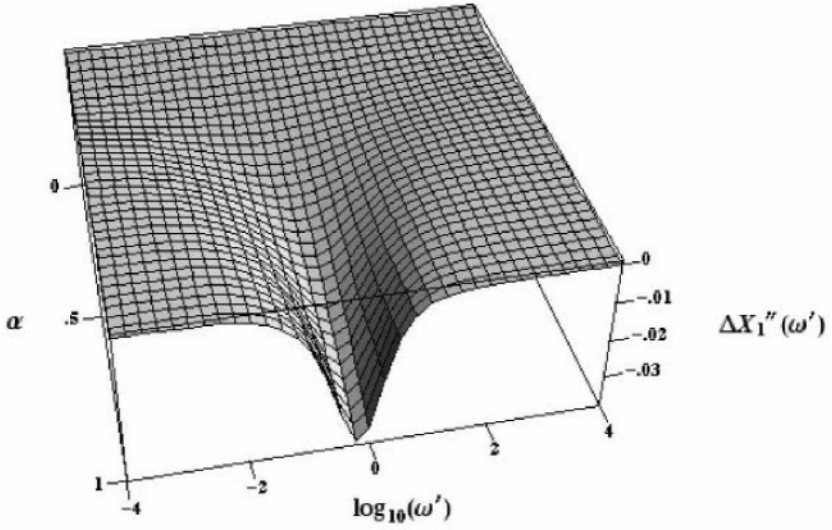


Figure 3. 3D plot of the imaginary part of the nonlinear dielectric increment $\Delta X_1''$ (first harmonic component of the electric polarization) as a function of ω' and α .

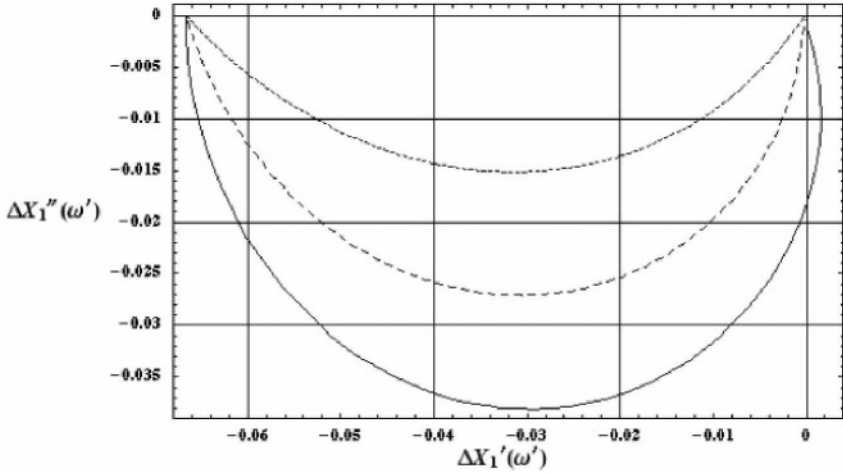


Figure 4. Cole-Cole plots of the nonlinear complex dielectric increment $\Delta X_1(\omega')$ for three different values of α . Full line : $\alpha = 1$ (Brownian limit) ; dashed line : $\alpha = 0.8$; dotted line : $\alpha = 0.5$.

frequency ω' and the fractional parameter α . It is worthwhile noting from these plots that $\Delta X_1'(\omega')$ and $\Delta X_1''(\omega')$ are always frequencies as α decreases. The Cole-Cole

diagrams (Fig. 4) demonstrate the influence of the anomalous exponent α with decreasing amplitudes of the arcs as α diminishes. It is always negative, with the exception of $\Delta X'_i(\omega')$ for $\alpha = 1$ (normal diffusion) that becomes positive in the high-frequency region.

4. Nonlinear dielectric response in presence of a pure ac electric field

In the absence of the dc bias field ($\gamma_0 = 0$), there are no longer constant terms in the dielectric response. Hence, by limiting ourselves again to the third order of the external electric perturbation, we shall evaluate the analytic expressions for the harmonic components of the electric polarization varying at the fundamental frequency ω (first harmonic) and in 3ω (third harmonic). From Eq. (21) in which we put $\gamma_0 = 0$, we have now to solve the following set of differential recurrence relations

$$F_k^n(\omega') x_{kn}(\omega') = \gamma_i \left[F_{k-1}^{n-1}(\omega') + F_{k+1}^{n-1}(\omega') - F_{k-1}^{n+1}(\omega') - F_{k+1}^{n+1}(\omega') \right], \quad (38)$$

where

$$x_{kn}(\omega') = 2(2n+1) \left[1 + \frac{2(i\omega k)^n}{n(n+1)} \right], \quad \omega' = \frac{\omega}{2D_R} = \omega\tau. \quad (39)$$

For $k = -1$, $n = 1$, we have

$$F_{-1}^1(\omega') = \frac{\gamma_1}{x_{-1,1}} \left[1 - F_{-2}^2(\omega') - F_0^2(\omega') \right], \quad (40)$$

where it suffices for our problem to evaluate F_{-2}^2 and F_0^2 up to the second order in the ac field only, which yields

$$F_{-2}^2(\omega') = \frac{1}{x_{-2,2}(\omega')} \left[\gamma_1 F_{-1}^1(\omega') \right] = \frac{\gamma_1^2}{x_{-1,1}(\omega') x_{-2,2}(\omega')}, \quad (41)$$

$$x_{-2,2}(\omega') = 10 \left[1 + (-2i\omega')^n / 3 \right]$$

and

$$F_0^2(\omega') = \frac{\gamma_1}{10} \left[F_{-1}^1(\omega') + F_1^1(\omega') \right] = \frac{\gamma_1}{5} \operatorname{Re} \left[F_{-1}^1(\omega') \right] = \frac{\gamma_1^2}{5} \operatorname{Re} \left[\frac{1}{x_{-1,1}(\omega')} \right], \quad (42)$$

so that

$$F_{-1}^1(\omega') = \frac{\gamma_1}{6 \left[1 + (-i\omega')^n \right]} - \frac{\gamma_1^3}{360 \left[1 + (-i\omega')^n \right]} \left[\frac{2(1 + \omega'^n \cos(\pi\alpha/2))}{1 + (i\omega')^n} + \frac{1}{1 + (-2i\omega')^n / 3} \right]. \quad (43)$$

This expansion gives correct results in so far as $\gamma_1 < 1$. In terms of the nonlinear electric susceptibility $\chi_i(\omega')$, Eq. (43) can be rewritten as

$$\begin{aligned}\chi_1(\omega') &= \frac{2F_{-1}^1(\omega')}{\gamma_1} \\ &= \frac{1}{3[1 + (-i\omega')^\alpha]} - \frac{\gamma_1^2}{180} \frac{1}{[1 + (-i\omega')^\alpha]^2} \left[\frac{2(1 + \omega'^\alpha \cos(\pi\alpha/2))}{1 + (i\omega')^\alpha} + \frac{3}{3 + (-2i\omega')^\alpha} \right].\end{aligned}\quad (44)$$

For $\alpha = 1$, we get

$$\chi_1(\omega')_{\alpha=1} = \frac{1}{3(1 - i\omega')} - \frac{\gamma_1^2}{180(1 + \omega'^2)} \frac{9 - i\omega'}{(1 - i\omega')(3 - 2i\omega')}, \quad (45)$$

which is in agreement with previously derived results [22,23]. More interesting experimentally in the application of a pure ac electric field only is the calculation of the third nonlinear harmonic component of the electric polarization given by the evaluation of $F_{-3}^1(\omega')$. Many data related to the study of disordered media are now available and the interest to an interpretation of their behavior is still growing. It is important to understand the typical features of such systems essentially characterized by their nonexponential relaxation patterns giving rise to slow diffusion. Among all these materials, ferroelectric liquid crystals in the chiral smectic-C phase [25-28] have caught the attention of many researchers. It is also the case of polymeric systems above the glass transition temperature. In particular, the third order of the nonlinear dielectric response for liquid crystals in the Goldstone mode yields negative values in the same manner as those observed for an equivalent study of free rotating dipoles in ordinary fluids (Langevin saturation effect). Setting $k = -3$ and $n = 1$ in Eq. (38) in order to calculate the third harmonic component in 3ω proportional to γ_1^3 , one obtains

$$x_{-31}(\omega') F_{-3}^1(\omega') = \gamma_1 F_{-2}^2(\omega'), \quad (46)$$

and using Eq. (41)

$$F_{-3}^1(\omega') = -\frac{\gamma_1^3}{x_{-4,1}(\omega') x_{-2,2}(\omega') x_{-3,1}(\omega')}, \quad (47)$$

where

$$x_{-3,1}(\omega') = 6[1 + (-3i\omega')^\alpha]. \quad (48)$$

Therefore, the explicit form for the electric susceptibility $\chi_3(\omega')$ is

$$\begin{aligned}\chi_3(\omega') &= \frac{2F_{-3}^1(\omega')}{\gamma_1^3} \\ &= -\frac{1}{60} \frac{1}{[1 + (-i\omega')^\alpha][3 + (-2i\omega')^\alpha][1 + (-3i\omega')^\alpha]} \\ &= -\frac{1}{60} \left[\frac{1}{(-3 + 2^\alpha)(-1 + 3^\alpha)} \frac{1}{1 + (-i\omega')^\alpha} + \frac{2^{2\alpha}}{(-3 + 2^\alpha)(2^\alpha - 3^{1+\alpha})} \frac{1}{3 + (-2i\omega')^\alpha} \right. \\ &\quad \left. + \frac{3^{2\alpha}}{(-1 + 3^\alpha)(-2^\alpha + 3^{1+\alpha})} \frac{1}{1 + (-3i\omega')^\alpha} \right],\end{aligned}\quad (49)$$

again in accord with the results of Refs. [21-23] for $\alpha = 1$.

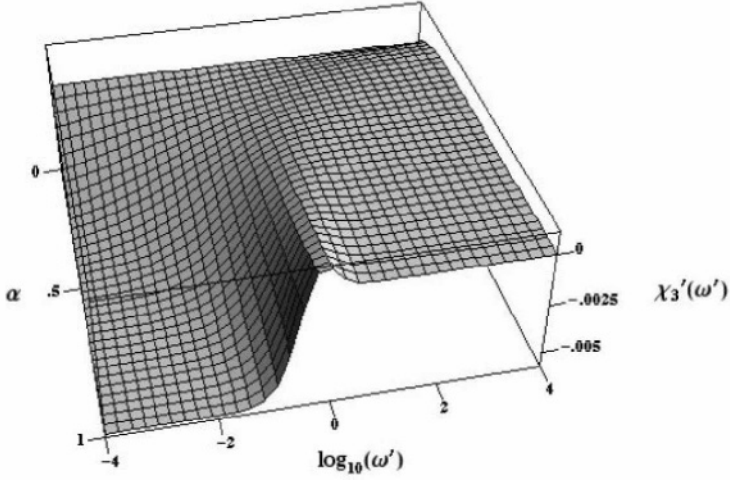


Figure 5. 3Dplot of the real part of the third harmonic component $\chi_3'(\omega')$ of the electric polarization as a function of ω' and α .

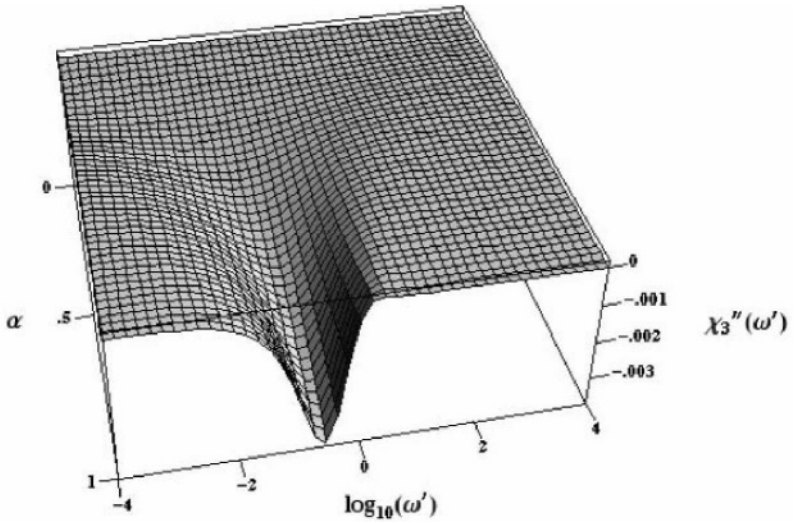


Figure 6. 3D plot of the imaginary part of the third harmonic component $\chi_3''(\omega')$ of the electric polarization as a function of ω' and α .

In Figs. 5 and 6 are shown the frequency evolution of the relaxation spectra of $\chi_3(\omega')$ as a function of α . The general pattern of all these plots is comparable to that already exhibited by the first harmonic component [nonlinear dielectric increment $\Delta X_1(\omega')$], with however, smaller amplitudes by a factor of almost two orders of magnitude. Some slight differences are nevertheless visible by looking at the Cole-Cole diagrams (Fig. 7) where the skewed arcs are more flattened due, especially, to the positive values of the real part $\chi_3'(\omega')$ in the high-frequency region. We have first checked our theoretical expression for the third-order nonlinear electric susceptibility $\chi_3(\omega')$ given by Eq. (49) on using experimental data recently obtained by Kimura et al. [29] on a ferroelectric liquid crystal, CS 1017 (Chisso): these measurements were made at 50°C with an ac electric field of angular frequency varying from 15 rad/s to $2.5 \cdot 10^6$ rad/s.

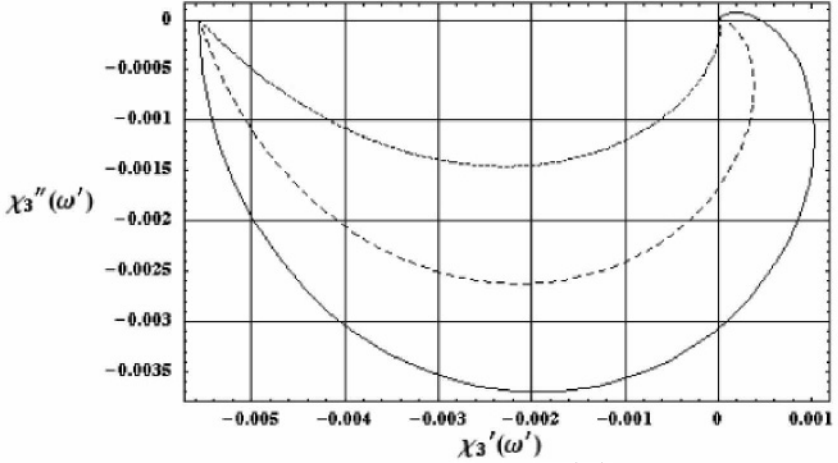


Figure 7. Cole-Cole plots of the third harmonic component $\chi_3(\omega')$ for three different values of α . Full line: $\alpha = 1$ (Brownian limit); dashed line: $\alpha = 0.8$; dotted line: $\alpha = 0.5$.

This comparison between theory and experiment is illustrated by nonlinear relaxation spectra in Fig. 8 where a quite correct agreement can be observed with the exception of a few points (within the limits of accuracy) at low frequencies due to conductivity and electrode polarization effects which are not taken into account in our analytical formulation. Fitting by a least mean squares leads to the numerical determination of α and τ , namely, $\alpha = 0.89$ and $\tau = 0.62 \cdot 10^{-3}$ s. These results are also presented in the form of Cole-Cole diagrams as shown in Fig. 9. We have made a second comparison with experiment by using data obtained by Furukawa et al. [30] on a polymer, polyvinyl acetate PVAc, at 50°C, in a frequency range lying from 0.01 Hz to 10 kHz. Here again, the agreement between theory and experiment appears to be satisfactory enough (Figs. 10 and 11). Our best fit procedure yields: $\alpha = 0.93$ and $\tau = 11$ ms.

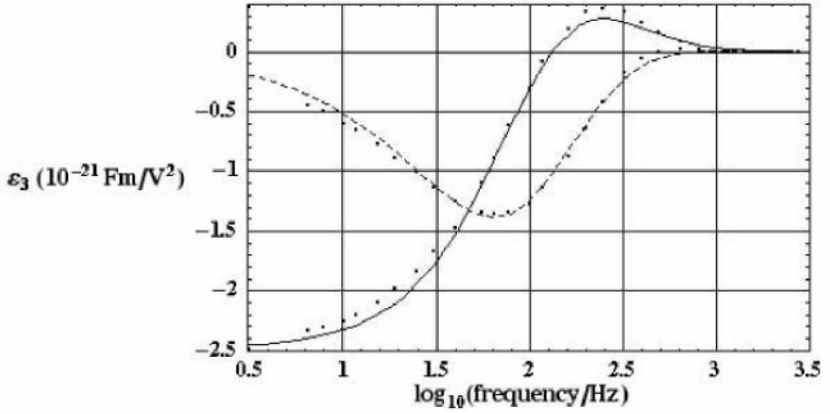


Figure 8. Third-order nonlinear dispersion (ϵ'_3) and absorption (ϵ''_3) spectra for CS 1017 (ferroelectric liquid crystal) at 50°C. Filled circles are experimental data taken from Kimura et al. [29]. The full and dashed lines represent our best fit procedure from Eq. (49) for the real (ϵ'_3) and imaginary (ϵ''_3) parts of the complex dielectric permittivity ϵ_3 , respectively.

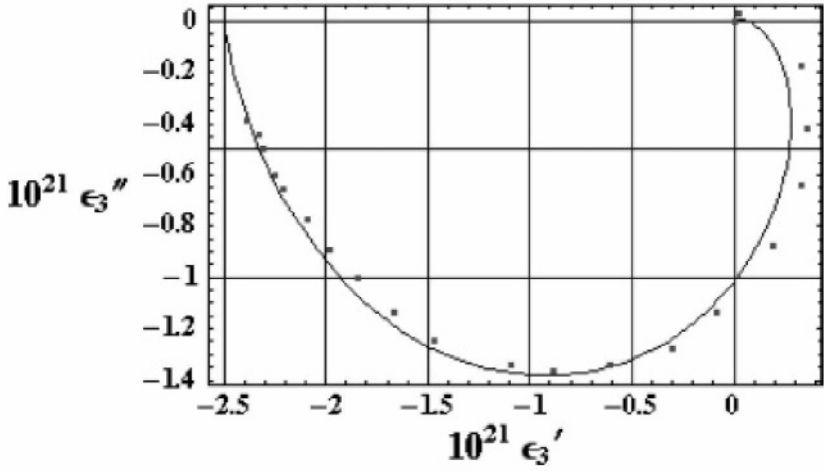


Figure 9. Cole-Cole plots of $\epsilon_3(\omega)$ for CS 1017 (same conditions as Fig. 8). Filled circles are experimental data taken from Kimura et al. [29]. Full line : best fit procedure.

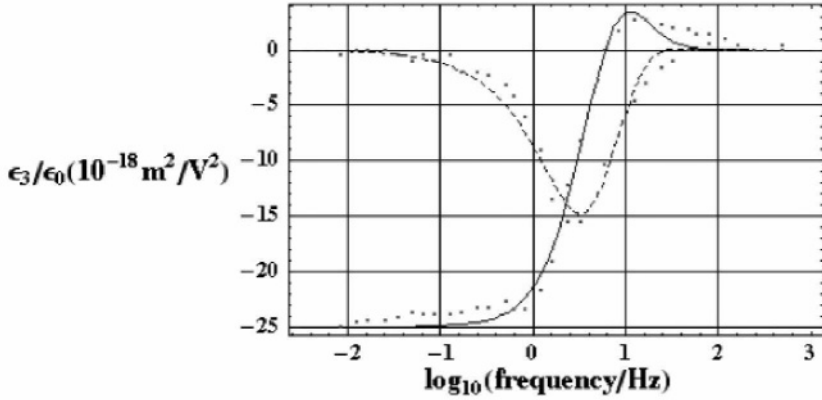


Figure 10. Third-order nonlinear dispersion (ϵ'_3 / ϵ_0) and absorption ($\epsilon''_3 / \epsilon_0$) spectra for PVAc (polymer) at 50°C. Filled circles are experimental data taken from Furukawa et al. [30]. The full and dashed lines represent our best fit procedure from Eq. (49) for the real (ϵ'_3 / ϵ_0) and imaginary ($\epsilon''_3 / \epsilon_0$) parts of the complex relative dielectric permittivity (ϵ_3 / ϵ_0).

5. Conclusion

In this paper, we have tried to introduce the fractional approach to the orientational motion of polar molecules acted by an external perturbation, such as a time-dependent electric field. This problem is treated in the context of non-inertial rotational diffusion (configuration space only) which leads to solve a fractional Smoluchowski equation. Hence, we consider the physical model corresponding to a slow relaxation process (subdiffusion) characterized by an anomalous exponent α ranging in the interval (0,1) ($\alpha = 1$ for normal diffusion).

The generalization of this diffusion equation including a fractional order rests on the model of the continuous time random walk. Here, because we are dealing with rotations rather than translations, it is preferable to speak on randomly distributed torques having an anomalous waiting time distribution function. We have derived in the frequency domain analytical expressions for the electric susceptibilities corresponding to nonlinear ac stationary responses and valid up to the third order in the electric field strength.

To illustrate these results, dispersion and absorption spectra for the first and the third harmonic components have been plotted in order to show the significant departure from the classical Brownian behavior as $\alpha \rightarrow 0$. Moreover, a comparison of our theoretical model with experimental data for the third-order nonlinear dielectric relaxation spectra of a ferroelectric liquid crystal and a polymer has led to a quite good agreement in fitting these dispersion and absorption plots.

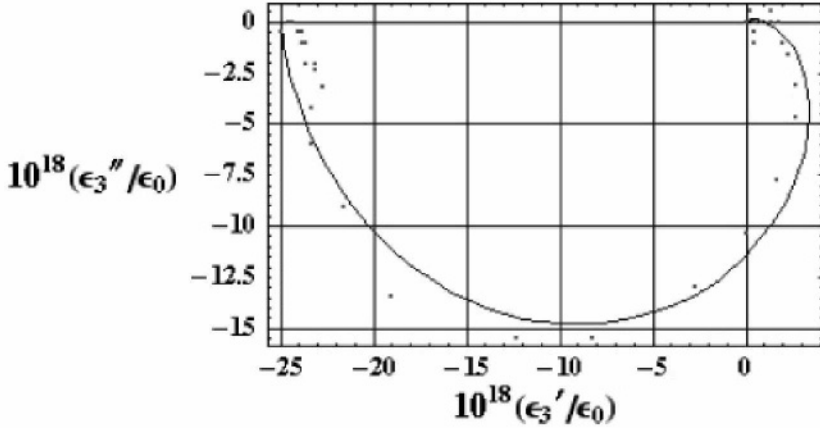


Figure 11. Cole-Cole plots of $(\epsilon_3 / \epsilon_0)(\omega)$ for PVAc (same conditions as Fig. 10). Filled circles are experimental data taken from Furukawa et al. [30]. Full line : best fit procedure.

To conclude, we indicate that our approach can be extended to the case of anisotropically polarizable molecules. Moreover, higher order responses can also be evaluated using the matrix continued fraction procedure in the manner developed for normal diffusion in our previous papers [18-20]. We also mention that the present theory could be applied with minute modifications to the case of ferrofluids subjected to time-dependent magnetic fields.

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References

1. Hilfer, R. (2002), *H*-function representations for stretched exponential relaxation and non-Debye susceptibilities in glassy systems, *Phys. Rev. E* **65**, 061510-1–061510-5.
2. Novikov, V. V. and Privalko, V. P. (2001) Temporal fractal model for the anomalous dielectric relaxation of inhomogeneous media with chaotic structure, *Phys. Rev. E* **64**, 031504-1–031504-11.
3. Kohlrausch, R. (1854) Theorie des elektrischen rückstandes in der leidener flasche, *Ann. Phys. Chem.* **91**, 179-214.
4. Williams, G. and Watts, D. C. (1970) Non-symmetrical dielectric relaxation behaviour arising from a single empirical decay function, *Trans. Faraday Soc.* **66**, 80-85.
5. Metzler, R. and Klafter, J. (2002) From stretched exponential to inverse power-law : fractional dynamics, Cole-Cole relaxation processes, and beyond, *J. Non-Cryst. Solids* **305**, 81-87.
6. Hilfer, R. (2000) *Applications of Fractional Calculus in Physics*, World Scientific, Singapore.
7. Alvarez, F., Alegria, A., and Colmenero, J. (1991) Relationship between the time-domain Kohlrausch-Williams-Watts and frequency-domain Havriliak-Negami relaxation functions, *Phys. Rev. B* **44**, 7306-7312.
8. Cole, K. and Cole, R. (1941) Dispersion and absorption in dielectrics, *J Chem. Phys.* **9**, 341-351.

9. Davidson, D. and Cole, R. (1951) Dielectric relaxation in glycerol, propylene glycol and *n*-propanol, *J. Chem. Phys.* **19**, 1484-1490.
10. Havriliak, S. and Negami, S. (1966) A complex plane analysis of α -dispersions in some polymer systems, *J. Polymer Sci.* **14**, 99-117.
11. Metzler, R., Barkai, E., and Klafter, J. (1999) Anomalous diffusion and relaxation close to thermal equilibrium: a fractional Fokker-Planck equation approach, *Phys. Rev. Lett.* **82**, 3563-3567.
12. Metzler, R. and Klafter, J. (2000) The random walk's guide to anomalous diffusion : a fractional dynamics approach, *Phys. Rep.* **339**, 1-77.
13. Metzler, R. and Klafter, J. (2001) Anomalous stochastic processes in the fractional dynamics framework : Fokker-Planck equation, dispersive transport, and non-exponential relaxation, *Adv. Chem. Phys.* **116** , 223-264.
14. Mainardi, F. (1996) Fractional relaxation-oscillation and fractional diffusion-wave phenomena, *Chaos, Solitons & Fractals* **7**, 1461-1477.
15. Coffey, W. T., Kalmykov, Y. P., and Titov, S. V. (2002) Anomalous dielectric relaxation in the context of the Debye model of noninertial rotational diffusion, *J. Chem. Phys.* **116**, 6422-6426.
16. Oldham, K. B. and Spanier, J. (1974) *The Fractional Calculus*, Academic Press, New York.
17. Metzler, R. and Klafter, J. (2000) The fractional Fokker-Planck equation : dispersive transport in an external force field, *J. Mol. Liquids* **86**, 219-228.
18. Déjardin, J.-L. and Kalmykov, Y. P. (2000) Nonlinear dielectric relaxation of polar molecules in a strong ac electric field : Steady-state response, *Phys. Rev. E* **61**, 1211-1217.
19. Déjardin, J.-L. and Kalmykov, Y. P. (2000) Steady state response of the nonlinear dielectric relaxation and birefringence in strong superimposed ac and dc bias electric fields: polar and polarizable molecules, *J. Chem. Phys.* **112**, 2916-2923.
20. Déjardin, J.-L., Kalmykov, Y. P., and Déjardin, P.-M. (2001) Birefringence and dielectric relaxation in strong electric fields, *Adv. Chem. Phys.* **117**, 275-481.
21. Déjardin, J.-L. (1993) Nonlinear response in dielectric relaxation including the induced polarization of polar molecules, *J. Chem. Phys.* **98**, 3191-3195.
22. Déjardin, J.-L. (1995) *Dynamic Kerr Effect*, World Scientific, Singapore.
23. Coffey, W. T. and Paranjape, B. V. (1978) Dielectric and Kerr effect relaxation in alternating electric fields, *Proc. R. Ir. Acad.* **78A**, 17-25.
24. Erdelyi, A., et al. (1981) *Higher Transcendental Functions*, Vol. III, Krieger, Malabar.
25. Meyer, R. B., Liebert, L., Strzelecki, L., and Keller, P. (1975) Ferroelectric liquid crystals, *J. Phys. (France)* **36**, L69-L71.
26. Zeks, B. and Blinc, R. (1991) *Ferroelectric Liquid Crystals, Principles, Properties and Applications*, Chap. 5, Gordon and Breach, Philadelphia.
27. Costello, P. G., Kalmykov, Y. P., and Vij, J. K. (1992) High-frequency dielectric behavior of a ferroelectric liquid crystal near the smectic-C*-smectic-A phase transition, *Phys. Rev. A* **46**, 4852-4858.
28. Glazounov, A. E. and Tagantsev, A. K. (2000) Phenomenological model of dynamic nonlinear response of relaxor ferroelectrics, *Phys. Rev. Lett.* **85**, 2192-2195.
29. Kimura, Y., Hara, S., and Hayakawa, R. (2000) Nonlinear dielectric relaxation spectroscopy of ferroelectric liquid crystals, *Phys. Rev. E* **62**, R5907-5910.
30. Furukawa, T. and Matsumoto, K. (1992) Nonlinear Dielectric Relaxation Spectra of Polyvinyl Acetate, *Jpn. J. Appl. Phys.* **31**, 840-845.

THEORY OF ANOMALOUS DIELECTRIC RELAXATION

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Abstract. The Cole-Cole behaviour of the complex susceptibility is derived from the diffusion limit of a random walk of permanent dipoles that is the discrete orientation model with a Lévy like distribution of waiting times at the sites. The method yields a generalisation of the Smoluchowski equation of the classical theory of the Brownian motion in a potential which describes the behaviour of the distribution function in configuration space with a fixed waiting time to a system which exhibits chaotic behaviour of the waiting times. It is indicated how the fundamental solution of the Smoluchowski equation in the absence of a potential may be obtained as a Lévy distribution by simply using the properties of the characteristic function which is the Mittag-Leffler function. Such a representation also yields in a simple manner both the mean square displacement of a dipole and the after effect function of the Cole-Cole process.

1. Introduction

From almost the earliest days of dielectric measurements [1] marked departures from the form of the frequency dependent complex susceptibility $\chi(\omega)$ predicted by the Debye equation have been observed. The best-known empirical formulae are the Cole-Cole equation [1]:

$$\frac{\chi(\omega)}{\chi'(0)} = \frac{1}{1 + (i\omega\tau_0)^\alpha} \quad 0 < \alpha \leq 1 \quad (1)$$

$\alpha=1$, corresponds to the Debye equation, $\chi'(0)$ is the static susceptibility, τ_0 is a characteristic time, the Cole-Davidson equation

$$\frac{\chi(\omega)}{\chi'(0)} = \frac{1}{(1 + i\omega\tau_0)^\beta}, \quad (0 < \beta \leq 1) \quad (2)$$

and the Havriliak-Negami equation, which is a combination of Eqs. (1) and (2):

$$\frac{\chi(\omega)}{\chi'(0)} = \frac{1}{[1 + (i\omega\tau_0)^\alpha]^\beta}. \quad (3)$$

Each of these equations exhibit *anomalous relaxation* (i.e., departure from the Debye pattern) behaviour. The Debye equation may be derived from the theory of the Brownian motion developed by Einstein and Smoluchowski (see Sections 2 and 3 below) indicating that just as in the Debye case the challenge is to provide theoretical justification for Eqs. (1-3). This has been already achieved for the Cole-Cole Eq. (1). That equation has been derived [2] by using a fractional probability density diffusion equation for the distribution function of the orientations of an assembly of non interacting dipoles. This diffusion equation is the fractional analogue of the Smoluchowski equation for the distribution function of orientations of non interacting

dipoles in the high friction or small inertial effects limit considered by Debye [3-5]. The fractional diffusion equation has also been written down and solved [5-7] for relaxation over the potential barriers in a bistable potential. In the normal diffusion case $\alpha=1$, this is the Debye-Fröhlich or site model [4,5,7] of dielectric relaxation, extended to a continuous distribution of orientations. The extension of the site model to a continuous distribution of orientations is of much importance both [5] in the theory of dielectric relaxation of nematic liquid crystals and in the theory of magnetic relaxation of fine single domain ferromagnetic particles. The most striking feature of the original Debye-Fröhlich model is that it again predicts Debye like relaxation behaviour, however the relaxation time τ_0 depends exponentially on the height of the potential barriers. The extension to a continuous distribution of orientations considerably improves the model [5-7] as it allows one both to calculate the prefactor of the overbarrier relaxation time and also to determine the contribution to the complex susceptibility of the relatively fast decay modes in the wells of the potential. For example in [5,6] it has been demonstrated that the overall relaxation behaviour may be closely approximated in the high friction limit, by the sum of two modes – one of which is the low frequency overbarrier mode – the second of which is a single high frequency mode characterising the near degenerate fast intrawell decay modes. If inertial effects are included an additional very high frequency (far infrared) mode of resonant character will appear [7] due to the oscillations of dipoles in the wells.

The fractional diffusion equation used in [2,5,6] has been justified for the free particle only, using renewal theory and the concept of the characteristic function of a random variable [5]. Recently Barkai et al [9], reviewed in [10], have proposed a more convincing method of derivation of the fractional Smoluchowski equation from the diffusion limit of a continuous time random walk [5,11].

It is the purpose of this paper to show how their method may be very easily adapted to the discrete orientation model of dielectric relaxation. Such an approach will provide in the continuum limit of the orientation sites, a justification for the fractional diffusion equation used as a starting point [1] in the explanation of the Cole-Cole behaviour. Moreover it will also justify the extension of the Debye-Fröhlich model to anomalous diffusion [5-7]. An important side result of this investigation is that it will also provide some insight into the meaning of the parameter α in the Cole-Cole equation. This is accomplished by using suggestions of Paul and Baschnagel [11] and Novikov and Privalko [12]. We shall first briefly outline the main aspects of the classical theory of dielectric relaxation due to Debye [3,4].

2. Einstein's theory of the Brownian motion

Einstein's theory [5,13] of the translational Brownian motion on which the Debye theory [3,4] of dielectric relaxation of an assembly of non interacting polar molecules is essentially based, relies on the *continuum limit* of a *discrete time* random walk. In such a walk the random walker is assumed to jump to one of its *nearest* neighbour sites situated at Δ in a fixed time τ , that is the elementary steps in the walk are taken at *uniform* intervals in time. Thus the only variable is the *direction* of the walker. The

problem is always to find that the walker will be in state n at some time t given that it was in a state m at some earlier time. Such a process which is *local* both in space and time can, in the continuum limit of a very large number of small steps of short duration, be modelled by the diffusion equation

$$\frac{\partial W}{\partial t} = D \frac{\partial^2 W}{\partial x^2} \quad (4)$$

The continuum limit may be stated more precisely by saying that both the step length Δ and the waiting time τ approach zero in such a way that

$$\lim_{\substack{\Delta \rightarrow 0 \\ \tau \rightarrow 0}} \frac{\Delta^2}{2\tau} = D \quad (5)$$

$$n\Delta \rightarrow x_0, m\Delta \rightarrow x, s\tau \rightarrow t, s = 1, 2, 3 \dots$$

where $W = W(x, t | x_0, 0)$ is the conditional probability density function of finding the walker at x at time t given that it was at x_0 at the time $t = 0$.

Equation (4) in the presence of an external force

$$F(x) = -\frac{\partial V(x)}{\partial x}, \quad (6)$$

e.g., the gravitational field of the earth, becomes the Smoluchowski equation [5,13]

$$\frac{\partial W}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial W}{\partial x} + \frac{W}{\zeta} \frac{\partial V}{\partial x} \right) \quad (7)$$

here $\zeta \dot{x}$ is the viscous drag on the Brownian particle assumed as a rigid sphere of radius a obeying Stokes' law so that

$$\zeta \dot{x} = 6\pi\eta a \dot{x} \quad (8)$$

where η is the viscosity of the surrounding fluid, in which the Brownian particle is suspended. By requiring that the equilibrium solution of Eq. (7) should be the Maxwell-Boltzmann distribution

$$W(x) = A \exp\left(-\frac{V(x)}{kT}\right), \quad (9)$$

Einstein [5,13] was able to deduce the fluctuation-dissipation theorem

$$D = kT / \zeta. \quad (10)$$

3. Application to dielectric relaxation

In the context of the present paper Debye [3] in his first model of dielectric relaxation adapted Einstein's theory to the rotational Brownian motion about a fixed axis of an assembly of non interacting dipolar molecules each of permanent dipole moment μ . He accomplished this by simply replacing the position coordinate x by the azimuth ϕ so that Eq. (7) becomes

$$\frac{\partial W}{\partial t} = \frac{\partial}{\partial \phi} \left(D \frac{\partial W}{\partial \phi} + \frac{W}{\zeta} \frac{\partial V}{\partial \phi} \right), \quad (11)$$

where

$$V(\phi) = -\mu E_m e^{i\omega t} \cos \phi \quad (12)$$

and

$$\mathbf{E}(t) = \mathbf{E}_m e^{i\omega t} \quad (13)$$

is the applied alternating field.

He then deduced, provided $\mu E_m \ll kT$ so that the response to the applied field is linear, that the mean dipole moment of a molecule is given by

$$\mu \langle \cos \phi \rangle = \frac{\mu^2 E_m}{2kT} \frac{e^{i\omega t}}{1 + i\omega\tau_D} = \frac{\mu^2 E}{2kT} \frac{\angle -\tan^{-1}(\omega\tau_D)}{\sqrt{1 + (\omega\tau_D)^2}}. \quad (14)$$

Thus, the average dipole moment has a part in phase with the applied field and a quadrature part. The quantity

$$\tau_D = \frac{\zeta}{kT} \quad (15)$$

is the Debye relaxation time for rotation about a fixed axis and

$$\zeta = 8\pi\eta a^3 \quad (16)$$

is the drag coefficient of a rotating sphere of radius a in a fluid of viscosity η . In his second (more realistic) model of the phenomenon Debye [4] considered rotation in space of a dipole specified by the polar angles ϑ, ϕ and obtained for the mean dipole moment in the direction of the field (the z direction)

$$\mu \langle \cos \vartheta \rangle = \frac{\mu^2 E}{3kT} \frac{\angle -\tan^{-1}(\omega\tau_D)}{\sqrt{1 + (\omega\tau_D)^2}} \quad (17)$$

In this instance

$$\tau_D = \frac{\zeta}{2kT} \quad (18)$$

is the Debye relaxation time for rotation in space. Substituting typical values of η and a into Eq. (18) using Eq. (16) suggests that for molecules τ_D is of the order of 10^{-10} sec indicating that the quadrature component of the dipole moment attains its maximum in the microwave band. Equation (11) and its three dimensional counterpart were also solved by Debye [4] for the after effect solution following the removal of a weak constant field $\mathbf{E}_0$ at $t = 0$ yielding

$$\mu \langle \cos \vartheta \rangle = \frac{\mu^2 E_0}{2kT} \exp\left(-\frac{2kT}{\zeta} t\right), \quad t > 0 \quad (19)$$

the foregoing results which all yield $\chi(\omega)$ in the form of the Cole-Cole equation with $\alpha=1$ pertain to linear response where the external field energy is much less than the thermal energy. Subsequently Debye's work was extended to nonlinear response, as far as terms cubic in the applied field, by Coffey and Paranjape [14] and to any order in the field strength by Déjardin and Kalmykov using matrix continued fractions [15]. Recent experiments by Jadzyn et al [16] are in substantial accord with the theory. The Debye theory has also been extensively applied to ferrofluids where the mechanism of reorientation of the magnetic moment inside the ferromagnetic particle is blocked, so that the particle behaves as a rigid dipole [5]. The Debye theory should now be a more accurate representation of reality than applied to molecules, as the ferromagnetic particles approximate closely to actual Brownian particles.

The other important model of dielectric relaxation yielding, in its crudest form based on a rate equation treatment, a complex susceptibility of the form of Eq.(1) with $\alpha=1$ is the Debye-Fröhlich model for a discrete set of orientations of a dipole. Thus considering one well only and using transition state theory [5] we have by the Arrhenius law

$$\tau_0 = \frac{2\pi}{\omega_A} \exp\left(\frac{\Delta V}{kT}\right), \quad (20)$$

where ω_A is the angular frequency of oscillation of a dipole in the well A of the potential, ΔV is the height of the potential barrier. More refined calculations [5] based on the Kramers theory of escape of particles over potential barriers [5,17,18] including a continuous distribution of orientations, allow one to replace the Arrhenius prefactor of the exponential in Eq.(20) by expressions involving the dissipative coupling to the bath. *Thus the fluctuation dissipation theorem is not violated as in the transition state theory.* The model incorporating the dissipative coupling has also been the basis for the theory of dielectric relaxation of nematic liquid crystals [5,19].

Having briefly summarised the classical theory of dielectric relaxation we shall now derive the fractional diffusion equation for rotation of dipoles in a potential, for simplicity we shall restrict ourselves to rotation about a fixed axis and we shall ultimately derive the Cole-Cole equation.

4. Fractional diffusion equation for the Cole-Cole behaviour

We consider an assembly of permanent dipoles constrained to rotate about a fixed axis and a set of discrete orientations on the unit circle with fixed angular spacing Δ ; a typical dipole may remain in a fixed orientation at a given site for an arbitrary long waiting time. It may then reorient to another discrete orientation site. This is the discrete orientation model.

Following the procedure suggested in [9,10] for the translational motion we first denote individual discrete orientations by $\{..., -1, 0, 1, ..., N, ...\}$. A typical dipole is supposed to have orientation $n=0$ at time $t=0$. The dipole having oriented to the site n at time t is fixed in that orientation that is *trapped*, for some random time. The random waiting times after which changes in orientation take place are denoted by $\{\tau_i\}$, $i=1,2,...$ these times are assumed to be independent identically distributed random variables with pdf $w(\tau)$. Thus the situation is unlike that in the Einstein theory where τ is fixed. A random walk with a distribution of waiting times between jumps such as that considered here, is called [5,11] a *continuous time random walk*. We assume that

- a. The pdf $w(\tau)$ is independent of the orientation of the dipole at time t , that is independent of n .
- b. The dipole when at orientation specified by n reorients only to its nearest neighbour sites, that is $n \pm 1$ as in Einstein's theory.
- c. The probability of orienting to $n+1$ is $A(n)$ and the probability of orienting to $n-1$ is $B(n)$ where $A(n)$ and $B(n)$ obey the normalisation condition

$$A(n) + B(n) = 1 \quad (21)$$

and are independent of the time.

The probability that a dipole executes a discrete change in its orientation in a time interval of length t is

$$\int_0^t w(\tau) d\tau \quad (22)$$

Hence the probability that the dipole has survived in a given orientation for a time t is

$$G(t) = 1 - \int_0^t w(\tau) d\tau = \int_t^\infty w(\tau) d\tau \quad (23)$$

because

$$\int_0^\infty w(\tau) d\tau = 1 \quad (24)$$

Hence introducing the Laplace transform

$$\tilde{G}(s) = \int_0^\infty G(t) e^{-st} dt \quad (25)$$

of the survival probability $G(t)$ at a site we have

$$\tilde{G}(s) = s^{-1} (1 - \tilde{w}(s)) \quad (26)$$

Now the waiting times are identically distributed random variables. Hence on introducing $Q_i(t)$, the probability that the dipole has changed i times in orientation in the time interval $(0, t)$ we will have for the Laplace transform $\tilde{Q}_i(s)$

$$\tilde{Q}_i(s) = \tilde{G}(s) [\tilde{w}(s)]^i \quad (27)$$

or

$$\tilde{Q}_i(s) = s^{-1} (1 - \tilde{w}(s)) [\tilde{w}(s)]^i \quad (28)$$

Inversion of Eq. (28) into the time domain, using the convolution theorem for Laplace transforms, emphasises the non Markovian nature of the process since $Q_i(t)$ will depend on the entire history of the process.

Let us now following [9,10] introduce $W(n, t)$ which is the probability of finding the dipole in discrete orientation n at time t . Let us further introduce $p_i(n)$ which is the probability that the dipole has orientation n after i changes in orientation then summing over all the orientation changes,

$$W(n, t) = \sum_{i=0}^\infty p_i(n) Q_i(t) \quad (29)$$

or

$$\tilde{W}(n, s) = \frac{(1 - \tilde{w}(s))}{s} \sum_{i=0}^\infty p_i(n) [\tilde{w}(s)]^i. \quad (30)$$

Now the evolution of $p_i(n)$ since only nearest neighbours are involved, is determined by the discrete time (i) and space (n) equation

$$p_{i+1}(n) = A(n-1)p_i(n-1) + B(n+1)p_i(n+1) \quad (31)$$

The continuous distribution of orientations, ϕ , is obtained by the replacement of $p_i(n)$ by $p_i(\phi)$ where $p_i(\phi)d\phi$ is the probability of finding the dipole after the i^{th} jump in the angle $\phi \rightarrow \phi + d\phi$. In like manner

$$A(n-1), B(n+1) \rightarrow A(\phi-\Delta), B(\phi+\Delta)$$

thus Eq. (31) becomes

$$p_{i+1}(\phi) = A(\phi-\Delta)p_i(\phi-\Delta) + B(\phi+\Delta)p_i(\phi+\Delta) \quad (32)$$

On expanding in a Taylor series about the point $\Delta=0$ we have as far as terms in Δ^2

$$A(\phi-\Delta)p_i(\phi-\Delta) = A(\phi)p_i(\phi) - \Delta \frac{\partial}{\partial \phi} [A(\phi)p_i(\phi)] + \frac{\Delta^2}{2} \frac{\partial^2}{\partial \phi^2} [A(\phi)p_i(\phi)] \quad (33)$$

Moreover by the principle of detailed balance if the system is close to thermal equilibrium at temperature T [9,10],

$$A(\phi) \cong B(\phi) \cong 1/2 \quad (34)$$

and

$$A(\phi) - B(\phi) \cong \frac{E(\phi)\Delta}{2kT} \quad (35)$$

where $E(\phi)$ is the magnitude of the electric field acting on the system. Equation (32) then becomes in the continuum limit as far as terms in Δ^2

$$p_{i+1}(\phi) = p_i(\phi) + \frac{\Delta^2}{2} \left[\frac{\partial^2}{\partial \phi^2} p_i(\phi) + \frac{\partial}{\partial \phi} \frac{\partial V}{\partial \phi} \frac{p_i(\phi)}{kT} \right] = p_i(\phi) + \frac{\Delta^2}{2} L p_i(\phi) \quad (36)$$

Now replacing n by ϕ , Eq. (30) may be written

$$\tilde{W}(\phi, s) = \frac{1 - \tilde{w}(s)}{s} p_0(\phi) + \frac{1 - \tilde{w}(s)}{s} \sum_{i=1}^{\infty} p_i(\phi) [\tilde{w}(s)]^i \quad (37)$$

or according to Eq. (36)

$$\tilde{W}(\phi, s) = \frac{1 - \tilde{w}(s)}{s} \delta(\phi) + \frac{1 - \tilde{w}(s)}{s} \sum_{i=1}^{\infty} \left[p_{i-1}(\phi) + \frac{\Delta^2}{2} L p_{i-1}(\phi) + O(\Delta^3) \right] [\tilde{w}(s)]^i. \quad (38)$$

We may now eliminate the summation in Eq. (38) by noting that,

$$\tilde{W}(\phi, s) \tilde{w}(s) = \frac{1 - \tilde{w}(s)}{s} \sum_{i=0}^{\infty} p_i(\phi) [\tilde{w}(s)]^{i+1} = \frac{1 - \tilde{w}(s)}{s} \sum_{i=1}^{\infty} p_{i-1}(\phi) [\tilde{w}(s)]^i \quad (39)$$

on change of the summation variable to $i = j - 1$. Thus

$$\tilde{W}(\phi, s) = \frac{1 - \tilde{w}(s)}{s} \delta(\phi) + \tilde{w}(s) \left[\tilde{W}(\phi, s) + \frac{\Delta^2}{2} L \tilde{W}(\phi, s) + O(\Delta^3) \right]. \quad (40)$$

We now explicitly consider the waiting time distribution. First we remark that the Einstein theory of the Brownian motion relies on the central limit theorem [5,11] that a *sum* of independent identically distributed random variables (the sum of the elementary displacements of the Brownian particle)

$$S_N = \sum_{n=0}^N X_n$$

becomes a Gaussian distribution in the limit $N \rightarrow \infty$ provided the first and second moments of X_n do not diverge. However there are famous exceptions for example [11] the Cauchy distribution,

$$f(x) = \frac{a}{\pi} \frac{1}{a^2 + x^2} \quad (41)$$

the second moment of this distribution is infinite. The Cauchy distribution is just one example of a whole class of distributions which possess long inverse power law tails e.g.,

$$p(x) = \frac{1}{|x|^{1+\sigma}}, \quad 0 < \sigma < 2 \quad (|x| \rightarrow \infty). \quad (42)$$

The tails prevent convergence to the Gaussian distribution for $N \rightarrow \infty$ however not the existence of a limiting distribution. These distributions are called [5,11] Lévy or stable distributions. If the concept of a Lévy distribution is applied to an assembly of temporal random variables such as the $\{\tau_i\}$ of the present paper then $w(\tau)$ is a long tailed pdf with long time asymptotic behaviour [9],

$$W(\tau) \sim \frac{\alpha A_\alpha}{\Gamma(1-\alpha)\tau^{1+\alpha}}, \quad 0 < \alpha < 1 \quad (\tau \rightarrow \infty). \quad (43)$$

The restriction to $0 < \alpha < 1$ ensures that the first moment of the waiting time distribution is divergent as is usual in a CTRW (corresponding to chaotic behaviour of the waiting times). Moreover in the frequency, s , domain the long time behaviour is manifested in the low frequency expansion [9]

$$\tilde{w}(s) = 1 - A_\alpha s^\alpha + c_1 (A_\alpha s^\alpha)^2 + \dots, \quad (44)$$

where it is obvious by the properties of the Laplace transform that the second term corresponds to the asymptotic behaviour given by Eq. (43). If we now substitute Eq. (44) into Eq. (40), on multiplying across by $A_\alpha^{-1} s^{-\alpha}$ and simplifying, we have

$$0 = s^{-1} (1 - c_1 A_\alpha s^\alpha + \dots) \delta(\phi) + (-1 + c_1 A_\alpha s^\alpha + \dots) \tilde{W}(\phi, s) + \frac{\Delta^2}{2A_\alpha} (s^{-\alpha} - A_\alpha + c_1 A_\alpha s^\alpha + \dots) [L\tilde{W}(\phi, s) + O(\Delta^3)] \quad (45)$$

If introducing the limiting procedure $A_\alpha \rightarrow 0, \Delta \rightarrow 0$ with

$$K_\alpha = \lim_{\substack{\Delta \rightarrow 0 \\ A_\alpha \rightarrow 0}} \frac{\Delta^2}{2A_\alpha} \quad (46)$$

finite, Eq. (45) becomes

$$-s^{-1} \delta(\phi) + \tilde{W}(\phi, s) = K_\alpha s^{-\alpha} L\tilde{W}(\phi, s) \quad (47)$$

or on inversion to the time domain

$$\frac{\partial W(\phi, t)}{\partial t} = K_\alpha {}_0 D_t^{1-\alpha} L W(\phi, t), \quad (48)$$

where

$${}_0 D_t^{-\alpha} g(t) = \frac{1}{\Gamma(\alpha)} \int_0^t \frac{g(t') dt'}{(t-t')^{1-\alpha}} \quad (49)$$

is the Riemann-Liouville fractional derivative [5].

Now in dielectric applications it is usual, to write Eq.(48) as,

$$\frac{\partial W}{\partial t} = \tau_0^{1-\alpha} D_t^{1-\alpha} L_s W \quad (50)$$

where $K_\alpha = \tau_0^{-\alpha}$, $\tau_0 = \zeta / (kT)$, and

$$L_s = L / \tau_0 \quad (51)$$

is the Smoluchowski operator of the normal Brownian motion. Equation (50) constitutes the extension of the classical theory of the Brownian motion excluding inertial effects to Cole-Cole behaviour. For the potential of Eq. (12) and the corresponding after effect solution Eq. (19), Eq.(50) immediately yields Eq.(1), [2]. For the Debye-Fröhlich model, on noting [5] that the eigenvalues of Eq. (50) are simply related to the eigenvalues of L_s by

$$\lambda = \lambda_s \tau_0^{1-\alpha} \quad (52)$$

one may easily generalise [5,6] that model to Cole-Cole relaxation. We briefly illustrate how Eq. (50) may be solved in the absence of a potential by using the method of characteristic functions [5].

5. Fundamental solution or Green function of the fractional Smoluchowski equation

We consider Eq. (50) in the absence of a potential and with a delta function initial distribution of orientations. The characteristic function which is the two sided Fourier transform over the space variable ϕ satisfies

$$\frac{\partial \tilde{W}}{\partial t} + \frac{k^2}{\tau_0^\alpha} D_t^{1-\alpha} \tilde{W} = 0 \quad (53)$$

where

$$\tilde{W} = \tilde{W}(k, t) = \langle e^{-ik\phi} \rangle$$

Hence we have

$$\tilde{W}(k, t) = E_\alpha \left[-k^2 (t / \tau_0)^\alpha \right] \quad (54)$$

where E_α is the Mittag-Leffler function [5] defined by

$$E_\alpha(z) = \sum_{n=0}^{\infty} \frac{z^n}{\Gamma(1 + \alpha n)}. \quad (55)$$

Since Eq. (54) is a characteristic function the second derivative of Eq. (54) with respect to k evaluated at $k=0$ will immediately yield the second moment of the distribution of the pdf $W(\phi, t)$ we have

$$\langle \phi^2 \rangle = \frac{2}{\Gamma(1 + \alpha)} \left(\frac{t}{\tau_0} \right)^\alpha, \quad 0 < \alpha \leq 1 \quad (56)$$

which is subdiffusive behaviour. Furthermore

$$\langle \phi^{2n+1} \rangle = 0, \quad \langle \phi^{2n} \rangle \propto (t / \tau_0)^{n\alpha} \quad (57)$$

This fact if (due to the statistically similar nature of the waiting times and step lengths) one may identify Δ^2 with $\langle \phi^2 \rangle$ supports the truncation of Eq. (45) using the limiting procedure of Eq. (46), to yield the diffusion Eq.(50). Such an identification is also essential in the Einstein theory in order to justify truncation of the Chapman-Kolmogorov integral equation used by Einstein [5] in order to obtain Eq. (4). Equation (57) has important implications in the possible treatment of anomalous diffusion using the Langevin equation method [5].

Finally the characteristic function Eq. (54) for $k=1$ yields the decay function for the Cole-Cole behaviour. The Cole-Cole Eq. (1) is determined from Eq. (54) by simply taking the one sided Fourier transform over the time variable and using linear response theory [5]. The pdf $W(\phi, t)$ may also be determined from Eq. (54) and (55) by evaluating the inverse Fourier transform over the k variable. It is [5] a Lévy distribution possessing the characteristic long time tail.

6. Discussion and Conclusions

We have seen that Cole-Cole behaviour may be described using probability density diffusion equations in essentially the same manner as the Debye relaxation by considering the diffusion limit of a CTRW. Moreover the fractional Smoluchowski equation may be solved just as the normal Smoluchowski equation using the method of characteristic functions. The advantage of using the CTRW formalism is that it is now possible to gain some insight into the meaning of the parameter α . It is the *order* of the fractional derivative in the fractional differential equation describing the continuum limit of a random walk with a chaotic set of waiting times (often known as a *fractal time random walk*). However a more physical useful definition of α is as the *fractal dimension* of the set of waiting times which is the scaling of the waiting time segments in the random walk with magnification. α thus measures the *statistical self similarity* (or how the whole looks like its parts [11]) of the waiting time segments. In order to construct such an entity in practice a whole discrete hierarchy of time scales is needed. For example a fractal time Poisson process [11] with a waiting time distribution assumes the typical form of the Lévy stable distribution in the limit of large τ . This is explicitly discussed in [11] where a formula for α is given and is also discussed in [12] where the fractal time process is essentially generated by considering jumps over the wells of a chaotic potential barrier landscape. The microscopic picture presented in [11,12] appears to completely support the commonly used experimental representation [1] of the Cole-Cole behaviour as a distribution of Debye like relaxation mechanisms with a continuous relaxation time distribution function.

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8. References

1. Scaife, B. K. P. (1998) *Principles of Dielectrics*, Oxford University Press, London, 1989; 2nd Edition.
2. Coffey, W. T., Kalmykov, Yu. P., and Titov, S. V. (2001) *J. Chem. Phys.* **116**, 6422.
3. Debye, P. (1913) *Ver. Deut. Phys. Gesell.* **15**, 777; reprinted 1954 in collected papers of Peter J.W. Debye Interscience New York.
4. Debye, P., *Polar Molecules* (1929) Chemical Catalog Co. New York; reprinted by Dover, New York, 1954.
5. Coffey, W. T., Kalmykov, Yu. P., and Waldron, J. T. (2003) *The Langevin Equation*, 2nd edition, World Scientific, Singapore.
6. Kalmykov, Yu. P., Coffey, W. T., and Titov, S. V., to be published.
7. Coffey, W. T., Kalmykov, Yu. P., and Titov, S. V. (2003) *Phys. Rev. E* **67**, in the press.
8. Fröhlich, H., *Theory of Dielectrics* (1958) 2nd Edition, Oxford University Press, London.
9. Barkai, E., Metzler, R. and Klafter J. (2000) *Phys. Rev. E* **61**, 132.
10. Metzler, R., and Klafter J. (2000) *Phys. Rep.* **339**, 1.
11. Paul, W., and Baschnagel, J. (1999) *Stochastic Processes from Physics to Finance*, Springer Verlag, Berlin.
12. Novikov, V. V. and Privalko, V. P. (2001) *Phys. Rev. E* **64**, 031504.
13. Mazo, R. (2002) *Brownian Motion: Fluctuations, Dynamics and Applications*, Oxford University Press, Oxford.
14. Coffey, W. T., and Paranjape, B. V. (1978) *Proc. R. Ir. Acad.* **78A**, 17.
15. Déjardin, J. L., and Kalmykov, Yu. P. (2000), *Phys. Rev.* **61**, 1211.
16. Jadzyn, J., Kedziora, P., and Hellemans, L. (1999), *Phys. Lett.* **251**, 49
17. Kramers, H. A. (1940) *Physica* **7**, 284.
18. Brown, W. F. (1963) *Phys. Rev.* **130**, 1677.
19. Urban S. and Wuerflinger A. (1997) *Adv. Chem. Phys.*, **98**, 143.

ROTATIONAL BROWNIAN MOTION AND NONLINEAR DIELECTRIC RELAXATION OF ASYMMETRIC TOP MOLECULES IN STRONG ELECTRIC FIELDS: THE LANGEVIN EQUATION APPROACH

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1. Introduction

Dielectric relaxation spectroscopy is a valuable tool in probing dynamical processes in condensed matter. Recently, this method has been extended to the nonlinear regime and applied to the investigation of liquid crystals, polymers, solids, and liquids (see, e.g., [1-10] and references cited therein). These investigations have shown that nonlinear dielectric spectra provide more information on the relaxation processes than can be obtained from linear spectra only. On the other hand, nonlinear experimental data offer an additional important test of theoretical models leading to a better understanding of the properties of the materials. However, the study of nonlinear dielectric spectra requires an adequate theoretical description of dielectric relaxation in strong electric fields.

The linear theory of electric polarization of dielectric fluids was formulated originally by Debye [11], who calculated the linear dielectric response in the context of the noninertial rotational diffusion model of spherical molecules. That response has a well-known representation in terms of the Debye equation for the complex dielectric permittivity and of the Cole-Cole diagram, which is a perfect semicircle. Linear-response theory was further extended by Perrin [12] and others [13,14] to asymmetric top molecules when the dielectric response becomes more complicated, as rotation about each molecular axis may contribute to the dielectric spectra. The permittivity in linear response is independent of the applied electric field strength. Many attempts have been made to generalize the Debye theory in order to take into account the nonlinear aspects of dielectric relaxation of polar fluids in high electric fields, however only symmetric top molecules have been usually treated (see [15] and [16] and references cited therein for a review). The theory of rotational Brownian motion of asymmetric tops in an electric field (in the *low field strength* limit) has been developed by Wegener *et al.* [17-19] in a particular application to the Kerr effect relaxation (the results of Wegener *et al.* [17-19] were reproduced recently by Hosokawa *et al.* [20]). A theory of nonlinear dielectric relaxation of asymmetric top molecules in *strong electric fields* was developed in Ref. [21]. Here, this theory is presented in details. As a particular example, the theory is used to evaluate the nonlinear dielectric relaxation in superimposed ac and strong dc bias electric fields for a system of rodlike molecules, where the dipole moment vector may be directed at an arbitrary angle to the long molecular axis. In an experimental context, this technique has been recently proposed by Hellemans *et al.* [7-

10] to study the dynamics of molecular liquids. It has been also demonstrated in [7-9] that the experimental data for symmetric top molecules with the dipole moment μ directed along the axis of symmetry are in complete agreement with the theory of Coffey and Paranjape [22]. However, for asymmetric top molecules, the result of Ref. [22] is not applicable.

The traditional theoretical approach to the problem habitually commences with the noninertial Langevin equation for the rotational Brownian motion of a molecule or with the corresponding Smoluchowski equation for the probability density distribution function W of orientations of the molecules in configuration space. The Smoluchowski equation can be solved by expanding W in terms of an appropriate complete set of orthogonal functions, usually as a series of spherical harmonics $Y_{l,m}$. This yields an infinite hierarchy of recurrence relations for the moments, namely, the expectation values of the spherical harmonics $\langle Y_{l,m} \rangle(t)$ (see, e.g., [16,23-25]). The underlying Langevin equation can also be reduced to the same moment system (*without recourse* to the Smoluchowski equation) by appropriate transformation of the variables and by direct averaging of the stochastic equation so obtained [16,23]. In many applications (e.g., for the problem in question), approximate solutions of this hierarchy can be obtained by using perturbation methods as the energy of molecules in external fields is usually (much) less than the thermal energy kT . When the perturbation approach is not applicable, one may use the matrix continued fraction method [16,23]. As shown in Refs. 16 and 23, this method is very convenient for the computation of the nonlinear response. In general, the same approach may be used for asymmetric tops by noting that the quantities of interest are averages involving Wigner's D functions [26,27].

The paper is arranged as follows. In Sect. 2, an infinite hierarchy of recurrence equations for the expectation values of Wigner's D -functions describing nonlinear relaxation of an assembly of noninteracting rigid asymmetric top molecules is derived in the context of the Langevin equation approach without recourse to the Fokker-Planck equation. In Sect.3, for the purpose of illustration, the linear response theory for asymmetric top molecules is given in the context of the approach developed. The perturbation solution of the hierarchy for the particular case of nonpolarizable rodlike molecules in superimposed ac and strong dc bias electric fields is obtained in Sect. 4.

2. Solution of the Euler-Langevin equation for an asymmetric top in the noninertial limit

We consider the three-dimensional rotational Brownian motion of a rigid asymmetric top molecule in an external potential V . The orientation of the molecule is described by the Euler angles $\Omega = \{\alpha, \beta, \gamma\}$ (here, the notations from Ref. [27] are adopted; see Fig. 1). The Euler angles completely determine the orientation of the molecular (body-fixed) coordinate system xyz with respect to the laboratory coordinate system XYZ . The dynamics of the molecule are described by the Euler-Langevin equation for the angular velocity $\omega(t)$ written in the body-fixed coordinate system xyz [14]:

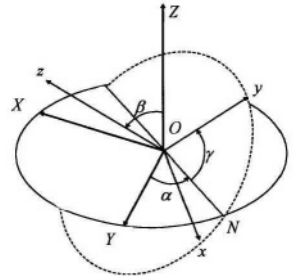


Figure 1. The Euler angles

$$\frac{d}{dt} \hat{I} \omega(t) + \omega(t) \times \hat{I} \omega(t) + \hat{\zeta} \omega(t) = -\nabla V[\Omega(t), t] + \lambda(t), \quad (2.1)$$

where $\hat{I}$ is the inertia tensor of the molecule, $\hat{\zeta} \omega(t)$ is the damping torque due to Brownian movement, $\hat{\zeta}$ is the rotational friction tensor, $\lambda(t)$ is the white noise driving torque, again due to Brownian movement, so that $\lambda(t)$ has the following properties:

$$\overline{\lambda_i(t)} = 0, \quad \overline{\lambda_i(t_1) \lambda_j(t_2)} = 2kT \zeta_{ij} \delta_{ij} \delta(t_1 - t_2). \quad (2.2)$$

Here, δ_{ij} is Kronecker's delta, the overbar means a statistical average over an ensemble of Brownian particles which *all* start at time t with the *same* angular velocity and orientation, and indices $i, j=1, 2, 3$ correspond to the Cartesian axes $x y z$ of the *molecular* coordinate system. The term $-\nabla V$ in Eq. (2.1) represents the torque acting on the molecule, $\nabla \equiv \delta / \delta \phi$ is the orientation space gradient operator (the properties of ∇ are described in detail in [28]), $\delta \phi$ is an infinitesimal rotation vector so that $\omega(t) = \delta \phi / \delta t$, $V(\Omega, t)$ is the potential energy of the molecule in the electric field, viz.,

$$V(\Omega, t) = -(\mu \cdot E) - (E \cdot \hat{\alpha} \cdot E) / 2, \quad (2.3)$$

where μ is the electric dipole moment vector, $\hat{\alpha}$ is the electric polarizability tensor (here the effects due to hyperpolarizability are neglected, however they may also be included in the theory by adding the corresponding terms in Eq. (2.3) [16]). The torque $-\nabla V$ in Eq. (2.1) can be expressed in terms of the angular momentum operator $\hat{J}$ [27]:

$$-\nabla V = -i \hat{J} V. \quad (2.4)$$

The components of $\hat{J}$ in the molecular coordinate system are given by [27]

$$\hat{J}_x = \frac{1}{\sqrt{2}} (\hat{J}^{-1} - \hat{J}^{+1}), \quad \hat{J}_y = -\frac{i}{\sqrt{2}} (\hat{J}^{-1} + \hat{J}^{+1}), \quad \hat{J}_z = \hat{J}^0, \quad (2.5)$$

where

$$\hat{J}^{\pm 1} = \frac{i}{\sqrt{2}} e^{\mp i\gamma} \left[\pm \cot \beta \frac{\partial}{\partial \gamma} + i \frac{\partial}{\partial \beta} \mp \frac{1}{\sin \beta} \frac{\partial}{\partial \alpha} \right], \quad \hat{J}^0 = -i \frac{\partial}{\partial \gamma}. \quad (2.6)$$

One can now determine the corresponding components of the orientation space gradient operator $\nabla = i \hat{J}$ from Eqs. (2.4)-(2.6). The Euler-Langevin Eq. (2.1) is a vector stochastic differential equation. Here, we shall use the Stratonovich definition [29] of a stochastic differential equation, as that definition always constitutes the mathematical idealization of the dielectric relaxation processes [23]. The Stratonovich definition allows us to apply the methods of ordinary analysis [23] at the transformation and solution of Eq. (2.1). In writing Eq. (2.1), it was assumed that the suspension of Brownian particles (molecules) is monodisperse, nonconducting, and sufficiently dilute to avoid interparticle correlation effects. Memory and quantum effects were also ignored (the last assumption fails in liquids and solutions only for the lightest polar molecules such as HF and HCl).

The Euler-Langevin Eq. (2.1) takes into account the inertial effects. The inclusion of these effects causes the theory of orientational relaxation of an asymmetric top to become very complicated even in the absence of an external potential (see, e.g., [30]). A radical simplification of the theory can be achieved in the noninertial limit, $I_i \dot{\omega} / (\omega \zeta_{ii}) \ll 1$, i.e., at low frequencies, when the inertia terms in Eq. (2.1) may be

neglected. Here, the angular velocity $\boldsymbol{\omega}$ may be immediately obtained from Eqs. (2.1) and (2.4) as

$$\boldsymbol{\omega}(t) = \delta\boldsymbol{\varphi} / \delta t = \hat{D} \{ \boldsymbol{\lambda}(t) - i\hat{\mathbf{J}}V[\boldsymbol{\Omega}(t), t] \} / (kT), \quad (2.7)$$

where $\hat{D} = kT\hat{\zeta}^{-1}$ is the diffusion tensor. The noninertial approximation is valid in the low-frequency region (< 10 GHz) for the majority of molecules in liquid solutions. In this approximation, one can readily obtain from Eqs. (2.4) and (2.7) the equation of motion of an arbitrary function $f(\alpha, \beta, \gamma)$:

$$\frac{d}{dt}f = \dot{\alpha} \frac{\partial}{\partial \alpha}f + \dot{\beta} \frac{\partial}{\partial \beta}f + \dot{\gamma} \frac{\partial}{\partial \gamma}f = (\boldsymbol{\omega} \cdot \nabla)f = \frac{1}{kT} \left[i \left((\hat{D}\boldsymbol{\lambda}) \cdot \hat{\mathbf{J}}f \right) + \left((\hat{D}\hat{\mathbf{J}}V) \cdot \hat{\mathbf{J}}f \right) \right]. \quad (2.8)$$

On noting that for a *symmetric* tensor $\hat{D}$ and for any $V(\boldsymbol{\Omega}, t)$ and $f(\boldsymbol{\Omega})$ the following mathematical identity holds [21,23]

$$2(\hat{D}\hat{\mathbf{J}}V) \cdot \hat{\mathbf{J}}f = V\nabla_{\boldsymbol{\Omega}}^2 f + f\nabla_{\boldsymbol{\Omega}}^2 V - \nabla_{\boldsymbol{\Omega}}^2 (Vf), \quad (2.9)$$

where the operator $\nabla_{\boldsymbol{\Omega}}^2$ is defined as [13]

$$\nabla_{\boldsymbol{\Omega}}^2 = -\hat{\mathbf{J}}\hat{D}\hat{\mathbf{J}} = - \sum_{k,m=x,y,z} D_{km} \hat{J}_k \hat{J}_m, \quad (2.10)$$

one has [21]

$$\begin{aligned} \frac{d}{dt}f[\boldsymbol{\Omega}(t)] &= \frac{i}{kT} \left(\hat{D}\boldsymbol{\lambda}(t) \cdot \hat{\mathbf{J}}f[\boldsymbol{\Omega}(t)] \right) + \frac{1}{2kT} \left[V[\boldsymbol{\Omega}(t), t] \nabla_{\boldsymbol{\Omega}}^2 f[\boldsymbol{\Omega}(t)] \right. \\ &\quad \left. + f[\boldsymbol{\Omega}(t)] \nabla_{\boldsymbol{\Omega}}^2 V[\boldsymbol{\Omega}(t), t] - \nabla_{\boldsymbol{\Omega}}^2 (V[\boldsymbol{\Omega}(t), t] f[\boldsymbol{\Omega}(t)]) \right]. \end{aligned} \quad (2.11)$$

Equation (2.11) is a stochastic differential equation with a multiplicative noise term $i(\hat{D}\boldsymbol{\lambda}) \cdot \hat{\mathbf{J}}f / (kT)$. In order to average Eq. (2.11) over an ensemble of particles which all have started with the same $\boldsymbol{\Omega}$, one must write Eq. (2.11) in integral form [23]:

$$\begin{aligned} f[\boldsymbol{\Omega}(t+\tau)] &= f(\boldsymbol{\Omega}) + \frac{i}{kT} \int_t^{t+\tau} \left(\hat{D}\boldsymbol{\lambda}(t') \cdot \hat{\mathbf{J}}f[\boldsymbol{\Omega}(t')] \right) dt' + \frac{1}{2kT} \int_t^{t+\tau} \left[V[\boldsymbol{\Omega}(t'), t'] \nabla_{\boldsymbol{\Omega}}^2 f[\boldsymbol{\Omega}(t')] \right. \\ &\quad \left. + f[\boldsymbol{\Omega}(t')] \nabla_{\boldsymbol{\Omega}}^2 V[\boldsymbol{\Omega}(t'), t'] - \nabla_{\boldsymbol{\Omega}}^2 \{ V[\boldsymbol{\Omega}(t'), t'] f[\boldsymbol{\Omega}(t')] \} \right] dt' \end{aligned} \quad (2.12)$$

with $\boldsymbol{\Omega}(t) = \boldsymbol{\Omega}$, and then evaluate the limit [23]

$$\begin{aligned} \dot{f}(\boldsymbol{\Omega}) &= \lim_{\tau \rightarrow 0} \frac{f[\boldsymbol{\Omega}(t+\tau)] - f(\boldsymbol{\Omega})}{\tau} = \frac{i}{kT} \lim_{\tau \rightarrow 0} \frac{1}{\tau} \left\{ \int_t^{t+\tau} \hat{D}\boldsymbol{\lambda}(t') \cdot \hat{\mathbf{J}}f[\boldsymbol{\Omega}(t')] dt' \right. \\ &\quad \left. + \frac{1}{2kT} \int_t^{t+\tau} \left[V[\boldsymbol{\Omega}(t'), t'] \nabla_{\boldsymbol{\Omega}}^2 f[\boldsymbol{\Omega}(t')] + f[\boldsymbol{\Omega}(t')] \nabla_{\boldsymbol{\Omega}}^2 V[\boldsymbol{\Omega}(t'), t'] \right. \right. \\ &\quad \left. \left. - \nabla_{\boldsymbol{\Omega}}^2 \{ V[\boldsymbol{\Omega}(t'), t'] f[\boldsymbol{\Omega}(t')] \} \right] dt' \right\}. \end{aligned} \quad (2.13)$$

The right-hand side of Eq. (2.13) again comprises two terms, namely: the noise-induced drift and deterministic drift. In order to evaluate the noise-induced drift term, we first note that a rotation through the infinitesimal angle $\delta\boldsymbol{\varphi}(t')$ transforms the function $f(\boldsymbol{\Omega})$ into $f[\boldsymbol{\Omega}(t')]$ as [27]

$$f[\boldsymbol{\Omega}(t')] = e^{i\delta\boldsymbol{\varphi}(t') \cdot \hat{\mathbf{J}}} f(\boldsymbol{\Omega}) \approx \left(1 + i\delta\boldsymbol{\varphi}(t') \cdot \hat{\mathbf{J}} \right) f(\boldsymbol{\Omega}), \quad (2.14)$$

where according to Eq. (2.7)

$$\delta\Phi(t') = \Phi(t') - \Phi(t) = \frac{1}{kT} \int_t^{t'} \hat{D} \left\{ \lambda(t'') - i\hat{\mathbf{J}}V[\Omega(t''), t''] \right\} dt''. \quad (2.15)$$

Thus, on noting Eqs. (2.14) and (2.15), we have

$$\frac{i}{kT} \lim_{\tau \rightarrow 0} \frac{1}{\tau} \int_t^{t+\tau} \hat{D}\lambda(t') \cdot \hat{\mathbf{J}}f[\Omega(t')] dt' = -\hat{\mathbf{J}}\hat{D}\hat{\mathbf{J}}f(\Omega) = \nabla_\Omega^2 f(\Omega). \quad (2.16)$$

Here, we have used Eqs. (2.2). The evaluation of the deterministic drift term [the last term in Eq. (2.13)] yields [21]

$$\frac{1}{2kT} \left[V(\Omega, t) \nabla_\Omega^2 f(\Omega) + f(\Omega) \nabla_\Omega^2 V(\Omega, t) - \nabla_\Omega^2 [V(\Omega, t) f(\Omega)] \right]. \quad (2.17)$$

Noting Eqs. (2.16) and (2.17), we obtain from Eq. (2.13)

$$\dot{f} = \nabla_\Omega^2 f - \frac{1}{2kT} \left[\nabla_\Omega^2 (Vf) - V \nabla_\Omega^2 f - f \nabla_\Omega^2 V \right]. \quad (2.18)$$

Equation (2.18) constitutes the averaged equation of motion of an arbitrary function $f(\alpha, \beta, \gamma)$. We remark that Ω in Eq. (2.18) and $\Omega(t)$ in Eq. (2.11) have *different meanings*, namely, the $\Omega(t)$ in Eq. (2.11) are stochastic variables while the Ω in Eq. (2.18) are the sharp (definite) values $\Omega(t) = \Omega$ at time t [23].

In rotational diffusion problems, the quantities of interest are averages involving Wigner's D functions defined as [27]

$$D_{M, M'}^J(\Omega) = e^{-iM\alpha} d_{MM'}^J(\beta) e^{-iM'\gamma}, \quad (2.19)$$

where $d_{MM'}^J(\beta)$ is a real function whose various explicit forms are given, for example, in Ref. [27]; a typical example is

$$d_{MM'}^J(\beta) = \frac{(-1)^{J-M'}}{2^J} \left[\frac{(J+M)!}{(J-M)!(J+M')!(J-M')!} \right]^{-1/2} (1 - \cos \beta)^{\frac{M'-M}{2}} \\ \times (1 + \cos \beta)^{\frac{M'+M}{2}} \frac{d^{J-M}}{(d \cos \beta)^{J-M}} \left[(1 - \cos \beta)^{J-M'} (1 - \cos \beta)^{J+M'} \right].$$

The orthogonality and normalisation conditions for D functions are [27]

$$\int_0^{2\pi} \int_0^{2\pi} \int_0^\pi D_{l_1, l_1'}^{j_1}(\Omega) D_{l_2, l_2'}^{j_2}(\Omega) \sin \beta d\beta d\alpha d\gamma = \frac{8\pi^2}{2j_1 + 1} \delta_{j_1 j_2} \delta_{l_1 l_2} \delta_{l_1' l_2'} \quad (2.20)$$

(the asterisk denotes the complex conjugate). In quantum mechanics, Wigner's D functions represent the wave functions of a rigid symmetric top [27].

Equation (2.18) written in terms of D functions yields

$$\frac{d}{dt} D_{n, m}^j = \nabla_\Omega^2 D_{n, m}^j - \frac{1}{2kT} \left[\nabla_\Omega^2 (V D_{n, m}^j) - V \nabla_\Omega^2 D_{n, m}^j - D_{n, m}^j \nabla_\Omega^2 V \right]. \quad (2.21)$$

Here, it is convenient to use the molecular coordinate system in which the diffusion tensor $\hat{D}$ is diagonal so that the operator ∇_Ω^2 , Eq. (2.10), is simplified to [13]

$$\nabla_\Omega^2 = - \left(D_{xx} \hat{j}_x^2 + D_{yy} \hat{j}_y^2 + D_{zz} \hat{j}_z^2 \right). \quad (2.22)$$

We remark that the principal axis system of the diffusion tensor $\hat{D}$ for an asymmetric top molecule may not coincide, in general, with the principal axis system that

diagonalises the moment of inertia tensor $\hat{I}$ [31]. Thus, if the orientation of the diffusion tensor principal axis system is unknown, the nondiagonalised diffusion tensor form, Eq. (2.10), must be used. Equation (2.22) contains three phenomenological constants, namely: the three-diagonal components of the diffusion tensor D_{xx} , D_{yy} , and D_{zz} . The values of D_{ii} may be estimated either in the context of the so-called hydrodynamic approach, where the components of the diffusion tensor depend only on the shape of the particle, or in terms of microscopic molecular parameters [31]:

$$D_{ii} = kT / \zeta_{ii} = \tau_j^i kT / I_i,$$

where I_i is the principal moment of inertia about the i -axis and τ_j^i is the angular velocity correlation time about that axis. Unfortunately, it is very difficult to evaluate τ_j^i for a model system, however these times can be measured experimentally using nuclear magnetic resonance techniques [31].

The operator ∇_Ω^2 defined by Eq. (2.22) can be represented as [13,21]

$$\nabla_\Omega^2 = -\frac{1}{2\tau_D} \left\{ \hat{\mathbf{J}}^2 + 2\Delta \hat{J}_z^2 + \Xi \left[(\hat{J}^{+1})^2 + (\hat{J}^{-1})^2 \right] \right\}, \quad (2.23)$$

where

$$\tau_D = \frac{1}{D_{xx} + D_{yy}}, \quad \Delta = \frac{D_{zz}}{D_{xx} + D_{yy}} - \frac{1}{2}, \quad \Xi = \frac{D_{xx} - D_{yy}}{D_{xx} + D_{yy}}, \quad (2.24)$$

the operator $\hat{\mathbf{J}}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$ is given by [27]

$$\hat{\mathbf{J}}^2 = -\frac{\partial^2}{\partial \beta^2} - \cot \beta \frac{\partial}{\partial \beta} - \frac{1}{\sin^2 \beta} \left(\frac{\partial^2}{\partial \alpha^2} - 2 \cos \beta \frac{\partial^2}{\partial \alpha \partial \gamma} + \frac{\partial^2}{\partial \gamma^2} \right), \quad (2.25)$$

and we have used the equality $\hat{J}_x^2 - \hat{J}_y^2 = (\hat{J}^{+1})^2 + (\hat{J}^{-1})^2$. Equation (2.23) can be simplified by using the known properties of the angular momentum operators and D functions, viz., [27]

$$\begin{aligned} \hat{\mathbf{J}}^2 D_{n,m}^j(\Omega) &= j(j+1) D_{n,m}^j(\Omega), & \hat{J}_z^2 D_{n,m}^j(\Omega) &= m^2 D_{n,m}^j(\Omega), \\ \hat{J}_v D_{n,m}^j(\Omega) &= -\sqrt{j(j+1)} C_{j,m,1,v}^{j,m+v} D_{n,m+v}^j(\Omega), \quad (v = \pm 1), \end{aligned}$$

and

$$D_{l_1,m_1}^{j_1}(\Omega) D_{l_2,m_2}^{j_2}(\Omega) = \sum_{j=|j_1-j_2|}^{j_1+j_2} C_{j_1,j_1,j_2,l_2}^{j,j_1+l_2} C_{j_1,m_1,j_2,m_2}^{j,m_1+m_2} D_{l_1+l_2,m_1+m_2}^j(\Omega).$$

Here, $C_{j_1,j_1,j_2,l_2}^{j,j_1+l_2}$ are the Clebsch-Gordan coefficients [27] the various definitions of which are available, e.g., in Ref. [26,27]; a typical example is

$$\begin{aligned} C_{a,\alpha,b,\beta}^{c,\gamma} &= \delta_{\gamma=\alpha+\beta} \sqrt{\frac{(a+b-c)!(a-b+c)!(-a+b+c)!(c+\gamma)!(c-\gamma)!(2c+1)}{(a+b+c+1)!(a+\alpha)!(a-\alpha)!(b+\beta)!(b-\beta)!}} \\ &\quad \times \sum_n \frac{(-1)^{b+\beta+n} (c+b+\alpha-n)!(a-\alpha+n)!}{n!(c-a+b-n)!(c+\gamma-n)!(a-b-\gamma+n)!}, \end{aligned}$$

where the summation index n assumes integer values for which all the factorial arguments are nonnegative. Thus

$$\nabla_{\Omega}^2 D_{n,m}^j = -\frac{j(j+1)}{2\tau_D} \left\{ \left[\frac{2\Delta m^2}{j(j+1)} + 1 \right] D_{n,m}^j + \Xi \left[C_{j,m,1,1}^{j,m+1} C_{j,m+1,1,1}^{j,m+2} D_{n,m+2}^j + C_{j,m,1,-1}^{j,m-1} C_{j,m-1,1,-1}^{j,m-2} D_{n,m-2}^j \right] \right\}.$$

Noting the above equations, one may show that for any potential V which may be expanded in D functions as

$$V(\Omega, t)/(kT) = \sum_{Q,S,R} v_{R,S,Q}(t) D_{S,Q}^R(\Omega), \quad (2.26)$$

the following differential-recurrence equation is valid [21]

$$\begin{aligned} \tau_D \frac{d}{dt} D_{n,m}^j = & - \left[\frac{j(j+1)}{2} + \Delta m^2 \right] D_{n,m}^j - \frac{j(j+1)}{2} \Xi \left[C_{j,m,1,1}^{j,m+1} C_{j,m+1,1,1}^{j,m+2} D_{n,m+2}^j + C_{j,m,1,-1}^{j,m-1} C_{j,m-1,1,-1}^{j,m-2} D_{n,m-2}^j \right] \\ & + \frac{1}{4} \sum_{R,S,Q} \sum_{J=j-R}^{j+R} v_{R,S,Q} C_{j,n,R,S}^{J,n+S} \left\{ [J(J+1) + 4\Delta m Q - j(j+1) - R(R+1)] C_{j,m,Q}^{J,m+Q} D_{n+S,m+Q}^J \right. \\ & + \Xi \left[J(J+1) C_{j,m+Q,1,1}^{J,m+Q+1} C_{j,m+Q+1,1,1}^{J,m+Q+2} C_{j,m,R,Q}^{J,m+Q} - j(j+1) C_{j,m,1,1}^{j,m+1} C_{j,m+1,1,1}^{j,m+2} C_{j,m+2,R,Q}^{J,m+2+Q} \right. \\ & \quad \left. \left. - R(R+1) C_{R,Q,1,1}^{R,Q+1} C_{R,Q+1,1,1}^{R,Q+2} C_{j,m,R,Q+2}^{J,m+Q+2} \right] D_{n+S,m+Q+2}^J \right. \\ & \left. + \Xi \left[J(J+1) C_{j,m+Q,1,-1}^{J,m+Q-1} C_{j,m+Q-1,1,-1}^{J,m+Q-2} C_{j,m,R,Q}^{J,m+Q} - j(j+1) C_{j,m,1,-1}^{j,m-1} C_{j,m-1,1,-1}^{j,m-2} C_{j,m-2,R,Q}^{J,m-2+Q} \right. \right. \\ & \quad \left. \left. - R(R+1) C_{R,Q,1,-1}^{R,Q-1} C_{R,Q-1,1,-1}^{R,Q-2} C_{j,m,R,Q-2}^{J,m+Q-2} \right] D_{n+S,m+Q-2}^J \right\}. \quad (2.27) \end{aligned}$$

As we have already mentioned, all the quantities $D_{r,s}^j$ in Eq. (2.27) are, in general, functions of the sharp (definite) values $\Omega(t) = \Omega$ at time t , which are themselves random variables with the probability density function $W(\Omega, t)$ such that $W(\Omega, t)d\Omega$ is the probability of finding Ω in the interval $(\Omega, \Omega + d\Omega)$. Therefore, in order to obtain equations for the moments governing the relaxation dynamics of the system, we must also average Eq. (2.27) over W . Thus, we have from Eq. (2.27) a hierarchy of differential-recurrence equations for statistical moments $\langle D_{n,m}^j \rangle$

$$\begin{aligned} \tau_D \frac{d}{dt} \langle D_{n,m}^j \rangle = & - \left\{ \frac{j(j+1)}{2} + \Delta m^2 \right\} \langle D_{n,m}^j \rangle \\ & - \frac{j(j+1)}{2} \Xi \left[C_{j,m,1,1}^{j,m+1} C_{j,m+1,1,1}^{j,m+2} \langle D_{n,m+2}^j \rangle + C_{j,m,1,-1}^{j,m-1} C_{j,m-1,1,-1}^{j,m-2} \langle D_{n,m-2}^j \rangle \right] \\ & + \frac{1}{4} \sum_{R,S,Q} \sum_{J=j-R}^{j+R} v_{R,S,Q} C_{j,n,R,S}^{J,n+S} \left\{ [J(J+1) + 4\Delta m Q - j(j+1) - R(R+1)] C_{j,m,Q}^{J,m+Q} \langle D_{n+S,m+Q}^J \rangle \right. \\ & + \Xi \left[J(J+1) C_{j,m+Q,1,1}^{J,m+Q+1} C_{j,m+Q+1,1,1}^{J,m+Q+2} C_{j,m,R,Q}^{J,m+Q} - j(j+1) C_{j,m,1,1}^{j,m+1} C_{j,m+1,1,1}^{j,m+2} C_{j,m+2,R,Q}^{J,m+2+Q} \right. \\ & \quad \left. \left. - R(R+1) C_{R,Q,1,1}^{R,Q+1} C_{R,Q+1,1,1}^{R,Q+2} C_{j,m,R,Q+2}^{J,m+Q+2} \right] \langle D_{n+S,m+Q+2}^J \rangle \right. \\ & \left. + \Xi \left[J(J+1) C_{j,m+Q,1,-1}^{J,m+Q-1} C_{j,m+Q-1,1,-1}^{J,m+Q-2} C_{j,m,R,Q}^{J,m+Q} - j(j+1) C_{j,m,1,-1}^{j,m-1} C_{j,m-1,1,-1}^{j,m-2} C_{j,m-2,R,Q}^{J,m-2+Q} \right. \right. \\ & \quad \left. \left. - R(R+1) C_{R,Q,1,-1}^{R,Q-1} C_{R,Q-1,1,-1}^{R,Q-2} C_{j,m,R,Q-2}^{J,m+Q-2} \right] \langle D_{n+S,m+Q-2}^J \rangle \right\}. \quad (2.28) \end{aligned}$$

If the system is in equilibrium, all averages in Eq. (2.28) are either constant or zero. Thus, in this case, one must construct from Eq. (2.27) a set of differential-recurrence relations for the appropriate equilibrium correlation functions (see, e.g., [23], Sect. 8.7).

Equation (2.28) is a general result, which may be applied to the anisotropic rotational diffusion problem. The advantage of the approach we have developed is that it is valid for any potential V . Another advantage of the present treatment is that it is not based on the quantum theory of a free asymmetric rotor (as is that of Favro [13]) so that many results obtained in the context of the anisotropic rotational diffusion model may be rederived from the general Eq. (2.28) in a much simpler way than before (see Sect. 3). In particular applications, Eq. (2.28) can considerably be simplified. For example, in isotropic rotational diffusion, where $D_{xx} = D_{yy} = D_{zz}$, both Δ and Ξ in Eq. (2.28) are equal to zero so that Eq. (2.28) reduces to [21]

$$\tau_D \frac{d}{dt} \langle D_{n,m}^j \rangle = -\frac{j(j+1)}{2} \langle D_{n,m}^j \rangle + \frac{1}{4} \sum_{R,S,Q} \sum_{j=|j-R|}^{j+R} v_{R,S,Q} C_{j,n,R,S}^{j,n+S} C_{j,m,R,Q}^{j,m+Q} \times [J(J+1) - j(j+1) - R(R+1)] \langle D_{n+S,m+Q}^j \rangle. \quad (2.29)$$

A further simplification can be achieved for axially symmetric problems, where one may ignore the dependence of the quantities of interest on the angles α and γ . On using a known property of the Wigner D functions, viz., [27] $D_{0,0}^j(\alpha, \beta, \gamma) \equiv P_j(\cos \beta)$, where $P_j(z)$ is the Legendre polynomial of the order j , we have from Eq. (2.29)

$$\tau_D \frac{d}{dt} \langle P_j \rangle = -\frac{j(j+1)}{2} \langle P_j \rangle + \frac{1}{4} \sum_R \sum_{j=|j-R|}^{j+R} v_{R,0,0}(t) \left(C_{j,0,R,0}^{j,0} \right)^2 \times [J(J+1) - j(j+1) - R(R+1)] \langle P_j \rangle.$$

On supposing that the electric field $\mathbf{E}$ is directed along the Z axis of the laboratory coordinate system, the polarization $P_z(t)$ is defined as

$$P_z(t) = N_0 \langle \mu_z \rangle(t), \quad (2.30)$$

where N_0 is the concentration of dipolar molecules and the μ_z is given by [32]

$$\mu_z(\Omega) = \mu \sum_{p=-1}^1 (-1)^p u^{(p)} D_{0,-p}^1(\Omega). \quad (2.31)$$

Here $u^{(\pm 1)} = \mp(u_x \pm iu_y)/\sqrt{2}$, $u^{(0)} = u_z$ are the irreducible spherical tensor components of the first rank [27] and u_x , u_y , and u_z are the components of a unit vector $\mathbf{u}$ in the direction of $\boldsymbol{\mu}$. Due to the cylindrical symmetry about the Z -axis, the moments $\langle D_{n,m}^j(t) \rangle$ with $n = 0$ only are required in the calculation of $P_z(t)$ (as well as the electro-optical birefringence) [17-19]. Hence, one can always insert in Eqs. (2.26) and (2.28) the indices $n, S \equiv 0$ so that from a mathematical viewpoint, Eq. (2.28) become a recurrence equation, where only two indices vary. Moreover, the form of Eq. (2.28) for the longitudinal nonlinear response for *asymmetric tops* becomes very similar to that which appears in evaluating the nonlinear response of *symmetric tops* when the external field has an arbitrary direction [16,24]. A general method of solution of such recurrence equations in terms of matrix continued fractions has been recently developed in Refs. 33-35 and applied to the evaluation of the nonlinear dielectric and Kerr-effect responses in [16,24]. Thus, the problem of the evaluation of the nonlinear response of asymmetric top molecules may be solved just as in [16,24] using matrix continued fractions. Indeed, on using the results of [33-35], one can show that Eq. (2.28) may be transformed into a matrix three-term differential-recurrence equation

$$\tau_D \frac{d}{dt} \mathbf{C}_n(t) = \mathbf{Q}_n^- \mathbf{C}_{n-1}(t) + \mathbf{Q}_n \mathbf{C}_n(t) + \mathbf{Q}_n^+ \mathbf{C}_{n+1}(t), \quad (n \geq 1), \quad (2.32)$$

where the elements of the column vector $\mathbf{C}_n(t)$ and of the matrices $\mathbf{Q}_n$, $\mathbf{Q}_n^+$, and $\mathbf{Q}_n^-$ are determined by Eq. (2.28). Equation (2.32) can be solved in terms of matrix continued fractions for all kinds of nonlinear response (transient, ac stationary, etc.) [16,23,24].

We remark that the recurrence Eq. (2.28) for the expectation values of Wigner's D functions may also be obtained from the corresponding Fokker-Planck (Smoluchowski) equation for the distribution function $W(\Omega, t)$ of the orientations of asymmetric top molecules, which is [36]

$$\frac{\partial}{\partial t} W = -\hat{\mathbf{J}} \hat{D} \left(\hat{\mathbf{J}} W + \frac{1}{kT} W \hat{\mathbf{J}} V \right) = \frac{1}{2kT} [W \nabla_\Omega^2 - V \nabla_\Omega^2 W + \nabla_\Omega^2 (VW)] + \nabla_\Omega^2 W. \quad (2.33)$$

The Langevin and Fokker-Planck equation treatments are equivalent and yield the same results. However, the Langevin equation approach has, in our opinion, the advantage that it allows one to derive Eq. (2.28) in a much simpler manner.

3. Linear response of an assembly of asymmetric tops

Here, we demonstrate how the linear response theory results for noninteracting dipolar asymmetric top molecules may be obtained from Eq. (2.28). Let us suppose that an external spatially uniform small dc electric field $\mathbf{E}$ ($\xi = \mu E / (kT) \ll 1$) had been applied to the system of asymmetric top molecules at $t = -\infty$ in the direction of the Z -axis of the laboratory coordinate system and at time $t = 0$ the field has been switched off. We are interested in the decay of the polarisation $P_Z(t)$ of the system of the molecules starting at $t = 0$ from the equilibrium state I with the Boltzmann distribution function

$$W_I(\Omega) = Z^{-1} e^{\mu_z(\Omega)E/(kT)} \approx \frac{1}{8\pi^2} \left[1 + \frac{\mu_z(\Omega)E}{kT} \right] \quad (3.1)$$

to the equilibrium state II with the uniform distribution function $W_{II}(\Omega) = 1/(8\pi^2)$, which is reached at $t \rightarrow \infty$. According to Eqs. (2.30) and (2.31), the behaviour of the electric polarisation $P_Z(t)$ is completely determined by $\langle D_{0,0}^1 \rangle(t)$, $\langle D_{0,-1}^1 \rangle(t)$, and $\langle D_{0,1}^1 \rangle(t)$. Equations of motion for these functions at $t \geq 0$ can be obtained from Eq. (2.27) by setting $v_{R,S,Q} = 0$, $j = 1$, $n = 0$, and $m = 0, \pm 1$. We have

$$\tau_D \frac{d}{dt} \langle D_{0,0}^1 \rangle(t) + \langle D_{0,0}^1 \rangle(t) = 0, \quad (3.2)$$

$$\tau_D \frac{d}{dt} \langle D_{0,\pm 1}^1 \rangle(t) + (1 \pm \Delta) \langle D_{0,\pm 1}^1 \rangle(t) = -(\Xi/2) \langle D_{0,\mp 1}^1 \rangle(t). \quad (3.3)$$

In Eqs. (3.2) and (3.3), the initial values of $\langle D_{0,p}^1 \rangle(t)$ at $t = 0$ are

$$\langle D_{0,p}^1 \rangle(0) = \int D_{0,p}^1(\Omega) W_I(\Omega) d\Omega.$$

Thus, we can obtain from Eqs. (2.19), (2.20), and (3.1) in the low field strength limit

$$\langle D_{0,0}^1 \rangle(0) \approx \xi u_z / 3, \quad \langle D_{0,\pm 1}^1 \rangle(0) \approx \mp \xi (u_x \pm i u_y) / (3\sqrt{2}), \quad [\mu E / (kT) \ll 1]. \quad (3.4)$$

The solutions of Eqs. (3.2) and (3.3) are

$$\langle D_{0,0}^1 \rangle(t) = \frac{\xi u_z}{3} e^{-(D_{xx}+D_{yy})t}, \quad \langle D_{0,\pm 1}^1 \rangle(t) = \mp \frac{\xi}{3\sqrt{2}} \left[u_x e^{-(D_{yy}+D_{zz})t} \pm i u_y e^{-(D_{xx}+D_{zz})t} \right], \quad (3.5)$$

where the relations

$$\tau_D^{-1}(1 + \Delta - \Xi/2) = D_{zz} + D_{yy}, \quad \tau_D^{-1}(1 + \Delta + \Xi/2) = D_{zz} + D_{xx}$$

have been taken into account. Now, one has from Eqs. (2.30), and (3.5)

$$P_Z(t) = E \frac{\mu^2 N_0}{3kT} \left\{ u_x^2 e^{-(D_{xx}+D_{yy})t} + u_y^2 e^{-(D_{xx}+D_{zz})t} + u_z^2 e^{-(D_{xx}+D_{yy})t} \right\}. \quad (3.6)$$

Having determined $P_Z(t)$, one may also evaluate from Eq. (3.6) other dielectric characteristics such as the complex susceptibility $\chi(\omega)$:

$$\chi(\omega) = \frac{\mu^2 N_0}{3kT} \left[\frac{u_x^2}{1 + i\omega/(D_{yy} + D_{zz})} + \frac{u_y^2}{1 + i\omega/(D_{xx} + D_{zz})} + \frac{u_z^2}{1 + i\omega/(D_{xx} + D_{yy})} \right], \quad (3.7)$$

which is the result of Perrin [12]. We remark that the quantum theory of a rigid asymmetric rotor (which was the basis of the previous theoretical approaches [13,17-19, 31,37]) has not been used here in order to derive Eq. (3.6).

4. Response in superimposed ac and strong dc bias fields: perturbation solution

For the purpose of illustration, we also calculate the dielectric response for rigid rodlike molecules in superimposed external ac and strong dc bias electric fields. As far as symmetric top molecules with the dipole moment μ directed along the axis of symmetry are concerned, this problem was solved by Coffey and Paranjape [22]. However, these results are not applicable to asymmetric top molecules. In what follows, let us suppose, for simplicity, that the diffusion tensor $\hat{D}$ has only two distinct components $D_{xx}=D_{yy}=D_{\perp}$ and $D_{zz}=D_{\parallel}$. This approximation is reasonable for rodlike molecules, where $D_{xx} \approx D_{yy}$, so that $D_{\parallel}$ and $D_{\perp}$ are the rotational diffusion coefficients about the long and short axes of the molecule, respectively. Thus,

$$\tau_D = (2D_{\perp})^{-1}, \quad \Delta = (D_{\parallel}/D_{\perp} - 1)/2, \quad \text{and} \quad \Xi = 0.$$

Furthermore, let us suppose that the molecules are subjected to superimposed external electric ac $\mathbf{E}_1(t)$ and strong dc bias $\mathbf{E}_0$ fields (both directed along the Z axis) and consider an ensemble of rigid *nonpolarisable* polar molecules, where the dipole vector μ is oriented at an angle Θ to the direction of the long axis of the molecule. Due to the cylindrical symmetry about the Z-axis, only the moments $\langle D_{n,m}^j \rangle(t)$ with $n=0$ are required in the calculation of $P_Z(t)$, so that from a mathematical viewpoint, Eq. (2.28) becomes a recurrence equation, where only two indices vary. Here, the polarisability effects are ignored (equations, which take into account these effects, are given in [21]). Without loss of generality, the molecular coordinate system for a rodlike molecule can always be chosen so that $u_y=0$, whence $u_x=\sin \Theta$, $u_z=\cos \Theta$ in Eq. (2.31). The potential energy of the molecule is then

$$V/(kT) = \sum_{Q=-1}^1 v_{1,0,Q} D_{0,Q}^1, \quad (4.1)$$

where $v_{1,0,0} = -\cos \Theta [\xi(t) + \xi_0]$, $v_{1,0,\pm 1} = \pm \sin \Theta [\xi(t) + \xi_0] / \sqrt{2}$, $\xi_0 = \mu E_0 / (kT)$, and $\xi(t) = \mu E(t) / (kT)$, so that Eq. (2.28) yields for $n = 0$

$$\tau_D \frac{d}{dt} \langle D'_{0,m} \rangle = -(\Delta m^2 + j(j+1)/2) \langle D'_{0,m} \rangle - \frac{1}{4} \sum_{Q=-1}^1 \sum_{J=|j-1|}^{j+1} v_{1,0,Q} C_{j,0,1,0}^{J,0} C_{j,m,1,Q}^{J,m+Q} [j(j+1) + 2 - J(J+1) - 4\Delta m Q] \langle D'_{0,m+Q} \rangle, \quad (4.2)$$

Insofar as the values of the field parameters ξ_0 and ξ are very small ($\ll 1$) for the majority of polar molecules even at field strengths $\sim 10^7$ V/m, one may apply perturbation theory in order to calculate the nonlinear response. Here, we shall restrict ourselves to the ac response nonlinear in the dc bias field ξ_0 (up to third order) and linear in the ac field $\xi_1 e^{i\omega t}$ (higher-order terms may be calculated in like manner). As shown in Ref. [21], one can obtain from Eqs. (2.30) and (4.2) the electric polarisation and nonlinear dielectric increment $\delta \epsilon = \epsilon_{nonlin}(\omega, \xi_0) - \epsilon_{lin}(\omega)$, i.e., the difference between the nonlinear dielectric permittivity $\epsilon_{nonlin}(\omega, \xi_0)$ and the linear permittivity $\epsilon_{lin}(\omega) = \epsilon_{nonlin}(\omega, 0)$. The increment $\delta \epsilon$ is given by

$$\delta \epsilon = \delta \epsilon' + i \delta \epsilon'' = A(\epsilon_s, \epsilon_\infty) F(\omega', \xi_0), \quad (4.3)$$

where [21]

$$\begin{aligned} F(\omega', \xi_0) = & -\frac{\xi_0^2}{30} \left\{ \frac{\cos^2 \Theta}{1+i\omega'} \left[\frac{2}{3} - \frac{2(1+\Delta)+i\omega'}{(3+i\omega')(1+\Delta+i\omega')} \right] \right. \\ & + \frac{\sin^2 \Theta}{3+\Delta+i\omega'} \left(3+\Delta + \frac{2(1+\Delta)(3+\Delta)+(6+5\Delta)i\omega'}{2(1+i\omega')(1+\Delta+i\omega')} \right) + \frac{\cos^2 \Theta}{3+i\omega'} \left(3 + \frac{3(1+\Delta)+(3+\Delta)i\omega'}{(1+i\omega')(1+\Delta+i\omega')} \right) \Bigg] \\ & + \frac{\sin^2 \Theta}{2(1+\Delta+i\omega')} \left[\frac{(1-2\Delta)(6+i\omega')}{3(3+i\omega')} + \cos^2 \Theta \left(\frac{3(1+\Delta)}{(3+\Delta+i\omega')(1+\Delta+i\omega')} + \frac{2(2\Delta-1)}{(1+i\omega')(3+i\omega')} \right) \right. \\ & - \frac{(1-2\Delta)(6+i\omega')}{(3+i\omega')} + \frac{3+2\Delta}{(1+i\omega')(3+\Delta+i\omega')} + \frac{2(6+2\Delta+i\omega')}{(3+\Delta+i\omega')} \Bigg] + \sin^2 \Theta \left(\frac{(1+\Delta)(1-2\Delta)}{(1+\Delta+i\omega')(3+i\omega')} \right. \\ & \left. \left. + \frac{(1+\Delta)(1+2\Delta)(3+4\Delta)}{(1+\Delta+i\omega')(3+4\Delta+i\omega')} + \frac{(1+2\Delta)(6+8\Delta+i\omega')}{(3+4\Delta+i\omega')} \right) \right] \Bigg\} \quad (4.4) \end{aligned}$$

and $\omega' = \omega \tau_D$. The function $A(\epsilon_s, \epsilon_\infty)$ takes into account the internal field effects; this function depends on the model of the local field used (appropriate equations for $A(\epsilon_s, \epsilon_\infty)$ are given, e.g., in Ref. [10]). For $\Theta = 0$ (symmetric top) or $\Delta = 0$ (isotropic diffusion), Eq. (4.4) reduces to the corresponding result of Coffey and Paranjape [22]:

$$F(\omega', \xi_0) \rightarrow -\xi_0^2 \frac{1+(1+i\omega')(2+i\omega'/3)}{45(1+i\omega')^2(1+i\omega'/3)}. \quad (4.5)$$

The principal difference between Eqs. (4.4) and (4.5) is that Eq. (4.4) contains the contribution of the rotation about the long molecular axis to $\delta \epsilon$.

The dielectric increment $\delta \epsilon$ of dilute solutions of mesogenic 10-TPEB molecules ($C_{10}H_{21}-\text{O}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{N}=\text{C}-\text{S}$, where $\text{O} = C_6H_4$) in benzene were measured in superimposed strong dc (1.1×10^7 V/m) and small (≈ 100 V/m) ac electric fields in Ref.

[10]. For the 10-TPEB molecule, the angle Θ is markedly different from zero, viz., $\Theta = 42^\circ \pm 2^\circ$ [10]. In the fitting, the experimental value of the relaxation time $\tau_D = 10.09, 8.57, \text{ and } 7.78 \cdot 10^{-10} \text{ s}$ at 6, 15 and 25 °C, respectively, [10] have been used so that the only adjustable parameter was Δ . The least mean squares fitting procedure yields $\Delta \approx 3.85$. The comparison of the real and imaginary parts of the experimental and theoretical $\delta\epsilon$ and of the nonlinear Cole-Cole plot for a dilute solution of 10-TPEB molecules in benzene at 6, 15 and 25 °C is shown in Fig. 2.

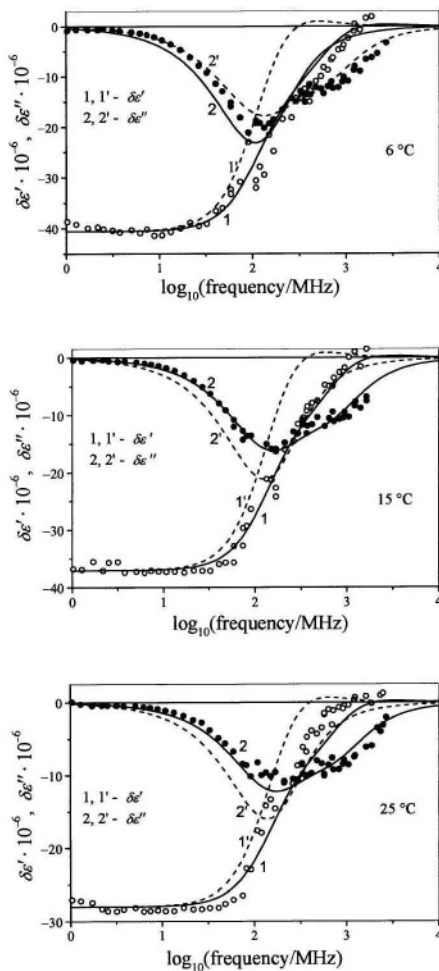


Figure 2. Nonlinear dielectric decrement $\delta\epsilon(f)$ [$f = \omega / 2\pi$] of solution of 10-TPEB molecules in benzene at 6, 15, and 25 °C Circles are the experimental data [10]; solid lines are the best fit from Eq. (4.4); dashed lines are the Coffey-Paranjape Eq. (4.5).

It appears that the theory correctly describes the shape of the observed spectra; here, five modes with different characteristic frequencies (due to molecular rotation about the long and short molecular axes) contribute to the spectra. It is of interest to compare the value of Δ so obtained with that estimated in the hydrodynamic limit when the Brownian particle is much larger than the fluid molecules and exhibits no slip with the fluid as it rotates; here the diffusion tensor depends only on the particle shape [31]. For long rods ($L \gg R$, where L and R are the half-length and radius of a rod), the hydrodynamic theory yields [38]

$$\Delta = \frac{x^2}{4 \ln(2x)} - \frac{1}{2}. \quad (4.6)$$

Here $x = L/R$ and equations for $D_{\parallel}$ and $D_{\perp}$ from Ref. [38] have been used in order to obtain Eq. (4.6). The value $\Delta \approx 3.85$ corresponds to a shape parameter $x \approx 6.7$ in Eq. (4.6) and reasonably characterises the geometrical structure of the 10-TPEB molecule [10].

Our approach can also be used for the evaluation of the dynamic Kerr effect, where the quantities of interest are $\langle D_{0,m}^2 \rangle(t)$ [17]. Moreover, it can be applied (with small modifications) to the calculation of the *nonlinear magnetic* response of ferrofluids [39]. Thus, the method we have developed provides a useful basis for future studies of the nonlinear response of various physical systems comprising Brownian asymmetric top particles.

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6. References

1. Furukawa, T., Tada, M., Nakajima, K., and Seo, I. (1988) Nonlinear Dielectric Relaxation in a Vinyliden Cyanide/Vinyl Acetate Copolymer, *Jpn. J. Appl. Phys. Part I* **27**, 200-204.
2. Kimura, Y. and Hayakawa, R. (1992) Nonlinear Dielectric Relaxation Spectra Calculated with a Free Rotation model of the Dipole Moment, *Jpn. J. Appl. Phys. Part I*, **31**, 3387-3391.
3. Furukawa, T. and Matsumoto, K. (1992) Nonlinear Dielectric Relaxation Spectra of Polyvinyl Acetate, *Jpn. J. Appl. Phys. Part I*, **31**, 840-845.
4. Kimura, Y., Hara, S., and Hayakawa, R. (2000) Nonlinear Dielectric Relaxation Spectroscopy of Ferroelectric Liquid Crystals, *Phys. Rev. E* **62**, R5907.
5. Glazounov, A. E. and Tagantsev, A. K. (2000) Phenomenological Model of Dynamic Nonlinear Response of Relaxor Ferroelectrics, *Phys. Rev. Lett.* **85**, 2192-2195.
6. Kimura, Y., Hayakawa, R., Okabe, N., and Suzuki, Y. (1996) Nonlinear Dielectric Relaxation Spectroscopy of the Antiferroelectric Liquid Crystal 4-(1-Trifluoromethyl-Pheptyloxycarbonyl) Phenyl 4-Octyloxybiphenyl-4-Carboxylate, *Phys. Rev. E* **53**, 6080-6084.
7. De Smet, K., Hellemans, L., Rouleau, J. F., Courteau, R., and Bose, T. K., Rotational Relaxation of Rigid Dipolar Molecules in Nonlinear Dielectric Spectra, *Phys. Rev. E* **57**, 1384 (1998).
8. Jadżyn, J., Kędziora, P., and Hellemans, L. (1999) Frequency Dependence of the Nonlinear Dielectric Effect in Diluted Dipolar Solutions, *Phys. Lett. A* **251**, 49-53.
9. Kędziora, P., Jadżyn, J., De Smet, K., and Hellemans, L. (1998) Nonlinear Dielectric Relaxation in Non-Interacting Dipolar Systems, *Chem. Phys. Lett.* **289**, 541-545.
10. J. Jadżyn, J., Kędziora, P., Hellemans, L., and De Smet, K. (1999) Relaxation of the Langevin Saturation in Dilute Solution of Mesogenic 10-TPEB molecules, *Chem. Phys. Lett.* **302**, 337-340.

11. Debye, P. (1929) *Polar Molecules*, Chemical Catalog, New York.
12. Perrin, F. (1934) Mouvement Brownien d'un Ellipsoïde (I). Dispersion Diélectrique pour les Molécules Ellipsoïdales, *J. Phys. Radium*, **5**, 497-511.
13. Favro, D. L. (1960) Theory of Rotational Brownian Motion of a Free Rigid Body, *Phys. Rev.* **119**, 53-62.
14. McConnell, J. (1981) *Rotational Brownian Motion and Dielectric Theory*, Academic, New York.
15. Watanabe, H. and Morita, A. (1984) Kerr Effect Relaxation in High Electric Fields, *Adv. Chem. Phys.* **56**, 255-409.
16. Déjardin, J. L., Kalmykov, Yu. P., and Déjardin, P. M. (2001) Birefringence and Dielectric Relaxation in Strong Electric Fields, *Adv. Chem. Phys.* **117**, 275-481.
17. Wegener, W. A., Dowben, R. M., and Koester, V. J. (1979) Time-Dependent Birefringence, Linear Dichroism, and Optical Rotation Resulting from Rigid Body Rotational Diffusion, *J. Chem. Phys.* **70**, 622-632.
18. Wegener, W. A. (1986) Transient Electric Birefringence of Dilute Rigid Body Suspensions at Low Field Strength, *J. Chem. Phys.* **84**, 5989-6004.
19. Wegener, W. A. (1986) Sinusoidale Electric Birefringence of Dilute Rigid Body Suspensions at Low Field Strength, *J. Chem. Phys.* **84**, 6005-6012.
20. Hosokawa, K., Shimomura, T., Furusawa, H., Kimura, Y., Ito, K., and Hayakawa, R. (1999) Two-Dimensional Spectroscopy of Electric Birefringence Relaxation in Frequency Domain: Measurement Method for Second-Order Nonlinear After-Effect Function, *J. Chem. Phys.* **110**, 4101-4108.
21. Kalmykov, Yu. P. (2002) Rotational Brownian Motion and Nonlinear Dielectric Relaxation of Asymmetric Top Molecules in Strong Electric Fields, *Phys. Rev. E*, **65**, 021101-11.
22. Coffey, W. T. and Paranjape, B. V. (1978) Dielectric and Kerr Effect Relaxation in Alternating Electric Fields, *Proc. R. Ir. Acad. Sec. A. Math. Phys. Sci.* **78**, 17-25.
23. Coffey, W. T., Kalmykov, Yu. P., and Waldron, J. T. (2003) *The Langevin Equation with Applications in Physics, Chemistry and Electrical Engineering*, World Scientific, Singapore, 2nd edition.
24. Déjardin, J. L., Déjardin, P. M., Kalmykov, Yu. P., and Titov, S. V. (1999) Transient Nonlinear Dielectric Relaxation and Dynamic Kerr Effect from Sudden Changes of a Strong dc Electric Field: Polar and Polarizable Molecules, *Phys. Rev. E* **60**, 1475.
25. Alexiewicz, W. (2000) Solution of the Smoluchowski Equation for Rotational Diffusion of Rigid Dipolar and Symmetric-Top Molecules in Dilute Solvents, *Acta Phys. Pol. B* **31**, 1051-1062.
26. Rose, M. E. (1957) *Elementary Theory of Angular Momentum*, Wiley, New York.
27. Varshalovich, D. A., Moskalev, A. N., and Khersonskii, V. K. (1998) *Quantum Theory of Angular Momentum*, World Scientific, Singapore.
28. Brenner, H. and Condiff, D. W. (1972), Transport Mechanics in Systems of Orientable Particles III. Arbitrary Particles, *J. Colloid Interface Sci.* **41**, 228-274.
29. Stratonovich, R. L. (1968) *Conditional Markov Processes and Their Application to the Theory of Optimal Control*, Elsevier, New York.
30. Lee, D. H. and McClung, R. E. D. (1987) The Fokker-Planck-Langevin Model for Rotational Brownian Motion IV. Asymmetric Top Molecules, *Chem. Phys.* **112**, 23-41.
31. Huntress, W. T. (1970) The Study of Anisotropic Rotation of Molecules in Liquids by NMR Quadrupolar Relaxation, *Adv. Magn. Reson.* **4**, 1-37.
32. Rosato, V. and Williams, G. (1981) Dynamic Kerr-Effect and Dielectric Relaxation of Polarizable dipolar Molecules, *J. Chem. Soc., Faraday Trans. 2*, **77**, 1767-1778.
33. Kalmykov, Yu. P. and Titov, S. V. (1998) The Complex Magnetic Susceptibility of Uniaxial Superparamagnetic particles in a High Constant Magnetic Field, *Fiz. Tverd. Tela (St. Petersburg)* **40**, 1642-1649 [(1998) *Phys. Solid State*, **40**, 1492-1499].
34. Kalmykov, Yu. P., Titov, S. V., and Coffey, W. T. (1998) Longitudinal Complex Magnetic Susceptibility and Relaxation Time of Superparamagnetic Particles with Cubic Magnetic Anisotropy, *Phys. Rev. B* **58**, 3267-3276.
35. Kalmykov, Yu. P. and Titov, S. V. (1999) Longitudinal Dynamic Susceptibility of Superparamagnetic Particles with Cubic Anisotropy, *Zh. Eksp. Teor. Fiz.* **115**, 101-114 [(1999) *JETP*, **88**, 58-65].
36. Nordio, P. L., Rigatti, G., and Segre, U. (1973) Dielectric Relaxation Theory in Nematic Liquids, **25**, 129-136.
37. Freed, J. H. (1964) Anisotropic Rotational Diffusion and Electron Spin Resonance Linewidths, *J. Chem. Phys.* **41**, 2077-2083.
38. Wegener, W. A. (1981) Diffusion Coefficients for Rigid Macromolecules with Irregular Shapes that Allow Rotational-Translational Coupling, *Biopolymers* **20**, 303-326.
39. Scherer, C. and Matuttis, H. G. (2001) Rotational Dynamics of Magnetic Particles in Suspensions, *Phys. Rev. E* **63**, 011504-7.

EXPERIMENTAL SOLUTIONS FOR NONLINEAR DIELECTRIC STUDIES IN COMPLEX LIQUIDS

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Abstract. Experimental solutions for nonlinear dielectric measurements in liquids and in soft matter systems are briefly discussed. Particular attention is paid the dual-field and aperiodic (pulse) high voltage excitation method, based on the author's experience.

In liquids and soft matter systems under strong electric field dielectric permittivity is described by [1-3]:

$$\epsilon^E = \epsilon + \epsilon_3 E^2 + \dots \quad (1)$$

where ϵ^E, ϵ are dielectric permittivities under strong electric field (E) and for $E \rightarrow 0$, respectively.

The measure of the “nonlinearity” is called the nonlinear dielectric effect (*NDE*) [1-3]:

$$\epsilon_{NDE} = \epsilon_3 = (\epsilon^E - \epsilon) / E^2 \quad (2)$$

where ϵ_{NDE} is the experimental measure of *NDE*.

The higher order terms, $\sim E^4, \dots$ were noted only for some macromolecular liquids [1] and in the immediate vicinity of the critical consolute temperature, for $T - T_C < 0.02K$ [4]. Experimental values of $\Delta\epsilon^E$ are very small [5]. Hence, measurements of *NDE* demand special experimental set-ups, in practice custom-built. There are two general principles for *NDE* measurements [1-24]. For the first one, a single strong electric field is applied [6-12]. The field usually follows the sine-wave pattern.

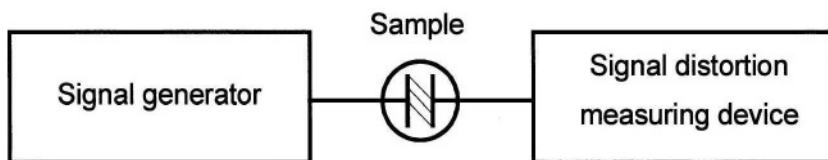


Figure 1. The single-field principle of *NDE* measurements

In this case the detection of *NDE* is associated charge-related distortions of the output signal. The single-field principle of *NDE* measurements in liquids/soft matter is shown Fig. 1. The nonlinear dielectric response of the sample can be measured using broad-band [6-11] or selective [11, 12] techniques. For the broad-band technique the application of an arbitrary waveform excitation signal is possible. On the other hand, advantage of selective techniques is a better signal to noise performance. In practice, regardless of the used registration technique the spectrum of the excitation signal should be perfectly well known and included into the output signal analysis. For technical reasons product *frequency* $\times$ *amplitude* of excitation signal have to be limited. Hence, the application of single-field *NDE* measurement techniques is limited to samples characterized large and very large values of $\Delta\epsilon^E$. This suggests high intensities of the electric field, often obtained due to a small gap of a measurement capacitor ($d=10\mu m-100\mu m$) [6-12]. It seems that for single-field *NDE* measurements a possible influence of such parasitic factors as surface related effects, electrostriction and ion-related heating should be carefully should be considered. To the best of the author knowledge the application of the single-field *NDE* techniques is restricted to ferroelectric liquid crystals or polymer films of extremely small ionic conductivity [6-12]. The second principle for *NDE* measurement is presented in Fig. 2. In this case the application of a strong, external electric field induces anisotropy within a sample and shifts its capacitance by ΔC^E , in a “nonlinear” way. In order to detect this shift a capacitance meter introduces a second, weak, measuring field. Hence this way of *NDE* studies may be called the “dual-field method” [13-24].

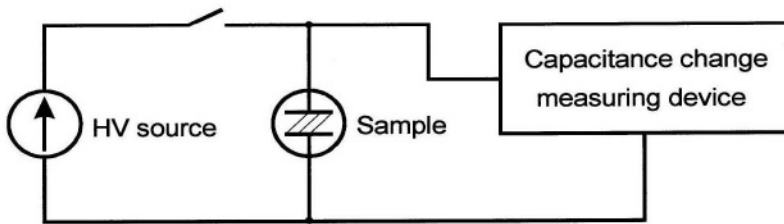


Figure 2. The dual-field principle of *NDE* measurements.

In *NDE* studies the question of reaching an appropriate signal/noise ratio is always a basic problem. For dual-field methods a resonant circuit in the input stage, due to its selective nature, solves this problem. A difficult issue which consequently appears is the *separation of the capacitance change measuring device from the influence of high voltage source* [1, 5]. This paper is focused on the implementation of dual-field *NDE* measurement methods with resonant circuit in the input stage [13-24]. The application of a strong electric field in the form of a short DC or AC pulse makes the reduction of the influence of heating of a sample due to the residual ionic conductivity possible [1, 5]. The resulted changes of the electric capacitance ΔC^E , and consequently $\Delta\epsilon^E$, are reflected in the shift of the measurement frequency: $\Delta f^E = f(E) - f(E=0)$. In our

experimental practice the duration of pulses of the strong electric field (Δt_D) can be changed from tens of second to $100\mu s$ [5, 13-22]. The lower limit of the pulse length enables tests in liquid samples of relatively high electric conductivity, up to $10\mu Sm^{-1}$. The upper limit is important for very viscous liquids, as for instance epoxy-resins, to reach the stationary conditions at $\Delta t_D \gg \tau$, where τ is the relaxation time of mesoscale processes.

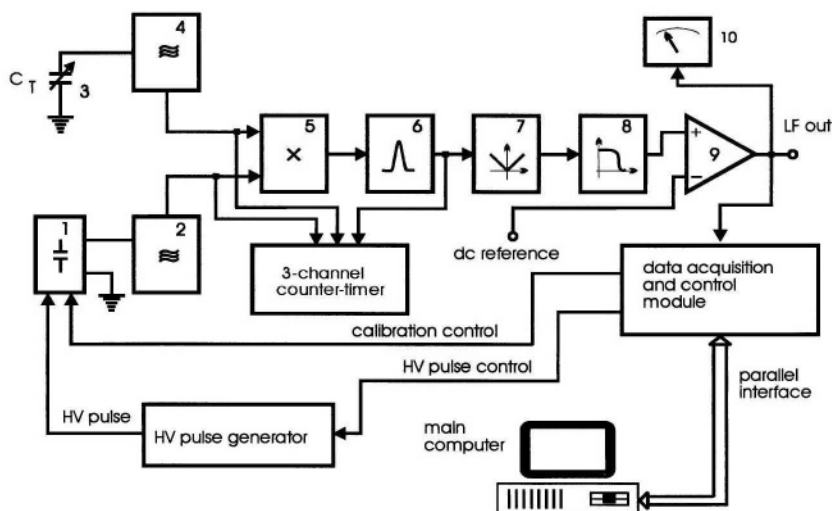


Figure 3. The dual-field, aperiodic (AC/DC pulse) HV excitation NDE set-up with superheterodyne based frequency demodulator. 1- The input stage (see fig.4) 2- Main generator 3-Tuning capacitor 4- Reference frequency generator 5- Mixer 6- Band-pass filter 7- Rectifier 8- Low-pass filter 9- Amplifier 10- Tuning indicator

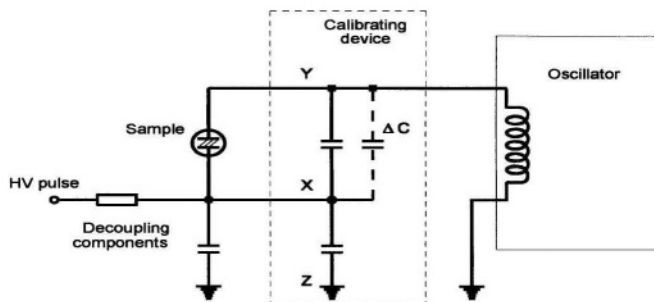


Figure 4. The input stage

The dual-field *NDE* set-ups can be used for liquid testing liquid and soft matter samples characterized by very small, small, medium and large *NDE* values, i.e. from $10^{-19} \text{ m}^2 \text{ V}^{-2}$ to $10^{-14} \text{ m}^2 \text{ V}^{-2}$ [2-5, 13-21]. In studies using these apparatuses the strong electric field induce the shift of capacitance by $\Delta C^E \approx 1 \div 10 \text{ fF}$ for a typical capacitance of the measurement capacitor with a sample $C \approx 100 \text{ pF}$ /. The value of ΔC^E should be detected with 2 – 3 digits resolution. For the majority of liquids the strong electric field is applied for $\Delta t_D = 1 \text{ ms}$. The detection of ΔC^E associated with such extreme conditions is possible by means of the superheterodyne idea, until recently used in the lab of the authors The scheme of the apparatus applied in our lab is presented in Fig. 3 [5]. The Input stage is shown in Fig. 4. There are two identical generator connected to a mixer. Its working frequency is equal to the difference of frequencies of generators. Hence of ΔC^E in the generator with a tested sample induces changes in the intermediate frequency. To avoid the influence of the amplitude modulation generators should overdrive the mixer. Next the signal passes the band-pass filter where the frequency modulation is converted into the amplitude modulation. After rectification the signal passes the eight order Butterworth low-pass filter to obtain the envelope of the signal. The signal can be now registered via digitizer. In practice superheterodyne based *NDE* apparatus exhibited few permanent

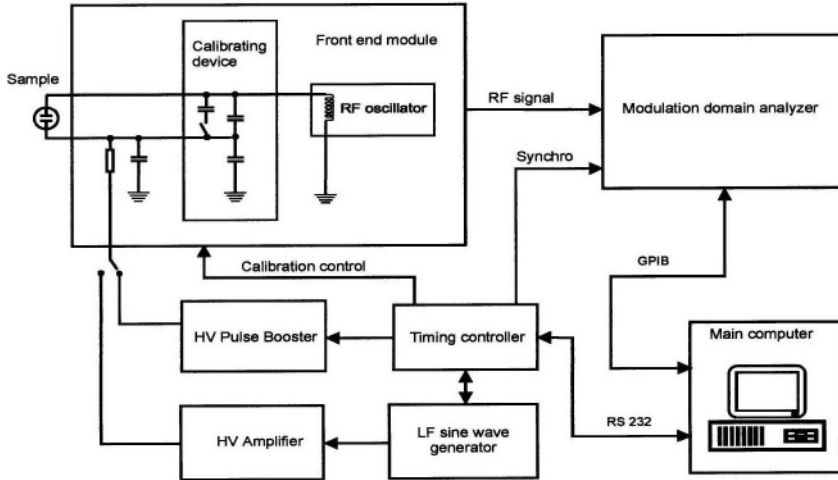


Figure 5. The dual-field, single-generator, aperiodic (pulse) HV excitation and MDA based nonlinear dielectric spectrometer.

problems. The most important is the noise induced by external disturbances and by the non-perfect grounding of parts of the apparatus. These problems are almost absent for the next design of the *NDE* apparatus, we apply at present (Fig. 5). It applies only a

single generator. The strong electric field induced changes of frequency $f(E) = f(E \rightarrow 0) + \Delta f^E$ which are registered using modulation domain analyzer (MDA) HP 53200, directly coupled to the generator with the measurement capacitor. MDA enables scanning and digitizing frequency versus time dependences. Hence, at the output one may obtain time-domain data $\Delta \epsilon^E(t)$. Our design of the generator enables studies from 26 kHz up to 15 MHz for the weak measuring field [15]. The apparatus presented in Fig. 5, allows also the application of a strong electric field in the form of a sine-wave train, as shown in Fig. 6. This opens a new, yet unexplored, way of *NDE* related insight into mesoscale properties of complex liquids. This way of the action of a strong electric field in this form enables test in liquid of relatively high electric conductivity. Now we may detect the “stationary” *NDE* value associated with the DC or sine-wave train of a given frequency. In both cases the analysis of the decay after switching of the strong electric field is possible. Fig. 6 presents the response to the signal in the form of a sine-wave train of a given length Δt_D in the isotropic phase of *n*-pentylcyanobiphenyl (5CB), 1 K above the isotropic - nematic transition.



Figure 6. The dual-field, single generator MDA based *NDE* apparatus in the Katowice lab. At the top the MDA analyzer is placed, below they are HV AC/DC pulse unit ($U_{HV} = 20V - 1500V$, $\Delta t_D = 100\mu s - 1000s$) and the HV amplifier ($U_{peak-peak} < 1000V$, $\Delta t_D \rightarrow arbitrary$ and $f_{HV} = DC \rightarrow 4kHz$). Below they are multimeter Keitley 195A for temperature measurement and the sine-wave frequency generator HP. At the main table they are the temperature stabilization unit (left side). Next they are the *NDE* measurement generator and the controller). The screen present the user-friendly software and the response of the isotropic 5CB sample to the action of a sine-wave train of a strong electric field.

The AC and DC component of the *NDE* as well as time-domain decay after switching-off the sign-wave pulse of a strong electric field is visible. In *NDE* studies a small solid (dust) or heterophase contamination may induce a strong “false” contribution. For the dual-field pulse *NDE* measurements methods this parasitic factor is immediately visible as a non-physical deformation of the output signal. Too large electric conductivity of a tested sample is clearly manifested by different values of the baseline before and after switching-off a strong electric field. Hence, these significant parasitic factors can be easily avoided in this case.

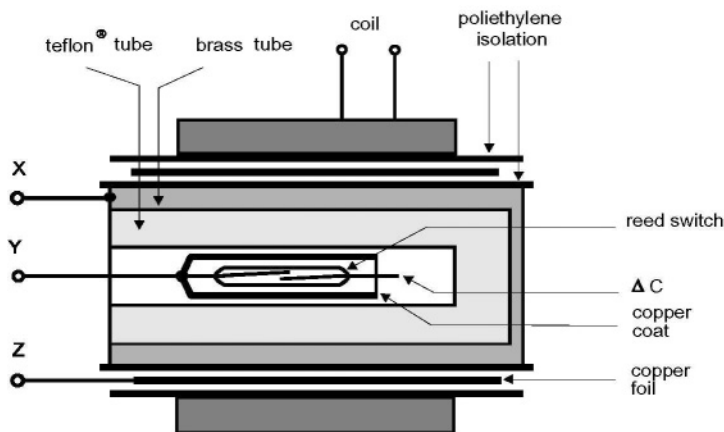


Figure 7. The calibration facility for *NDE* measurements applied in Katowice lab.

In *NDE* studies a basic problem is the calibration, i.e. calculation of $\Delta\epsilon^E$ basing on obtained in experiment values of Δf^E or ΔC^E . The calibration process based on a reference liquid seems to be not reliable for *NDE* studies. There is no commonly accepted reference liquid for *NDE*. In our studies we apply a calibration unit shown in Fig. 7. It based on a reed delay switch mounted in a copper jacket. One of its contacts sticks out about 1 mm outside the copper coat. The switching on/off results in the change of the capacitance between the stick and the copper by $\Delta C^{cal} = 26 \text{ fF}$. It was measured using Solartron 1260A impedance analyzer. The total “parasitic” electric capacitance introduced by the calibration unit is equal only 3pF. It is noteworthy that the calibration unit is attached permanently to the resonant circuit, also when the strong electric field is switch on. The value of the response of a sample induced by the strong electric field is compared with the response of the resonant circuit related to ΔC^{cal} , to obtain the value of ΔC^E . Measurement cells applied for *NDE* studies have a form of flat parallel or axial-cylindrical capacitor liquids. In our case we apply a flat-parallel capacitor with a diameter 20 mm and gaps 0.2 mm – 1 mm made from Invar [13-20]. Its capacitance with a given sample ranged from 20 pF to 130 pF. Changes of capacitance due to the action of a strong electric field were equal to

$\Delta C^E = 0.1 \text{ fF} - 10 \text{ fF}$ and are registered with 3-digit resolution. For the vast majority of tested samples (2-5, 13-21) the strong electric field was applied in the form of DC pulses with duration $\Delta t_D = 0.5 \text{ ms} - 10 \text{ ms}$. This factor and the careful cleaning of samples enabled necessary reduction of the heating effect. Within the capacitor tested samples were in contact only with Invar, quartz and Teflon. For linear and nonlinear dielectric studies under pressure, at present up to 700 MPa, we designed a special, small volume capacitor: only 0.5 cm^3 of a liquid sample is needed. The pressure is transmitted to the sample via deformation of specially prepared Teflon film [14-17]. In Fig. 3 and 4 dual-filed *NDE* set-ups used aperiodic strong electric field excitation. In the mid seventies another type of the dual field *NDE* apparatus was constructed (Fig. 8) [23], in which the resonant circuit is not an essential part of the radio-frequency (HF) generator, as in the case of set-ups presented in Figs. 3 and 4.

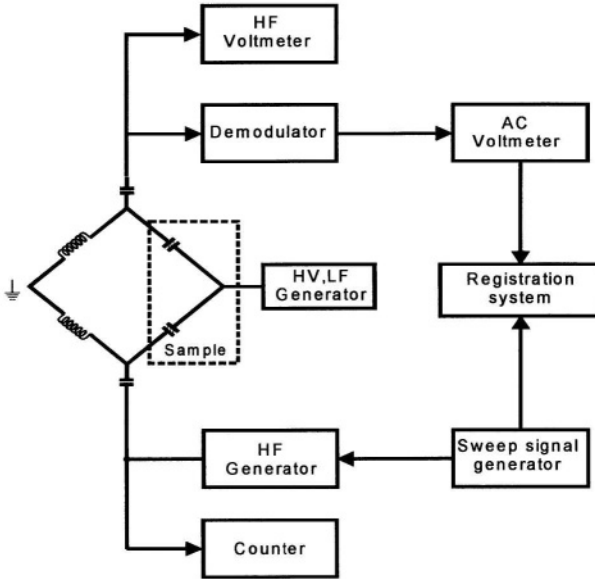


Figure 8. The dual-field and continuous, period HV excitation *NDE* apparatus [22].

In Fig. 8, the independent, external HF generator is used for scanning of the resonant curve under sine-wave, high voltage electric field from HV, LF generator. The significant advantage of this method is the fact that it gives also for the nonlinear dielectric absorption $\Delta \epsilon^{E//}$. For this method of *NDE* measurements the periodic, sign-wave strong electric field excitation, with $f_{HV} \approx 85 \text{ Hz}$ in refs. [23, 24], is applied few minutes. Usually, the strong electric field is applied for few minutes. Its intensity has to be higher than for dual-field, pulse methods (Figs. 3, 4), to obtain the appropriate signal to noise ratio. This may cause serious problems for liquids even with a medium-range electric conductivity. It is noteworthy that for the set up presented in Fig. 8 the HV is

introduced to the sample using a double, symmetric measurement capacitor [23, 24]. In Fig. 3 and 4 the application of a strong electric field without an influence on the system was solved by introducing a “block” capacitor of high capacitance, in practice $10nF$. This capacitor should of good quality, silver-mica type is recommended. In practice the application of a double, symmetric measurement capacitor is less convenient and associated with much larger amount of a liquid sample. In the opinion of the authors the unequivocal calibration of experimental data for this method also remains an open question.

In the last two decades broad-band dielectric spectroscopy (*BDS*) appeared to be one of the most powerful tools for studying molecular interactions and transport and relaxation processes in complex liquids and soft matter systems [25]. Probably, these can be associated with the novel class of spectrometers enabling almost continuous scanning of frequencies over tens of decades. It seems that *BDS* reach its maturity, both regarding technical solutions and applications. Hence, a question may arise for a possible successor of *BDS*, i.e. the “linear” dielectric spectroscopy. It seems that nonlinear dielectric spectroscopy, can play this role. One of novel features of *NDE*, in comparison with *BDS*, is the direct sensitivity to mesoscale inhomogeneities, basically important for any complex liquids and soft matter system.

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References

1. Chełkowski A. (1980, 1990) Dielectric Physics, PWN-Elsevier, Warsaw.
2. Chrapeć, Rzoska S. J., and Ziolo J. (1988) Properties of the nonlinear dielectric effect in critical nitrobenzene in n-alkane solutions in a broad range of temperatures, *Chem. Phys.* 122, 471-478.
3. Rzoska S. J. (1993) Kerr effect and nonlinear dielectric effect on approaching the critical consolute point, *Phys. Rev.* E48, 1136-1143.
4. Chrapeć J. and Rzoska S. J. (1989) Nonlinear dielectric effect investigation in the immediate vicinity of the critical point, *Phys. Lett.* A139 343-346.
5. Górny M., Ziolo J. and Rzoska S. J. (1996) A new application of nonlinear dielectric effect for studying relaxation processes in liquids, *Rev. Sci. Instrum.* 67, 4290-4293.
6. Furukawa T. (2004) Nonlinear dielectric and related studies for polymeric systems, *this volume*.
7. Furukawa T., Tada, M., Nakajima K., and Seo, I. (1988) Nonlinear dielectric relaxations in a vinylidene cyanide/vinyl acetate copolymer, *Jpn. J. Appl. Phys.* 27 200-204.
8. Kimura Y (2004) Frequency-domain nonlinear dielectric relaxation spectroscopy: Its application to ferroelectric liquid crystals, *this volume*
9. Kimura, Y., Hara, S. and Hayakawa, R. (2000) Nonlinear dielectric relaxation spectroscopy of ferroelectric liquid crystals, *Phys. Rev.*, **E62**, R5907-5910.
10. Orihara H., Fajar A., Bourny V. (2002) Observation of the soft-mode condensation in the Sm-A-Sm-C*(alpha) phase transition by nonlinear dielectric spectroscopy. *Phys. Rev.* **E65**, 040701.
11. Ishibashi Y., Nonlinear Dielectric Spectroscopy (1998) *J. Korean Phys. Soc.*, **32** 407-410.
12. Prasad S.K., G. G. Nair and Rao S. (1999) Non-linear dielectric response of ferroelectric liquid crystals, *Liquid Crystals* **26**, 1587-1591.
13. Drozd-Rzoska A. (1999) Quasicritical behavior of dielectric permittivity in the isotropic phase of n-hexylcyanobiphenyl in a large range of temperatures and pressures, *Phys. Rev.* **E59**, 5556-5560.
14. Drozd – Rzoska A., Pawlus S., Rzoska S. J. (2001) Pretransitional behavior of dielectric permittivity on approaching a clearing point in mixture of nematogens with antagonistic configurations of dipoles, *Phys. Rev.* **E64**, 051701.

15. Drozd-Rzoska A. and Rzoska S. J. (2002) Complex relaxation in the isotropic phase of n-pentylcyanobiphenyl in linear and nonlinear dielectric studies, *Phys. Rev.* **E65**,041701.
16. Rzoska S. J., Paluch M., Pawlus S., Drozd-Rzoska A., Jadzyn J., Czupryński K. and Dąbrowski R. (2003) Complex dielectric relaxation in supercooling and superpressing liquid-crystalline ciral isopentylcyanobiphenyl, *Phys. Rev.* **E68** 031705.
17. Drozd-Rzoska A., Rzoska S.J, Górny M. and Ziolo J. (2002) On critical behavior of linear and nonlinear dielectric permittivity on approaching a critical consolute point, *IEEE TDEI* **9** 112-117.
18. Rzoska S. J., Ziolo J., Drozd-Rzoska A. (1997) Stretched-relaxation after switching-off a strong electric field in a critical solution under high pressure, *Phys. Rev.* **E56** 2578-2583.
19. Rzoska S. J. and Ziolo J. (1999) Dynamics of glassy clusters appearing by nonlinear dielectric effect studies, *Phys. Rev.*, **E59**,2460-2464.
20. Rzoska S. J., Drozd-Rzoska A., Ziolo J. (2000), Dynamics of critical fluctuations in a binary mixture of limited miscibility under strong electric field, *Phys. Rev.* **E61** 960-964.
21. Małecki J., Nowak J. (1999) Intermolecular interactions in benzene solutions of 4-heptyl-3'-cyano-biphenyl studied with non-linear dielectric effects, *J. Mol. Liq.* **81** 245-253
22. Orzechowski K, Kosmowska M. (2004). Dielectric properties of critical conducting mixtures, *this volume*.
23. Nackaerts R., de Maeyer M., Hellemans L. (1979) Field dissociation on ion-pairs in a non-polar medium, *J. Electrostatics*, **7**, 169-186.
24. Kędziora P., J. Jadzyn, de Smet K., and L. Hellemans (1999) Linear and Nonlinear dipolar relaxation of 4,4'-n-hexylcyanobiphenyl, *J. Mol. Liq.* **80**, 19-25.
25. Kremer F. A. and Schönhals A. (2003) Broadband dielectric spectroscopy, *Springer Verlag, Berlin*.

COMMENTS ON NONLINEAR DIELECTRIC EFFECT MEASUREMENTS IN LIQUIDS

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The summary of the early years of *NDE* studies, 7 – 8 decades ago, can be found in the monograph “*Dielectric Physics*” by August Chelkowski (PWN-Elsevier, Warsaw, 1980). In the fifties *NDE* studies were introduced in **Poznań** (Poland) by Arkadiusz Piekara. In **Poznań** *NDE* tests focused on intermolecular interactions and intramolecular rotations. Results of this period of *NDE* studies are concluded in the book mentioned above. The mentioned *NDE* measurements were conducted for a single frequency of a weak measuring field, mainly for low - molecular liquids. In such systems the strong electric field induces the strong electric field related nonlinear response in the range of *femtofarads* for a measurement capacitor with a sample: $C \approx 100 \text{ pF}$. Worth recalling is the fact that the strong electric field had to be applied in the form of strong electric field pulses of few milliseconds length, to avoid heating. In the late sixties and seventies *NDE* studies were conducted also in UK [Jones P., Krupkowski G. (1974) *J. C. S. Faraday II*, **70**, 1253-1266]) using novel counter-based experimental techniques. However extreme technical problems caused that these groups were continued. Since the late seventies *NDE* studies are carried out in the Institute of Physics, Silesian University, Katowice, i.e. in the most industrial region of Poland, 370 km south of **Poznań** and Warsaw. They were introduced by Jerzy Ziolo who originated the “Katowice nonlinear dielectric spectroscopy group”. In the late seventies three main *NDE* experimental techniques were established:

1. The first one bases on two electric fields: a strong measuring (radio frequency) and a strong electric field DC pulse (length: few *milliseconds*) inducing anisotropy in the sample. It delivers values of strong electric change $\Delta\epsilon'_E$ for a given, single measurement frequency. Only recently a scan of frequencies from 20 kHz to 15 MHz appeared to be possible. It shows the ability for testing medium and low-conductivity, bulk samples with dielectric permittivity from 2 up to 60. This technique is applied mainly by groups in Poland (for references see authors papers in this volume). The sensitivity of this method enables measurement in a bulk sample, with capacitor gap 0.3 mm – 1 mm. This factor and the additional solid construction of the measurement capacitor causes that some parasitic artefacts, as for instance electrostriction effect or “false” responses from impurities (small dust particles, small gas bubbles) do not influence on result [for references see other author’s papers in this volume]
2. For the second *NDE* experimental method the strong electric field is applied in form of 85 Hz sine-wave acting on two connected in a parallel way resonant units. These units are fed from a radio-frequency weak electric field generator with

slowly swept frequency radio-frequency weak measuring field. After detection both $\Delta\epsilon'_E$ and $\Delta\epsilon''_E$ can be obtained. This method prefers liquids with particularly low electric conductivity and small dielectric permittivity. This method was developed in the lab. of L. Hellemans from Leuven (Belgium) [Hellemans L., de Maeyer M, (1982) High electric field effects and permittivity changes in non-polar liquids] *J. C. S. Faraday II* **78**, 401-416]

3. The third *NDE* measurement technique applies only one strong electric field, with frequency up to about 1 MHz. The *NDE* is calculated from small distortion ($\sim E^2$) appeared in the initially almost ideal sine-wave input signal. This method prefers samples with low electric conductivity and very large dielectric permittivity: This method is applied by Japanese groups (T. Furukawa, Sci. Univ. of Tokyo, Y. Kimura, Tokyo University): [see this volume]
4. The next method designed for biological samples and hence associated with relatively weak intensities of the field is applied by Kell et al. (Aberyswyth, UK): [see this volume]

Noteworthy are different areas of applications and limitations for the above techniques. Nowadays, it seems that a design of the user-friendly, nonlinear dielectric spectrometers start to be possible. This is associated with novel developments in electronic engineering, particularly the possibility of comprehensive applications of analogue and digital highly integrated units. Moreover, the application of solutions, originally developed for mobile telephones, as modulation-domain analyzers, seems to be particularly promising.

EFFECT OF CONSTRAINTS ON ELECTROSTRICTION

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Abstract: The effect of constraints on the measurement electromechanical coupling from polymer films is quantified. This information is essential to the application of electrostrictive materials. Theoretical analyses are shown to be in good accord with the experimental results.

1. Introduction

Electrostriction refers to the strain induced in a material by an applied electric field. It is a second-order property, occurring at twice the applied frequency with a magnitude proportional to square of the field strength. Whether one is correcting non-linear dielectric measurements for the errors arising from electrostriction, or developing devices (transducers, sensors, etc.) based on electrostrictive materials, accurate and reproducible measurements are obviously essential. In addition to trivial measurement errors, electromechanical strains can depend on various factors, such as sample processing (e.g., crystallinity, orientation, residual polarization) and the test conditions (e.g., field strength, frequency, waveform, sample configuration, clamping method). These myriad potential problems are reflected in the literature. For example, reported values of the electrostrictive coefficient for poly(vinylidene fluoride-co-trifluoroethylene), which is one of the most studied electroactive polymers, vary by more than four orders of magnitude [1].

One recognized but oft-overlooked aspect of the problem is the effect of the constraining pressure on the measured sample displacement. Constraints of some sort are always required for electromechanical measurements, if only to maintain the electrodes in contact with the sample. When measuring the longitudinal strain (thickness strain, parallel to the field), the electrodes are sputtered or vapor deposited on the sample major faces. Such electrodes severely constrain the lateral expansion of the film, reducing the apparent electrostriction. Alternatively, lateral pressure, for example in the form of dead-weighting, is brought to bear on electrodes in physical contact with the sample. This pressure serves an additional purpose, in helping to maintain flatness to avoid out-of-plane bending contributions to the measured strain.

For applications, the confining pressure is often determined by the geometry of the device. The performance is then a function both of the inherent electrostriction and the magnitude of this constraint. Thus, the electromechanical characterization of materials required knowledge of the response in the absence of constraint. Since direct measurements would be subject to error, the constraint-free response has to be calculated from experimental data. An early analysis of the effect of constraints by Gent and Lindley [2], valid for quite large aspect ratios (film thickness to width ratio, t/w) assumes incompressibility. This leads to the prediction of very large constraint effects, as the sample tries to maintain constant volume. Expressed as the ratio of the strain in the limits of high and zero pressure,

$$f = \frac{3}{4} (1 + w^2/2t^2)^{-1} \quad (1)$$

For rubber, in which Poisson's ratio, ν , is quite close to 0.5, the accuracy of the relation of Gent and Lindley has been experimentally verified [3]. Arridge [4] extended the analysis to compressible materials, with the results becoming a function of ν , as well as sample geometry. An analytical form of this solution was published recently by Yeoh et al. [5]

$$f = \left(\frac{4}{3} + \left(1 - \frac{\tanh(\alpha w/2)}{\alpha w/2} \right) \right) / \left(3(1 - 2\nu) \right)^{-1} \quad (2)$$

where

$$\alpha = \left(12(1 - 2\nu)/t^2 \right) \quad (3)$$

Finally, Furukawa and Matsumoto [6] derived an analysis valid for infinitely small aspect ratio ($w \gg t$), corresponding to a condition of maximum constraint. Their result depends only on the value of Poisson's ratio of the sample

$$f = (1 - 2\nu)(1 + \nu)/(1 - \nu) \quad (4)$$

2. Experimental

We measure electrostrictive strains using two methods. An absolute measure of strain comes from the relative change in the capacitance of an air gap, responding to the sample's change in thickness. The second method uses a commercial instrument, a MTI-1000 Fotonic Sensor, with which the displacement is determined from the intensity of light reflected from the top surface of the sample. The data must be calibrated, for example using a micrometer. The Fotonic Sensor allows measurements to be made at various locations on the film surface, in order to verify sample uniformity. In the present experiments, the sample dimensions were $w = 25.4$ mm and $t = 0.11$ mm, and Poisson's ratio, calculated from the measured shear and bulk moduli, was equal to 0.492.

3. Results

Plotted in Figure 1 is the electrostriction of a vinylidene fluoride film, measured as a function of the confining pressure (applied to the film faces, parallel to the electric field). The strain decreases by a factor of 11 in going from negligible pressure to the plateau corresponding to fully constrained. (The actual ratio of the free to totally constrained strain may be somewhat slightly larger, since we cannot measure at zero pressure due to the weight of the top electrode, nor is the constraint effect necessarily maximized.) In the table below, we compare the measured effect of the constraint to the predictions of the above analyses. The incompressibility assumption [2] strongly over-estimates the effect of the constraints. Allowing for compressibility [5], the value calculated from eq. 2 underestimated the constraint effect by roughly 50%. We can also see that for $w/t = 230$, the calculated result is equivalent to eq. 4 for an infinitely thin film.

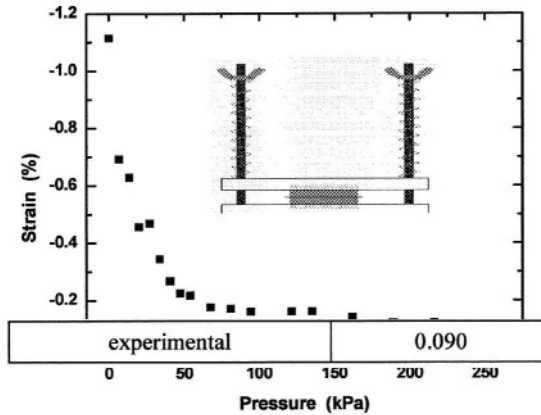


Figure 1. Electrostrictive strain in the thickness direction (parallel to a 10 MV/m, 0.01 Hz field) with various confining pressures applied to the film. The constraints were applied using calibrated springs (inset).

	F
Gent and Lindley [2]	3×10^{-5}
Yeoh et al. [5]	0.045
Furukawa and Matsumoto [6]	0.047
experimental	0.090

A possible source of the disagreement between the calculated effect of constraints and the experimental data could be artifacts from film non-uniformity. At low pressures, out-of-plane bending of the sample would give rise to displacements greater than the change in sample thickness due to electrostriction, thus increasing the apparent value of f . We believe that this contribution must be very small, since the films were cast from solution, and because the measured strain was found to be independent of the surface position at which measurements were made (using the Fotronics sensor).

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6. References

1. Elhami, K., Gauthier-Manuel, B., Manceau, J.F., Bastien, F. (1995) Electrostriction of the copolymer of vinylidene-fluoride and trifluoroethylene *J. Appl. Phys.* **77**, 3987-3990.
2. Gent, A.N., Lindley, P.B. (1959) The compression of bonded rubber blocks, *Proc. Inst. Mech. Engs. (London)* **173**, 111-117.
3. Mott, P.M., Roland, C.M. (1995) Uniaxial deformation of rubber cylinders *Rubber Chem. Technol.* **68**, 739-745.
4. Arridge, R.G.C. (1975) Stresses and displacements in lamellar composites: Part I, *J. Phys. D: Appl. Phys.* **8**, 34-52.
5. Yeoh, O.H., Pinter, G.A., Banks, H.T. (2002) *Rubber Chem. Technol.* **75**, 549-561.
6. Furukawa, T., Matsumoto, K. (1992) Nonlinear dielectric relaxation spectra of polyvinyl acetate, *Jpn. J. Appl. Phys.* **31**, 840-845.

DOUGLAS KELL COMMENTS ON ‘METHODOLOGY’ DURING THE WORKSHOP.

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My main comments on methodology pertain to the phenomena of ‘electrode polarisation’. Even when looking at the fundamental (linear response for AC, time-dependent current for step functions) it was obvious from many of the presentations that these had not been taken into account. In the very lossy (conductive) media characteristic of biology it is easy to replace the biological test sample with a purely conductive substance otherwise similar in conductivity to it. When this is done it is obvious that part of the dielectric response observed is not due to the biology but to the difficulty of forcing current across the electrode/electrolyte interfaces. In faradaic electrochemistry the nonlinear Tafel equation [1] describes the current/voltage (strictly current/overpotential) relations, and nonlinearities can be observed at very low values [2]. A summary of the nonlinear properties of different electrode materials was given in [3]. At the workshop, I pointed out in particular that there was a great need for reversible electrodes that (i) would not therefore produce harmonics when excited at a single frequency and (ii) were biocompatible – i.e. whose components or electrochemical products were non-toxic. These, when developed, would almost certainly be of value to practitioners of nonlinear dielectric spectroscopy whose interests were in purely physical or chemical problems.

References

1. Bockris, J. O. M. & Reddy, A. K. N. (1970). *Modern Electrochemistry, Vols 1 and 2* Plenum Press, New York.
2. McAdams, E. T. & Jossinet, J. (2000). Nonlinear transient response of electrode - electrolyte interfaces. *Med. Biol. Eng. Comput.* **38**, 427-432.
3. Woodward, A. M., Jones, A., Zhang, X., Rowland, J. & Kell, D. B. (1996). Rapid and non-invasive quantification of metabolic substrates in biological cell suspensions using nonlinear dielectric spectroscopy with multivariate calibration and artificial neural networks. Principles and applications. *Bioelectrochem. Bioenerg.* **40**, 99-132.

A NEW TECHNIQUE OF DIELECTRIC CHARACTERIZATION OF LIQUIDS

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Abstract. Quasi-optical dielectric resonators (QDR) with conducting endplates (CEP) are proposed and justified for measurement of complex permittivity of liquids. The structure of electromagnetic fields in the form of whispering gallery (WG) modes is calculated accurately in terms of Maxwell equations which allow one to characterize liquids from the first principles. A radially two-layered QDR has been shown to be rather convenient for microwave characterization of liquids including ones with large microwave loss. For experimental studies of a number of liquids in K_u -band, the QDR in the form of a Teflon disk sandwiched between the duralumin CEP was used. Here, water has shown an unusual property. The sign of the frequency shift indicates that properties of the resonator with water layer adjacent to the solid state dielectric become nearly the same as with metal layer. The proposed measurement technique can be used also for studies of nonlinear properties of liquids.

1. Introduction

The microwave technique of liquid media dielectric characterization does not differ in the main from the technique for characterization of solids [1,2]. However, the application of a traditional technique in case of liquids becomes often much more difficult because of evident inability of liquid substances to keep their own forms in space. The technique of microwave characterization of condensed matter allows one to determine complex permittivity $\epsilon = \epsilon' - i\epsilon''$ of the substances. Here, the resonator approach, i.e. the most sensitive one when applied to liquids with a large loss tangent, $\tan \delta = \epsilon'' / \epsilon'$, comes across serious difficulties conditioned by an abrupt decrease of quality factor Q of the resonant structures with such liquids.

The problems of electrodynamics analysis arising therewith do not allow one to determine ϵ directly. The latter may turn out to be an important problem in studies of permittivity in both weak and strong electromagnetic fields because it decreases accuracy and reliability of the analysis of experimental and theoretical results at their comparison and/or fitting. In present work, the results of the development of a new approach to liquids permittivity characterization in the microwave range are given on

the basis of quasi-optical dielectric resonator (QDR) which are named else as dielectric resonators with whispering gallery modes (WGR) (see for example [3]).

2. The resonator with conducting endplates

The interest to QDR is caused by the potential for their use in microwave technique [4], in particular for the microwave characterization of dielectrics [5, 6] and conductors, including the studies of superconductors surface resistance [7]. However, the rigorous electrodynamic analysis of the open QDR is unavailable that presents some problems in using them for measurement purposes. A consistent analysis of the field distribution in QDR with conducting endplates (CEP) makes it possible to calculate its resonance frequencies and quality factors depending on both disk dielectric and endplate conductor properties and also dimensions of dielectric disk sandwiched between CEP [8]. In fact, QDR with CEP is a quasi-optical analogue of Hakki-Coleman resonator [9], in a classic version of which the lower modes are excited.

In practice, the WG modes are not easy to use due to increase of the resonant frequency spectrum density at higher frequencies and difficulties of mode identification. However for the millimeter wave range, QDR is the ultimate choice due to its moderate dimensions at high frequencies and much higher Q -factors as compared with the other types. Experimental and theoretical studies of resonant frequency evolution of QDR with CEP under variation of endplate diameter have enabled to solve a problem of the wave identification [10].

In works [8, 10] the spectral characteristics of QDR with perfect CEP were studied. The cylindrical resonator (Figure 1) was made of one-axial crystal, the anisotropic axis of which coincides with resonator longitudinal axis and was characterized by tensor of permittivity $[\epsilon_{ij}]$ with non-zero components ϵ_z and $\epsilon_\perp$ in parallel and perpendicular directions were obtained from the dispersion equation [8, 10]:

$$a_H a_E = a, \quad (1)$$

$$\text{here} \quad a_H = X_H - X, \quad a_E = \epsilon_z X_E - X; \quad a = \left[\frac{k_0 k_z n}{q_0^2 q_H r_0^2} (1 - \epsilon_\perp) \right]^2;$$

$$k_0 = (\omega' - i\omega'')/c; \quad \omega' \text{ and } \omega'' \text{ are the real and imaginary parts of resonant frequency } (\omega'' \geq 0); \quad c \text{ is the velocity of light; } X_j = \frac{1}{q_j r_0} \frac{J_n'(q_j r_0)}{J_n(q_j r_0)};$$

$$X = \frac{1}{q_0 r_0} \frac{H_n^{(1)'}(q_0 r_0)}{H_n^{(1)}(q_0 r_0)}; \text{ the prime denotes differentiation with respect to argument.}$$

Index j stands for H and E ; $J_n(x)$ and $H_n^{(1)}(x)$ are the n -th order Bessel and Hankel cylindrical functions of the first kind; $n=0,1,2,\dots$, $k_z = m\pi/l$ (where l is the resonator height, $m = 0; 1; 2,\dots$), $q_H = \sqrt{\epsilon_\perp k_0^2 - k_z^2}$, $q_E = q_H \sqrt{\epsilon_z / \epsilon_\perp}$ and

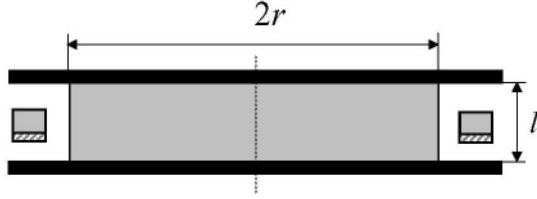


Figure 1. Cylindrical quasi-optical dielectric resonator with conducting endplates.

$q_0 = \sqrt{k_0^2 - k_z^2}$ are accordingly the azimuthal, axial and radial components of the wave vector inside and outside the resonator.

Axial components of the resonant electromagnetic fields take the form

$$\begin{aligned} E_z &= D_n G_E(r) \cos(k_z z) e^{i(n\varphi - \alpha t)}; \\ H_z &= C_n G_H(r) \sin(k_z z) e^{i(n\varphi - \alpha t)}, \end{aligned} \quad (2)$$

where $G_j = \begin{cases} J_n(q_j r), & r \leq r_0 \\ \frac{J_n(q_j r_0)}{H_n^{(1)}(q_0 r_0)} H_n^{(1)}(q_0 r), & r \geq r_0 \end{cases}$, C_n and D_n are the constants

related to each other by $a_H J_n(q_H r_0) C_n = -\sqrt{a} J_n(q_E r_0) D_n$.

Independent EH - and HE -modes can take place in the resonator. In the case of validity of condition $\left| \sqrt{a_H / a_E} \right| \gg 1$ eigen oscillations have a nature of HE -mode, otherwise they have a nature of EH -mode.

Transversal components of the field are expressed in terms of axial components (2) as

$$q^2 E_\varphi = \frac{1}{r} \frac{\partial}{\partial \varphi} \frac{\partial}{\partial z} E_z - i k_0 \frac{\partial}{\partial r} H_z; \quad q^2 E_r = \frac{\partial}{\partial r} \frac{\partial}{\partial z} E_z + i \frac{k_0}{r} \frac{\partial}{\partial \varphi} H_z \quad (3)$$

$$q^2 H_\varphi = i k_0 \varepsilon_\perp \frac{\partial}{\partial r} E_z + \frac{1}{r} \frac{\partial}{\partial \varphi} \frac{\partial}{\partial z} H_z; \quad q^2 H_r = \frac{\partial}{\partial r} \frac{\partial}{\partial z} H_z - i \frac{k_0 \varepsilon_\perp}{r} \frac{\partial}{\partial \varphi} E_z$$

where $q^2 = \begin{cases} q_H^2, & r \leq r_0 \\ q_0^2, & r \geq r_0 \end{cases}$.

3. Two-layered (along radius) QDR with CEP

Consider two-layered (along radius) QDR with CEP in which the layers are made of different one-axial single crystals with axes of anisotropy directed in parallel with the resonator longitudinal axis (Figure 2).

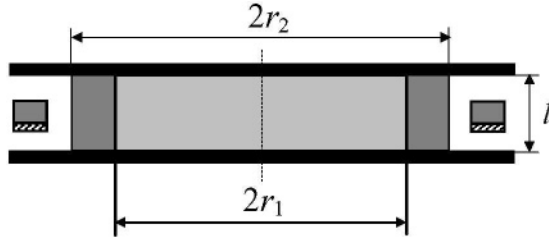


Figure 2. Two-layered quasi-optical dielectric resonator with conducting endplates.

In this case tensors of dielectric and magnetic permittivity are as follows

$$[\epsilon_{ij}] = \begin{cases} \begin{pmatrix} \epsilon_{\perp\nu} & 0 & 0 \\ 0 & \epsilon_{\perp\nu} & 0 \\ 0 & 0 & \epsilon_{z\nu} \end{pmatrix}, & \nu = 1, \quad r \leq r_1 \\ \begin{pmatrix} \epsilon_{\perp\nu} & 0 & 0 \\ 0 & \epsilon_{\perp\nu} & 0 \\ 0 & 0 & \epsilon_{z\nu} \end{pmatrix}, & \nu = 2, \quad r_1 < r \leq r_2 \\ \delta_{ij}, & \nu = 3, \quad r > r_2 \end{cases}$$

$$\mu_\nu = \begin{cases} \mu_1, & \nu = 1, \quad r \leq r_1 \\ \mu_2, & \nu = 2, \quad r_1 < r \leq r_2 \\ 1, & \nu = 3, \quad r > r_2 \end{cases}$$

where $\epsilon_{z\nu}$ and $\epsilon_{\perp\nu}$ are the components of the tensor $[\epsilon_{ij}]$ for a ν -layer in directions which are parallel and perpendicular with regard to the crystal optical axis; r_1 and r_2 are the resonator layer radii; δ_{ij} is Kronecker symbol.

The axial components of mode electromagnetic fields of two-layered QDR mode can be expressed by the following

$$E_{z\nu} = G_{E\nu}(r) \cos(k_z z) e^{i(n\varphi - \omega t)};$$

$$H_{z\nu} = G_{H\nu}(r) \sin(k_z z) e^{i(n\varphi - \omega t)},$$

$$\text{where } G_{j\nu} = \begin{cases} A_{jn} J_n(q_{j1} r), & r \leq r_1 \\ B_{jn} J_n(q_{j2} r) + C_{jn} N_n(q_{j2} r), & r_1 \leq r \leq r_2 \\ D_{jn} H_n^{(1)}(q_0 r), & r \geq r_2 \end{cases} \text{ characterizes the field}$$

distribution along the radius in resonators ν -layer. Here $A_{jn}, B_{jn}, C_{jn}, D_{jn}$ are the constants determined by the boundary and mode excitation conditions in QDR; $N_n(x)$ is the cylindrical Neiman function. Inside the dielectric layers, the field radial

components $q_{j\nu}$ of the wave vector are equal to $q_{H\nu}^2 = \mu_\nu \varepsilon_{\perp\nu} k_0^2 - k_z^2$ and $q_{E\nu}^2 = q_{H\nu}^2 \varepsilon_{z\nu} / \varepsilon_{\perp\nu}$

The field transversal components are expressed in terms of $E_{z\nu}$ and $H_{z\nu}$:

$$\begin{aligned} q^2 E_{\varphi\nu} &= \frac{1}{r} \frac{\partial}{\partial \varphi} \frac{\partial}{\partial z} E_{z\nu} - i \mu_\nu k_0 \frac{\partial}{\partial r} H_{z\nu}; \\ q^2 E_{r\nu} &= \frac{\partial}{\partial r} \frac{\partial}{\partial z} E_{z\nu} + i \mu_\nu \frac{k_0}{r} \frac{\partial}{\partial \varphi} H_{z\nu}; \\ q^2 H_{\varphi\nu} &= i \varepsilon_{\perp\nu} k_0 \frac{\partial}{\partial r} E_{z\nu} + \frac{1}{r} \frac{\partial}{\partial \varphi} \frac{\partial}{\partial z} H_{z\nu}; \\ q^2 H_{r\nu} &= \frac{\partial}{\partial r} \frac{\partial}{\partial z} H_{z\nu} - i \varepsilon_{\perp\nu} \frac{k_0}{r} \frac{\partial}{\partial \varphi} E_{z\nu}, \end{aligned}$$

where $q^2 = q_{H\nu}^2$ at $\nu = 1; 2$ and $q^2 = q_0^2$ at $\nu = 3$.

Spectral properties of anisotropic radially two-layered resonator are determined by the solutions of the following characteristic equation

$$\begin{aligned} &(\chi_0 \gamma_\beta^E - \chi_0 \gamma_\alpha^E)(\chi \mathcal{G}_\alpha^H - \chi \mathcal{G}_\beta^H) Z_J^H Z_N^H + (\chi_0^2 - \gamma_\beta^E \gamma_\beta^H)(\mathcal{G}_\alpha^E \mathcal{G}_\alpha^H - \chi^2) Z_J^E Z_J^H + \\ &+ (\chi_0^2 - \gamma_\alpha^E \gamma_\alpha^H)(\mathcal{G}_\beta^E \mathcal{G}_\beta^H - \chi^2) Z_N^E Z_N^H + (\chi \mathcal{G}_\beta^E - \chi \mathcal{G}_\alpha^E)(\chi_0 \gamma_\alpha^H - \chi_0 \gamma_\beta^H) Z_J^E Z_N^E + \\ &+ (\chi_0^2 - \gamma_\alpha^E \gamma_\beta^H)(\chi^2 - \mathcal{G}_\beta^E \mathcal{G}_\alpha^H) Z_N^E Z_J^H + (\chi_0^2 - \gamma_\beta^E \gamma_\alpha^H)(\chi^2 - \mathcal{G}_\alpha^E \mathcal{G}_\beta^H) Z_J^E Z_N^H = 0. \end{aligned}$$

In this equation, the following designations are used: $\chi_0 = n k_z (q_0^{-2} - q_{H2}^{-2}) / k_0 r_2^2$;

$\chi = n k_z (q_{H1}^{-2} - q_{H2}^{-2}) / k_0 r_1^2$; $\gamma_\xi^j = \sigma_2^j \xi_{22}^j - \alpha_0$; $\mathcal{G}_\xi^j = \sigma_2^j \xi_{21}^j - \sigma_1^j \alpha_{11}^j$, where ξ

takes on values α or β : $\alpha_{p\tilde{p}}^j = \frac{1}{q_{jp} r_{\tilde{p}}} \frac{J'_n(q_{jp} r_{\tilde{p}})}{J_n(q_{jp} r_{\tilde{p}})}$, $\beta_{2\tilde{p}}^j = \frac{1}{q_{j2} r_{\tilde{p}}} \frac{N'_n(q_{j2} r_{\tilde{p}})}{N_n(q_{j2} r_{\tilde{p}})}$,

where $p, \tilde{p} = 1; 2$ and prime means differentiation with respect to argument;

$$\sigma_\nu^j = \varepsilon_{z\nu} \quad \text{at} \quad j = E; \quad \sigma_\nu^j = \mu_\nu \quad \text{at} \quad j = H; \quad \alpha_0 = \frac{1}{q_0 r_2} \frac{H_n^{(1)'}(q_0 r_2)}{H_n^{(1)}(q_0 r_2)};$$

$$Z_R^j = \frac{R_n(q_{j2} r_1)}{R_n(q_{j2} r_2)}, \text{ where } R \text{ means the functions } J \text{ or } N.$$

Away from the frequency degeneration region, the independent EH - and HE -modes exist in the resonator. In the case when

$$\left| \frac{\chi^2 (Z_J^E - Z_N^E) (\gamma_\beta^H Z_J^H - \gamma_\alpha^H Z_N^H) + (\mathcal{G}_\alpha^E Z_J^E - \mathcal{G}_\beta^E Z_N^E) (\gamma_\alpha^H \mathcal{G}_\beta^H Z_N^H - \gamma_\beta^H \mathcal{G}_\alpha^H Z_J^H)}{\chi_0 [(\mathcal{G}_\alpha^H Z_J^H - \mathcal{G}_\beta^H Z_N^H) (\mathcal{G}_\beta^E Z_N^E - \mathcal{G}_\alpha^E Z_J^E) + \chi^2 (Z_J^H - Z_N^H) (Z_J^E - Z_N^E)] + \chi (\mathcal{G}_\alpha^E - \mathcal{G}_\beta^E) (\gamma_\alpha^H - \gamma_\beta^H) Z_J^E Z_N^E} \right| \gg 1$$

the eigen *HE*-modes are excited in the resonator, otherwise *EH*-modes are established.

4. The QDR frequency as a function of hole diameter in the dielectric cylinder

In practice, when using QDR a hole in the dielectric disk, concentric on the disk longitudinal axis, is often necessary. Therefore, the elucidation of the effect of a hole upon the resonator frequencies is of interest [11]. This, in its turn, initiates the formulation of the more general problem of studying the resonator spectrum at arbitrary diameter of the hole in the dielectric disk (see Figure 2). During the spectrum investigation, the hole diameter $2r_1$ is varied from zero to the highest possible value. The exterior diameter of the dielectric cylinder is $2r_2 = 77.7$ mm and its height is $l = 7.1$ mm. The interior diameter $2r_1$ is changed by means of a step-by-step removal of the dielectric Teflon material. In order to maximally reduce the plastic deformations, which are brought at fixation of the dielectric disk in the process of material removal, an appropriate fastening arrangement was made. The radius variation step is selected in such a way as to prevent “jumps” (at analysis of measurement results) between dependences for modes with different index sets *nsm*. The *EH*_{n11}- and *HE*_{n10}-mode frequency dependences on radial thickness $r_2 - r_1$ are shown in Figure 3a and 3b. At $r_2 - r_1 < 4$ mm the *Q*-factor decreases sharply and the measurement error increases along with it. This experimental result is consistent with the theoretical calculation one. According to this result the resonator’s radiation quality is dropped to such low values that the radiation loss dominance over the dielectric and metal losses becomes obvious (Figure 4a and 4b).

One can see from Figure 3a and 3b that WG modes propagate within QDR until, as was to be expected, the inside air-dielectric boundary coincides with the inside caustic line in the resonator. In our case, the caustic line is $r_2 - r_1 \cong 8$ mm distant from the

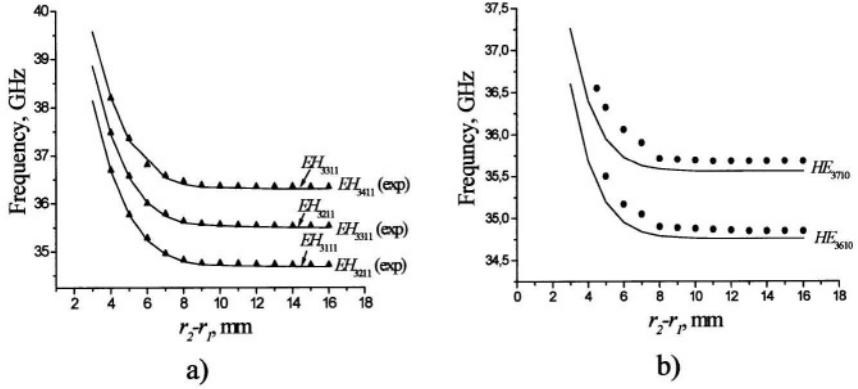


Figure 3. The EH_{n11} -mode (a) and HE_{n10} -mode (b) frequency dependences on radial thickness $r_2 - r_1$. The lines represent the results of calculations.

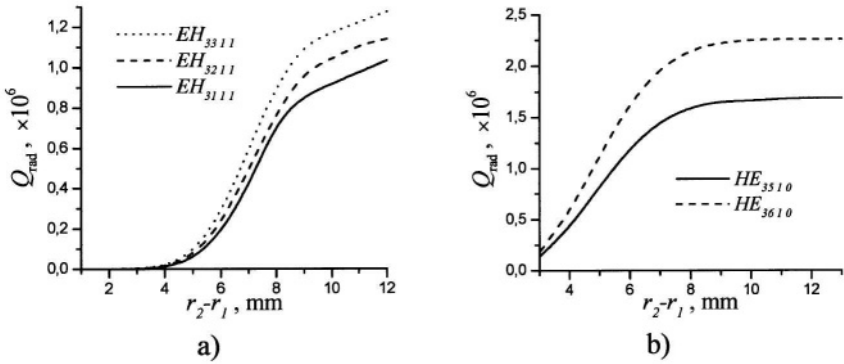


Figure 4. The EH_{n11} -mode (a) and HE_{n10} -mode (b) radiation quality-factor dependences on radial thickness $r_2 - r_1$ obtained theoretically.

dielectric cylinder periphery. At $r_2 - r_1 > 8$ mm, the ring resonator eigen frequencies are nearly independent of a hole diameter $2r_1$, while at $r_2 - r_1 < 8$ mm the frequencies increase when diameter $2r_1$ grows. The obtained experimental and theoretical results indicate an evolution nature of a whispering gallery wave transformation into waveguide modes at the continuous transition of QDR without a hole to the ring QDR (with a hole).

It is obvious, that the studied peculiarity of the QDR with CEP should also take place in the resonator without CEP because the presence of impedance walls does not

cause fundamental changes of electromagnetic field on the interface of two dielectric media.

5. Liquid permittivity measurement using two-layered QDR

It seems that a radially two-layer QDR is rather convenient for microwave characterization of liquids [12]. It is clear from physical considerations that measurement of both resonant frequencies and quality factor of the resonator with liquid filling its internal area enables one to determine ϵ' and $\tan \delta = \epsilon''/\epsilon'$ of liquid at known values of ϵ'_d and $\tan \delta_d$ for the dielectric, which the resonator is made of. Here, it is necessary to solve a number of problems under condition of the known dispersion equation and field structure: 1) to compose programs for computer calculations of values ϵ' and $\tan \delta = \epsilon''/\epsilon'$ by the measured frequency f and quality factor Q ; 2) to identify wave modes (oscillations) used for measurements; 3) to optimize the resonator dimensions from the point of view of measurement sensitivity increase. The latter is especially important at properties measurements of liquids with a large loss tangent.

For experimental measurements the resonator with diameter $D = 2r_2 = 78\text{mm}$ and height $l = 7\text{mm}$ was made of Teflon. The diameter $2r_1$ was varying in the process of the experiment. The Teflon disk was sandwiched between two duralumin endplates which allowed the calculation of eigen frequencies and field components as stated above. The HE_{nms} wave modes were excited in the resonator where $n=30-36$, $m=1$ and $s=0$ were azimuthal, radial and axial indices, accordingly.

The resonator was used for ϵ' measurements of a number of liquids, namely, benzene, machine oil, spirit and water and also for the loss tangent measurement of benzene. Next section deals with the water properties measurements. The data related to the resonator frequency and quality factor measurement depending on wall thickness $r_2 - r_1$ of a ring in the resonator at $r_2 = \text{const}$ are presented in Figure 5 and 6. These data enable one to determine values $\epsilon' = 1.8$ and $\tan \delta = 3 \cdot 10^{-3}$ for benzene (at the frequency about 36GHz).

6. About sign of frequency shift of the resonator with water

The opened opportunity seems to be attractive for studying liquids with large microwave loss such as water, because in the resonators studied we can control the weight coefficient of liquid loss in the resonator total losses by means of changing the radius r_1 (see Figure 2). Research into the frequency properties of QDR with water shows that water in a surface layer adjacent to solid-state dielectric causes the same sign of frequency shift as metal [13]. This effect seemed unusual in comparison with that of filling QDR with other dielectric liquids. The same QDR as in section 5 is used for experimental studies. In order to rule out the possibility of measurement errors

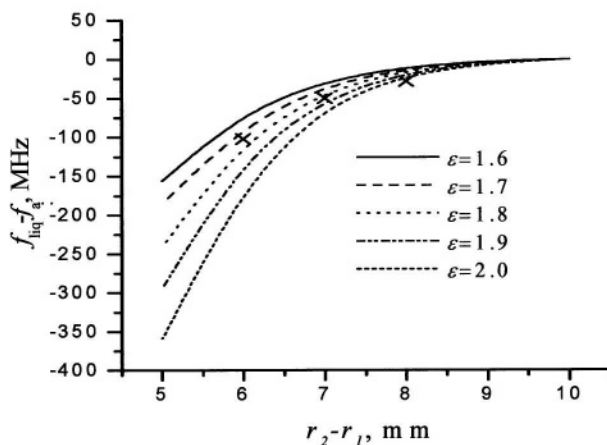


Figure 5. The shift frequency dependences on radial thickness $r_2 - r_1$ for the QDR with benzene, f_{liq} and f_a are frequencies of QDR with and without liquid. The lines represent the results of calculations.

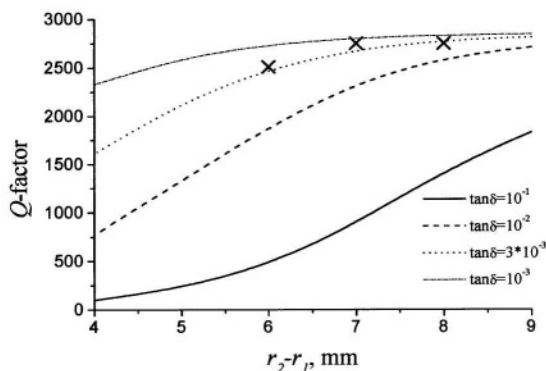


Figure 6. The Q -factor dependences on radial thickness $r_2 - r_1$ for the QDR with benzene. The lines represent the results of calculations.

conditioned by the absence of measurable absolute reproducibility at the resonator structure reassembling, the measurement procedure is carried out as follows. At every value of $r_2 - r_1$, firstly, the frequency f_a is measured for the QDR with air-filled groove, then the frequency f_{liq} is measured for the resonator with liquid, following which the frequency shift $\Delta f = f_{liq} - f_a$ is determined and applied to the plot (Figure 7). It is worthy to note, that the horizontal line in Figure 7 corresponds to air filling of the ring groove. One can see that Δf decreases with the availability of benzene filling ($\epsilon = 1.9$). However, water presence within the QDR gives an opposite effect, namely, Δf increases with the

increase of water volume. The latter indicates that as if we have some substance with $\epsilon' < 1$ which is placed in the area of electromagnetic field concentration. The direct calculations based on the dispersion equation for the radially two-layer QDR with CEP [8, 10] lead to the conclusion that for adequate description of Δf dependence on $r_2 - r_1$ in the case of water, it is necessary to take in account known dielectric properties of water in K_a -band ($\epsilon' = 20$ and $\tan \delta = 1.7$). In this connection it is interesting to note that the sign of Δf in QDR with a metal ring within the ring groove is positive also that seems some proof of that electromagnetic field structure is nearly the same in these both cases.

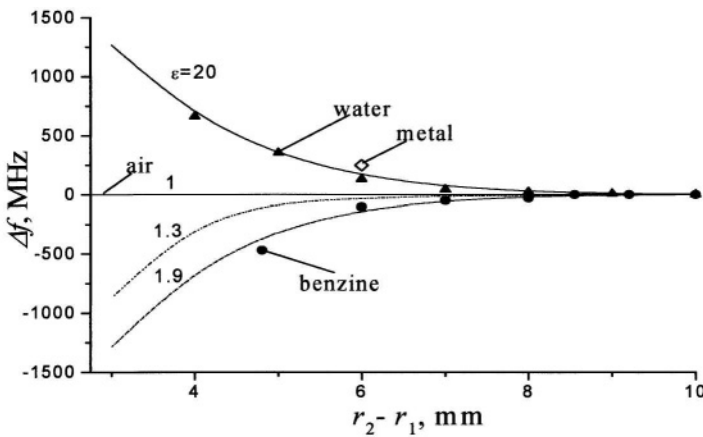


Figure 7. Frequency shift $\Delta f = f_{\text{res}} - f_a$ as a function of difference $r_2 - r_1$. The lines represent the results of calculations.

Without accurate calculation of Δf we could come to conclusion that a thin layer of water with a negative sign of permittivity exists near the boundary with Teflon wall, and such a conclusion has been made in [13]. It was based on calculating extraordinary occurrence at work with software. Annino and Cassettary [14] pointed out the error in [13] (see Comment and Reply on the Comment [14]). The discovered effect is not observed for such liquids as benzene. Probably, other high-loss tangent liquids will show the same effect as water. A phenomenon of the “anomalous” frequency shift in QDR with water has been discovered due to application of a dielectric resonator with higher order traveling azimuthal waves, i.e. WG modes [7,8,10,11], in the field concentration area of which an interface of solid-state dielectric and water can be placed. Recently effect of “anomalous” frequency shift of resonator with water has been confirmed in experiments with QDR containing cylindrical capillary filled with water [15]. The discovered feature is caused by larger dielectric permittivity of water than one of material which the resonator made of and in addition by the higher imaginary part if water permittivity than the real. Under these conditions as accurate calculations show electromagnetic field distribution is sensitive enough to presence of water layer in the resonator. The feature is rather attractive for physical study in microwave

electrodynamic structures because it is uncommon. On the other hand, it is quite possible that the feature can be useful at measurements of high-loss liquids.

7. Whispering gallery modes in liquids with small loss tangent

The study of the radially two-layered QDR properties promoted to the authors to use such a resonator for microwave characterization of above-described liquids. An attempt to excite WG modes directly in liquids became a next step. Present work considers the excitation of GW modes in two liquids, namely, machine oil and benzine. The experimental set-up enables one to measure eigen frequencies f and Q -factor of the QDR [11]. The measuring cell is a thin cylinder with external diameter $D=78\text{mm}$, height $l=6\text{mm}$ and wall thickness $h=1\text{mm}$ made of foam plastic ($\epsilon' \approx 1$). This material turns out to be convenient for carrying out measurement of oil. Unfortunately, porosity and partial solubility of the foam plastic are taking place for the case when we use benzine. Measurements of benzine and machine oil were carried out in the open QDR with and without the duralumin CEP [16]. The former variant is the best one because it allows one to find field structure in the resonator from Maxwell equations directly and, hence, to calculate ϵ' and ϵ'' of liquids with better accuracy than it was possible earlier. The resonance curve oscillogram of the open QDR with WG modes in one of liquids is presented in Figure 8.

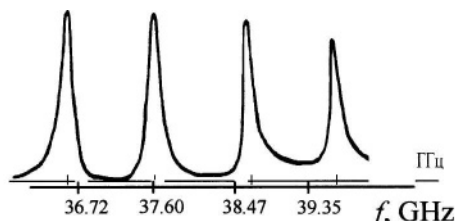


Figure 8. The resonance curve oscillogram of the open QDR with WG mode waves in benzine.

The analytical treatment of experimental values of frequencies and quality factors of the open QDR with clean low-octane benzine gives the values $\epsilon' = 1.88$ and $\tan \delta = 3.3 \cdot 10^{-3}$ at frequency $f_0 = 40\text{GHz}$ that agrees well with the data in section 5. In case of the machine oil, the dispersion equation allows one to obtain $\epsilon' = 2.18$ and Q -factor measurement of the open QDR allows one to find $\tan \delta = 2.8 \cdot 10^{-3}$. Measurement errors of permittivity and loss tangent make up $\Delta \epsilon' / \epsilon'' < 1\%$ and $\Delta \tan \delta / \tan \delta < 15\%$. The latter is conditioned in the main by the frequency instability of a microwave generator in the network scalar analyzer. The WG mode excitement directly in liquids simplifies considerably the measurement technique in case of liquids with low and moderate values of loss tangent and allows one to enhance the measurement accuracy of absolute values of liquids complex permittivity in the microwave range.

8. On the possibility to study nonlinear dielectric properties of liquids

Strictly speaking, the ideal physical systems with linear response dependence on external fields are absent in nature. Studies of nonlinear properties of substances give valuable information about the interaction mechanisms of the fields with substances. In this respect many works have been carried out in solid-state physics. Suffice it to remember such topics of modern physics as nonlinear optics, quantum radiophysics and electronics, plasma physics etc. Apparently the nonlinear properties of liquids were rather poorly studied. One of the reasons of this is the complexity of both the experimental studies and development of suitable theoretical models. Here, water provides a striking example of this. Many works were devoted to its study, however, a microscope model of the sub-molecular structure of water has not been developed yet.

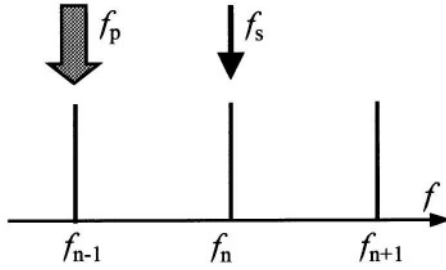


Figure 9. Whispering gallery spectrum of QDR with pump and signal frequencies, n is azimuthal index which is more than 10.

In this connection the development of a reliable measurement technique allowing one to determine directly not only liquid permittivity but also its dependence on electromagnetic and static electric fields becomes very important. In this respect the QDR with CEP can be a convenient instrument. In fact, a static field can be created with the help of CEP by applying voltage to them. Naturally, if there is an available equipment providing a maximum difference of potentials $U_{\max}$, one can achieve electric field $E_{\max} = U_{\max}/l$. It is clear that the field value $E_{\max}$ grows up with increase of ε' because l decreases in proportion to $\sqrt{\varepsilon'}$. One can conveniently measure dependence of ε' on high-frequency field E_{ω} by using the pumping technique where a substance is acted by a field at a certain frequency f_p and a response is measured at another, i.e. biased, frequency f_o . Such an approach is easily realized with the use of the QDR because it has a quasi-equidistant spectrum of resonant frequencies. One of them is taken as the signal frequency f_o and another as the pump frequency f_p . Here, it is convenient to use inequality $f_p < f_o$ both for the frequency isolation between two channels and the guarding of receiver from a high-power signal at the frequency f_p (Figure 9). Such an approach has been earlier developed for the study of nonlinear properties of high- temperature superconductors [17].

9. Conclusions

Thus, the work opens approaches to a new microwave technique of complex permittivity $\varepsilon = \varepsilon' - i\varepsilon''$ measurement of different liquids. Here, microwave loss in liquids has no importance in principle. The technique in principle enables one to determine the absolute values ε of liquids without a measurement device calibration which gives an opportunity to increase the measurement accuracy and promises possibilities of microwave characterization of liquids with high loss tangent. Here, the measurement process in a strong static and microwave field is performed rather simply. The two-layered quasi-optical dielectric resonators seem to be suitable for nonlinear and critical phenomena in different dielectric liquids.

10. References

1. Brandt, A.A. (1963) *Microwave study of dielectrics*, Fizmatgiz, Moscow (in Russian).
2. Afsar, M.N., Button, K.J. (1985) Millimeter-wave dielectric measurement of materials, *Proc. IEEE*, **73**, 131-153.
3. Aninno, G., Cassettari, M., Longo, I., and Martinelly, M. (1997) Whispering Gallery Modes in a Dielectric Resonator: Characterization at Millimeter Wavelength, *IEEE Trans. Microwave Theory Tech.*, **45**, no. 11, 2025-2033.
4. Cherpak, N.T., Filipov, Yu.F., Kharkovsky, S.N., and Kirichenko, A.Ya. (1993) Quasi-optical dielectric resonators in millimeter wave experiments, *The International Journal of Infrared and Millimeter Waves*, **14**, 617-627.
5. Cherpak, N.T., Izhyk, E.V., Kirichenko, A.Ya., and Velichko, A.V. (1996) Dielectric constant characterization of large-area substances in millimeter waveband, *The International Journal of Infrared and Millimeter Waves*, **17**, no.5, 819-831.
6. Krupka, J., Derzakowski, K., Abramowicz, A., Tobar, M.E., and Geyer, R.G. (1999) Use of whispering-gallery modes for complex permittivity determinations of ultra-low-loss dielectric materials, *IEEE Trans. Microwave Theory Tech.*, **47**, no. 6, 752-759.
7. Cherpak, N.T., Barannik, A.A., Filipov, Yu.F., Prokopenko, Yu.V., and Vitusevich, S.A. (2003) Accurate microwave technique of surface resistance measurements of large-area HTS films using sapphire quasi-optical resonator, *IEEE Trans. on Applied Supercond.*, **13**, no. 2, 3570-3573.
8. Prokopenko, Yu.V., Filipov, Yu.F., and Cherpak, N.T. (1999) Quasi-optical dielectric resonator with uniaxial anisotropy and conducting endplates. Field structure and quality factor, *Radiofizika i Elektronika*, **4**, 50-54, (in Russian).
9. Hakki B.W., and Coleman, P.D. (1960) Dielectric resonator method of measuring inductive capacities in the millimeter range, *IEEE Trans. Microwave Theory Tech.*, **8**, 402-410.
10. Cherpak, N.T., Barannik, A.A., Prokopenko, Yu.V., Filipov, Yu.F., and Smirnova, T.A. (2002) Frequency spectrum evolution of quasi-optical dielectric resonators with conducting endplates, *Telecommunications and Radioengineering*, **57**, no. 12, 46-55.
11. Barannik, A.A., Prokopenko, Yu.V., Filipov, Yu.F., Smirnova, T.A. and Cherpak, N.T. (2001) Ring quasi-optical dielectric resonator with conducting endplates, *Radiofizika i Elektronika*, **6**, 201-205 (in Russian).
12. Barannik, A.A., Prokopenko, Yu.V., Filipov, Yu.F., Smirnova, T.A. and Cherpak, N.T. (2003) *Quasi-optical dielectrometer*, Declaration patent for invention, no. 59568 (Ukraine).
13. Cherpak, N.T., Barannik, A.A., Prokopenko, Yu.V., Smirnova, T.A., and Filipov, Yu.F. (2003) On the negative value of dielectric permittivity of water surface layer, *Appl. Phys. Letters*, **83**, 4506-4508.
14. Annino, G., and M.Cassettari, M. (2004) Comment on "On the negative value of dielectric permittivity of water surface layer"; Cherpak, N.T., Barannik, A.A., and Prokopenko, Yu.V. "Reply to Comment on "On the negative value of dielectric permittivity of water surface layer", *Appl. Phys. Letters (to be published)*
15. Kirichenko, A.Ya., Lavrinovich, A.A., and Cherpak, N.T. (2004) Spectral characteristic properties of quasi-optical dielectric resonator with inhomogeneity in the form of a small water-filled hole, *Pis'ma v ZhTF (to be published)*.

16. Barannik, A.A., Prokopenko, Yu.V., Filipov, Yu.F., and Cherpak, N.T. (2003) Whispering gallery microwaves in liquids, *Dopovidi NAN Ukrainy (Reports of NAS of Ukraine)*, no.3, 77-79 (in Ukrainian).
17. Velichko, A.V., Cherpak, N.T., Izhyk, E.V., Kirichenko A.Ya., and Chukanova, I.N. (1997) High-frequency response to millimeter wave irradiation of YBaCuO thin film and ceramic, *Physica C*, **277**, 101-112.

NONLINEAR DIELECTRIC LOSSES AND DYNAMICS OF INTRINSIC CONDUCTIVITY OF DIELECTRICS

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1. Abstract

The phenomenological approach to dynamics of the intrinsic electric conductivity of dielectrics in the electric field was used for analyzing the respective contribution to dielectric losses. The proposed differential equation contains only two parameters – the effective time τ_F of conductivity decay in electric field, and time τ_R describing the rate of conductivity recovery after switching field off. The proposed approach predicts the *linear dependence* of specific conductivity of dielectrics *on the sample thickness* experimentally confirmed by Du Pont [1] for Teflon FEP. The field, time and frequency dependences of intrinsic conductivity $G(t, \omega, E)$ and related dependences of dielectric losses component $\epsilon''(\omega, E)$ was calculated, analyzed and illustrated by published experimental data.

2. Introduction

The problems related to the electric conductivity in dielectrics belong to difficult and unrewarding tasks. Difficult, because an exact description of the mechanisms of electric conductivity in dielectrics requires a set of partial differential equations which are unsolvable analytically. Moreover, the application of the electric field usually involves some additional processes which disturb the observed time dependence of conductivity. For this reason, large number of research papers as well as monographs devoted to the electrical conductivity of dielectrics focuses on special problems like the generation and annihilation of charge carriers and transport mechanisms.

The electrical conductivity of dielectrics attracted our attention since our involvement in the study of the nonlinear dielectric effect (NDE) of low conducting, polar liquids [1-5]. More systematic investigations [6] and the theoretical description [7] begun in the sixtieth. The attempts to apply the gas conductivity model proposed by Thomson and Thomson [1,8] to the solid phase, are recognized. However, implementing the di-

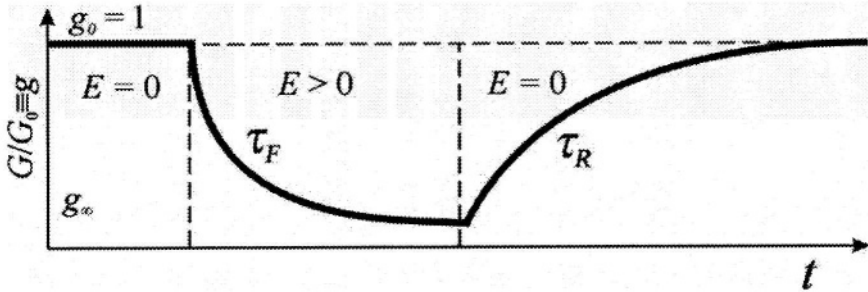


Figure 1. Decay and recovery of intrinsic conductivity of dielectrics (schematically, see text).

mensionless form of Thomson's equations gives the opportunity for the discussion of the selected stationary and non-stationary states [9,10].

Usually, the very well known phenomenon which accompanies the application of electric field to low conductivity media is the decrease of the electric conductivity G and its recovery after switching the field off, schematically shown in Figure 1. Essentially, it is a very complex process involving several contributions of different origin.

The dynamics of intrinsic, specific conductivity should lead to nonlinear dependence of dielectric losses (ϵ'') on electric field strength. *The aim of this work is to find (at least) an approximate picture of this effect.* To this the goal we have to formulate the function $G(E, t)$ that would reproduce the experimentally observed dependences schematically shown on Figure 1.

However difficulties in obtaining a rigorous theoretical description of electrical conductance of dielectrics lead us to abandon the idea of modeling the mechanisms responsible for the observed processes, and choosing a phenomenological approach. We would seek therefore, an analytical solution $G(E, t)$ describing the conductivity decay in static electric field E and its recovery following switching field off, and finally we need a function $\epsilon''(E, \omega)$ to simulate the DC conductivity background which obscures the dielectric spectra at low frequencies. Similar approach reported earlier [11,12] has lead to the explanation of the unusual stability of the electret charge as well as to understand the known effect of the improved stability of the electrets related to their thinning.

3. Phenomenological approach

Taking into account the mathematical difficulties, in the model proposed below, we would not attempt the description of the mechanisms responsible for the conductivity evolution in electric field. Therefore we will confine our consideration to a phenomenological approach aimed at approximating the time dependences of current and conductivity. Next, we would propose the following semi-empirical differential equation describing the conductivity decay and its recovery:

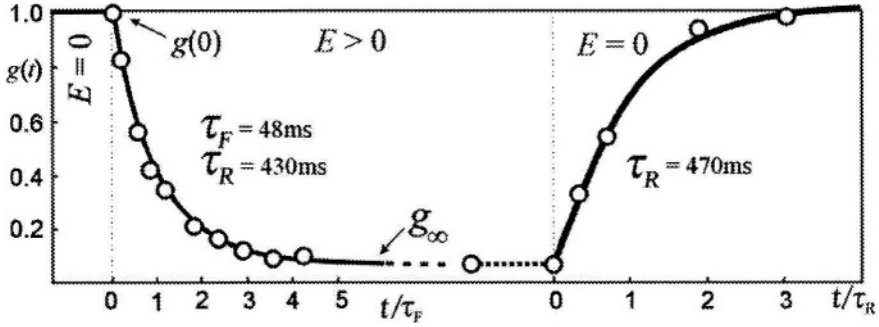


Figure 2. Decay and recovery of conductivity of nitrobenzene. Full lines show the best fit of Equation (2) to experimental points (circles). Figure 2. Decay and recovery of conductivity of nitrobenzene. Full lines show the best fit of Equation (2) to experimental points (circles).

$$\frac{dg(t)}{dt} = \frac{1 - [g(t)]^2}{\tau_R} - \frac{g(t)}{\tau_F} \quad (1)$$

where function $g(t) \equiv G(t)/G_0$ denotes the relative specific conductivity, while G_0 is the equilibrium value for $E = 0$. The equation contains only two parameters: times τ_F and τ_R – the effective time of conductivity decay in electric field, and the time of the conductivity recovery after switching field off, respectively (see Figure 1).

Equation (1) resembles the Thomsons' model suggests the approximate intuitive physical meaning of the parameters. Namely, τ_F , in crude approximation, expresses the mean time of flight $\tau_F \cong l / (E \sqrt{u^+ u^-})$, whereas the approximate relation $\tau_R \cong l / \sqrt{\alpha \beta}$ describes the rate of conductivity recovery. In the above relations l denotes the distance between electrodes and u – the carrier mobilities, α – recombination coefficient and β – the rate of the carrier-pairs creation. Denoting $\Delta \equiv \tau_R^2 + 4\tau_F^2$, the solution of Equation (1) becomes:

$$g(t) = \frac{\sqrt{\Delta}}{2\tau_F} \frac{\sinh \left[\frac{\sqrt{\Delta}}{\tau_F \tau_R} t + \ln \left| \frac{\sqrt{\Delta} + \tau_R + 2g(0)\tau_F}{\sqrt{\Delta} - \tau_R - 2g(0)\tau_F} \right| \right]}{\cosh \left[\frac{\sqrt{\Delta}}{\tau_F \tau_R} t + \ln \left| \frac{\sqrt{\Delta} + \tau_R + 2g(0)\tau_F}{\sqrt{\Delta} - \tau_R - 2g(0)\tau_F} \right| \right] + \operatorname{sgn} \left| \frac{\sqrt{\Delta} + \tau_R + 2g(0)\tau_F}{\sqrt{\Delta} - \tau_R - 2g(0)\tau_F} \right|} - \frac{\tau_R}{2\tau_F} \quad (2)$$

With the advantage of being analytical, the solution (2) can be used to compare with experimental data. Below, we would show only one example - decay and recovery of conductivity in nitrobenzene (Figure 2). However, similar fit made for higher alcohols proves that to a reasonable degree of approximation, the proposed phenomenological approach might reproduce dynamics of intrinsic conductivity of dielectrics.

Very important and interesting is boundary case – the dynamic equilibrium in electric field achieved for $t \rightarrow \infty$ with the respective minimum value of the conductivity g_∞ (see Figure 2). Evaluating the approximate formula

$$\tau_R/\tau_F \cong n_0 u E / (\beta l), \quad (3)$$

g_∞ can be express as

$$\lim_{t \rightarrow \infty} g(t) \equiv g_\infty = \frac{1}{2} \left(\sqrt{\left(\frac{\tau_R}{\tau_F} \right)^2 + 4} - \frac{\tau_R}{\tau_F} \right) = \frac{2\beta l}{\sqrt{n_0^2 u^2 E^2 + 4\beta^2 l^2} + n_0 u E} \quad (4)$$

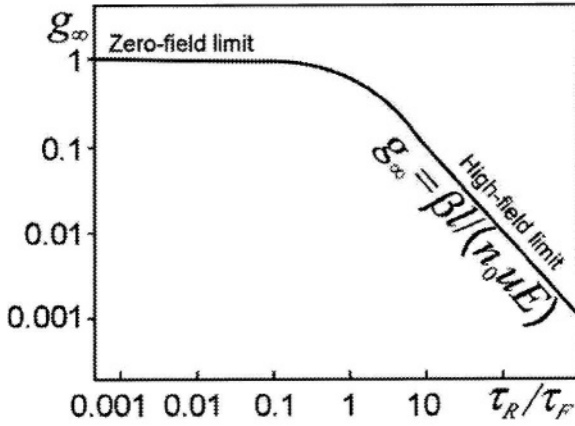


Figure 3. Conductivity g_∞ versus ratio according to Equation (4).

In Figure 3 a plot of the above dependence is displayed. Two limiting values can be seen:

- (a) For small values of the fraction τ_R/τ_F , i.e. in *weak-field limit* $E \ll \beta l / n_0 u$, one gets $g_\infty = 2\beta l / (2\beta l + n_0 u E) \approx 1$. Such a situation often is observed in the high conductivity materials, where the carrier creation rate β reaches relatively large values.

- (b) On the other hand, in the strong field limits, i.e. when $E \gg \beta l / n_0 u$, we get

$$g_\infty = \beta l / (n_0 u E) \quad (5)$$

and the *current density does not depend* on the electric field strength.

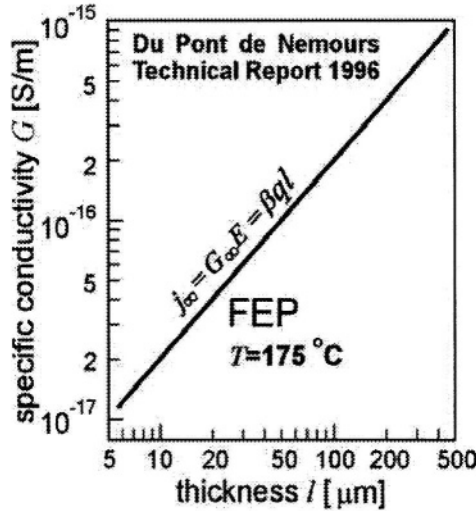


Figure 4. Dependence of the intrinsic conductivity G of Teflon® FEP on sample thickness [13].

Effectively, under the strong field, almost all the generated current carriers reach the electrodes which means, that the current density j_{∞} is determined by the rate of carrier generation β and, as follows from Equation (5), linearly depends on sample thickness (l):

$$j_{\infty} = G_{\infty} E = \beta q l \quad (6)$$

where q denotes the carrier charge. Although difficult to predict, such behavior of specific conductivity has been confirmed by Du Pont laboratories [13] (Figure 4). This particular form of the conductivity dependence $G_{\infty}(l)$ reflects the volume character of the carrier generation process. Under equilibrium conditions, on the other hand, their annihilation in the electric field occurs within two-dimensional space of the electrodes surface.

4. Conductivity in alternating electric field

Numerous studies of dielectrics are carried in the alternating electric fields in a wide range of frequencies ω . The dielectric relaxation studies in low frequency range are difficult to accomplish owing to a troublesome background effect related to the DC conductivity. The phenomenological approach proposed here, provides a means to evaluate and to account for the relative contribution of this conductivity. Adopting the

sinewave electric field of the form $E = E_0 \sin(\omega t)$ we may, similarly as before (Equation (1)), write down the rate equation of relative electrical conductivity as

$$\frac{dg(t)}{dt} = \frac{1 - g^2(t)}{\tau_R} - \frac{\sin(\omega t)g(t)}{\tau_F} \quad (7)$$

where $\tau_F \cong l/(E_S u)$ is now related to the effective field strength value E_S . Unfortunately, this equation cannot be solved analytically and numerical methods have to be used.

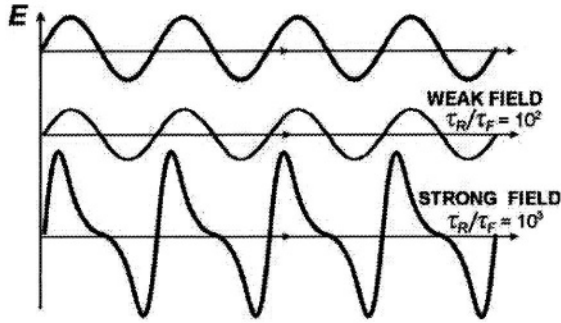


Figure 5. Current density as a function of time for two selected values of τ

Dependence of the conductivity on time and the electric field strength leads to a nonlinear relationship between the current densities and these parameters. The density of current j versus time is illustrated in Figure 5 for two τ_R/τ_F ratios, (for two selected values of the electric field strengths, respectively). The outcome of the calculation is that, irrespective of the field strength, the τ_R/τ_F ratio is the decisive factor rather, than the magnitude E_S itself. Practically, we apply a strong field when the following condition on the E_S/l ratio is satisfied:

$$\frac{\tau_R}{\tau_F} \cong \frac{G_0}{\beta q} \frac{E_S}{l} > 1 \quad (8)$$

For the „strong” field, in this meaning, the *sine-like* function of the current density appears distorted. For this reason, in the case of the AC electric field, we have to define an *average* electric conductivity

$$\langle G(\omega) \rangle = \frac{\int_0^{T/2} G(\omega, t) E(\omega, t) dt}{\int_0^{T/2} E(\omega, t) dt} \quad (9)$$

Results of the numerical calculations performed in a wide range of frequencies and τ_R/τ_F ratios (or electric field – see Equation (3)) are shown in Figure 6. These calculations performed in very wide range of electric field and frequency, provided an evidence that in alternating field the unique parameter τ_R/τ_F is significant, in contrary to the steady field case where the two separate times describing the time evolution of conductivity are involved (see Equation (2)). This property was tested empirically by the calcu-

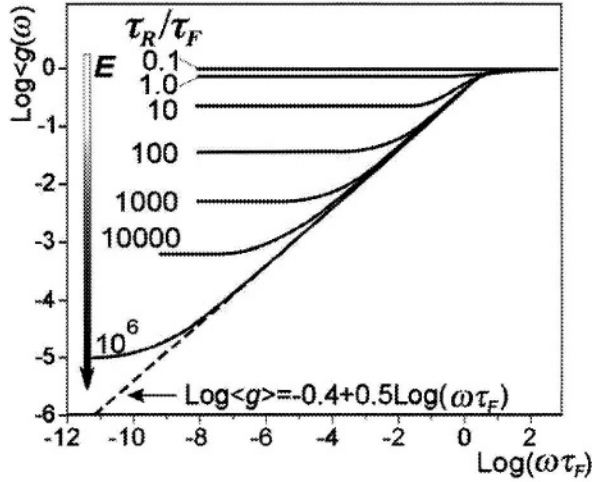


Figure 6. Logarithm of the average conductivity $\text{Log}\langle g \rangle$ as a function of frequency ω . The ratio τ_R/τ_F which can view as a measure of the electric field, is the parameter.

lations performed in the range of 10 orders of magnitude for τ_F and 15 orders of magnitude for the ratio τ_R/τ_F .

The ratio τ_R/τ_F directly relates to the rate of carrier generation β (Equation (3)). It can be determined by measuring g_∞ in a steady electric field because, according to Equation (4),

$$\frac{\tau_R}{\tau_F} = \frac{1 - g_\infty^2}{g_\infty} \quad (10)$$

Two measurements must be made to achieve this goal: (i) with the carefully chosen time $t > \tau_F$ one obtains G_∞ , (ii) during $t \ll \tau_F$ one measures G_0 in a pulse mode. Sometimes, it is more convenient to apply the above unambiguous relation between $\langle g(\omega) \rangle$ and τ_R/τ_F , outlined with the results in Figure 6. Hence, resorting only to two measurements of the conductivity – in low frequency range (G_∞), and in high frequencies (G_0) – we can experimentally determine the effective value of τ_R/τ_F ratio. It ought to be observed however, that in the case of AC field E means the effective electric field strength.

5. Component of dielectric losses related to intrinsic conductivity

We will now use the well-known relationship between specific electrical conductivity and dielectric losses:

$$\varepsilon''(\omega) = G/\varepsilon_0\omega \quad (11)$$

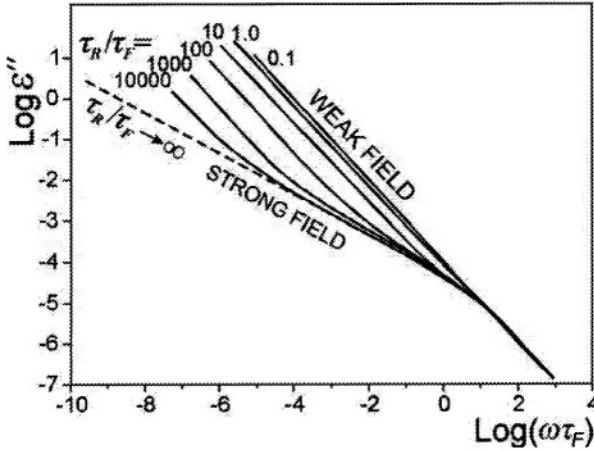


Figure 7. Logarithm of the dielectric losses *versus* $\text{Log}(\omega\tau_F)$. The equilibrium conductivity was assumed as $G_0 = 10^{-13} \text{ S/m}$.

When conductance G does not depend on external parameters, as it is commonly assumed, one obtains the well-known, hyperbolical relation between dielectric losses and frequency. However in our case, when conductance depends on time and intensity of electric field, the dependence is more complex.

Results of our calculations are shown in Figure 7. As an example we have assumed the rather low conductivity sample with initial, equilibrium conductivity $G_0 = 10^{-13} \text{ S/m}$. The obtained results show that for $\tau_R/\tau_F \leq 1$, e.g. for *weak* electric field

$$E_S < \beta q l \tau_F / (G_0 \tau_R)$$

as one might expect, the hyperbolical dependence of dielectric losses is predicted. One obtains such dependence also at *high* frequencies ($\omega\tau_F > 10$). However for stronger fields and lower frequencies the model predicts a clear cut deviation from hyperbolical dependence.

Schematically the results for the frequency dependence of the intrinsic conductivity and dielectric losses are shown in Figure 8. The conductivity dependence $G(E, \omega)$ is characterized by two dynamical equilibrium states: starting from the value G_0 at fre-

quency $\omega > \omega_F$ and reaching G_∞ at low frequency range for $\omega \ll \omega_F$, with almost linear region in between. The dielectric losses $\epsilon''(E, \omega)$ are characterized by two linear branches.

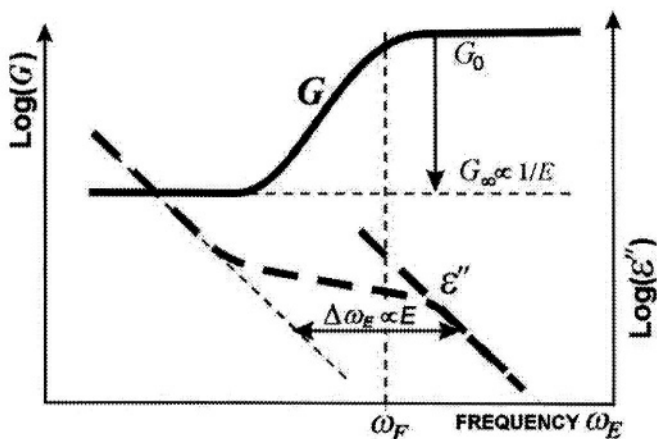


Figure 8. Schematic representation of the frequency dependence of logarithm of intrinsic conductivity G and related dielectric losses ϵ'' contribution.

6. Comparison with experimental results

The characteristic frequency $\omega_F = 1/\tau_F$ can be evaluated assuming that the decay time τ_F is, roughly speaking, equal to the mean time of flight $\tau_F \cong l/(Eu)$ of the current carriers. In dielectric liquids the carriers mobility are usually of the order of $10^{-6} - 10^{-10} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. Apply 1V to the sample of 1mm thick the characteristic frequency f_F is of the order of $10^{-1} - 10^3 \text{ Hz}$. In solid state the effective mobilities may take values in much broader range, and consequently the discussing phenom-

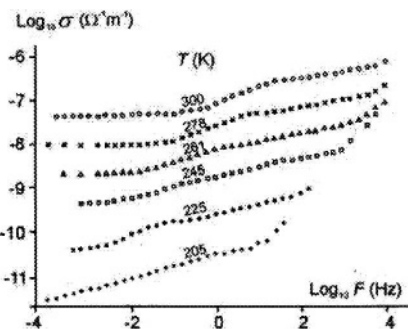


Figure 9. The frequency dependence of the conductivity of chalcogenide glass [14]. A drop in conductivity is clearly seen.

ena can be observed in respective wider range of frequency.

In similar procedure one may evaluate the critical intensity E_c of electric field using equations (3) and (8) and assuming $\tau_R/\tau_F = 1$:

$$E_c = \frac{bql}{G_0} = \frac{j_\infty}{(dj_\infty/dE)_{E=0}}$$

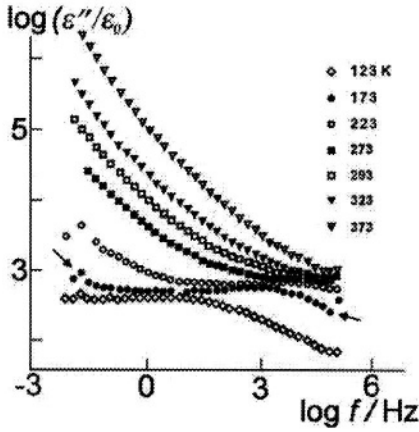


Figure 10. The frequency dependence of the dielectric losses of the ionic conductor Hollandite $K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$ [15]. The arrows indicate the most characteristic dependence (comp. Figure 8).

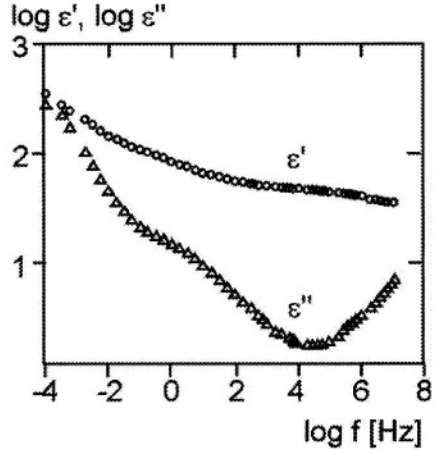


Figure 11. The low frequency dielectric relaxation of $PbTiO_3$ -PVDF composite [16]. The two linear branches can be distinguish in frequency dependence of dielectric losses ϵ'' (comp. Figure 8).

In practice, for weakly conducting sample E_c is of the order of 1V or even less.

In literature one can find results of experimental study of intrinsic conductivity and dielectric losses in low frequencies, below 10 Hz. In Figure 9 we quote the results of conductivity measurements published by Jonscher and Frost [14] for chalcogenide glass in low frequency range. The shape of the plot suggests that the mechanism we propose and discuss may be responsible for the observed drop in conductivity.

With the next two figures (10-11) we refer to the results of frequency dependence of the dielectric losses in ionic conductor Hollandite [15] and $PbTiO_3$ -PVDF composites [16], correspondingly. In both cases the characteristic two linear branches can be identified. In literature one can find many similar results, although the slopes of the linear branches are usually far from unity. Moreover, for an unambiguous interpretation of these data it would be required to examine the effect of magnitude of the electric field on the magnitude of the decrease in electrical conductivity or on the magnitude of the frequency shift in the case of dielectric losses.

7. Conclusions

A semi-empirical approach to dynamics of intrinsic electrical conductivity of dielectrics with two parameters τ_F and τ_R was proposed. These parameters have some *intuitive, approximate* physical meaning: τ_F denotes the effective time of conductivity decay, which may be associated with time of flight $\tau_F \cong l / \left(E \sqrt{u^+ u^-} \right)$ of current carriers in electric field, whereas τ_R denotes the recovery time of conductivity after switching off the field, and can be approximated as square root of the product of the recombination coefficient α and the carriers creation rate β , i.e. $\tau_R \cong 1 / \sqrt{\alpha \beta}$.

The proposed approach predicts the *linear dependence of specific conductivity of dielectrics on the sample thickness*. The results already reported by Du Pont [13] for Teflon FEP confirms the above predictions.

The phenomenological model was applied for calculation the field dependence of dielectric losses component $\varepsilon''(E)$ related to dynamics of the intrinsic conductivity $G(E, t)$ of dielectrics.

Numerical methods were used for calculating $\varepsilon''(E, \omega)$. We found, that the influence of field E becomes essential, when its frequency $\omega < \omega_F \cong 1 / \tau_F$ and $\tau_R / \tau_F \gg 1$ or $E \gg \beta l / (n_0 u)$. The conductivity dependence $G(E, \omega)$ is characterized by two dynamical equilibrium states: starting from the value G_0 at frequency $\omega > \omega_F$ and reaching G_∞ at low frequency range $\omega \ll \omega_F$, with almost linear transition in between (Figures 7,8).

The dielectric losses $\varepsilon''(E, \omega)$ are characterized by two linear branches (Figures 6,8). Such behavior can be found in published experimental data.

8. References

1. Małecki, J. (1976) Investigation of tautomeric $A-H \dots B \leftrightarrow A \dots H-B$ equilibrium by linear and non-linear dielectric polarization, *J. Chem. Soc. Faraday Trans. II*, **72**, 1214-1220.
2. Małecki, J. (1976) Theory of non-linear dielectric effects in liquids, *J. Chem. Soc. Faraday Trans. II*, **72**, 104-112.
3. Eigen M., and De Mayer L. (1963) *Techniques of Organic Chemistry*, in S. L. Fries, E. S. Lewis and A. Wessberger (Eds), Vol. VIII, part 2, *Interscience*, New York (Eds. S. L. Fries, E. S. Lewis and A. Wessberger, Vol. VIII, part 2)
4. Małecki, J. and Nowak J. (1999) Intermolecular interactions in benzene solutions of 4-heptyl-3'-cyanobiphenyl studied with non-linear dielectric effects, *J. Mol. Liquids* **81**, 245-252.
5. Małecki, J. (1988) Non-linear dielectric behavior and chemical equilibria in liquids, *Electrochim. Acta* **33**, 1235-1241.
6. Małecki, J., and Krowarsch, A. (1963) Badanie przewodnictwa elektrycznego cieczy dielektrycznych metodą impulsową, *PTPN, Prace Kom. Mat.-Przyr*, **11**, (2), 113-124.

7. Małecki, J. (1963) Przewodnictwo elektryczne cieczy dielektrycznych w słabym polu elektrycznym. Teoria i porównanie z wynikami doświadczalnymi, *PTPN, Prace Kom. Mat.-Przyr.* **11**, (2), 125-136.
8. Silver, M., (1965), *J. Chem. Phys.* **42**, 1011
9. Małecki, J., and Pierański, P. (1976) Thomson model of ion conduction in liquid dielectric. I. Steady state, *Acta Phys. Polon.* **A50**, 581-596.
10. Pierański, P. and Małecki, J. (1976) Thomson model of ion conduction in liquid dielectric. II. Steady states, *Acta Phys. Polon.* **A50**, 597-609.
11. Małecki, J. (1999) Linear decay of charge in electrets, *Phys. Rev. B* **59**, 9954-9960.
12. Hilczer, B., and Małecki, J. (1986) *Electrets*, Elsevier, Amsterdam, Oxford, New York, Tokyo.
13. Du Pont de Nemours Technical Report No. 240670C (unpublished).
14. Jonscher, A.K., and Frost, M.S. (1976) *Thin Solid Films* **37**, 267-273.
15. Jonscher, A.K., Deori, K.L., Reau, J.M., and Moali, J. (1979) *J. Materials Science* **14**, 1308.
16. Kułek, J., and Hilczer, B. (1998) Dielectric, piezoelectric and pyroelectric response of PbTiO₃-PVDF composites, *J. Korean Physical Society* **32**, S1079-S1081.

DIELECTRIC PROPERTIES OF CRITICAL CONDUCTING MIXTURES

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1. Introduction

Binary liquid mixtures with immiscibility gap offer possibility to investigate continuous phase transitions in conditions very convenient for experimentalists. Both the upper (UCST) and lower critical solution temperature (LCST) belong to [3,1] universality class as, for example, critical point of a pure liquids. The phase diagram of a system with the UCST is schematically presented in Figure 1.

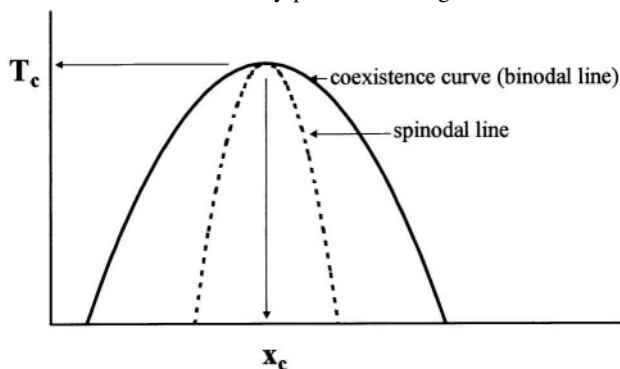


Figure. 1. The phase diagram $T(x)$ for a binary mixture with the UCST

Close to the critical point many macroscopic properties have critical divergence. The most spectacular anomalies are observed in light scattering [1-5], heat capacity [6-9], sound attenuation [5,10,11], but also in electric permittivity [12-23,28], conductivity [15,17,18,24-29] and non-linear dielectric effect (NDE) [30-37]. The reason of the observed anomalies are large and long-living concentration fluctuations. Systems lose their individual behaviors and achieve universal properties. The critical behaviors can be described by universal critical exponents, whereas the critical amplitudes - responsible for the magnitude of the observed effects are characteristic for the investigated systems and reflect their physical and chemical properties. Consequently, convenient selection of the investigated mixture may express or suppress some critical and pre-critical anomalies. This paper is devoted to the description of different dielectric

properties of binary critical mixtures. It will be proved that addition of small amounts of ionic species to non-ionic critical systems increases the amplitude of dielectric critical phenomena.

2. Electric permittivity

Electric permittivity measurements are simple, not expensive, precise, but unexpectedly, many conflicting results are obtained initially. In some experiments a sharp increase of permittivity was found [38-40], whereas in others smooth character and only small negative curvature close to T_c were observed [41-43]. However, in eighties it was found [12-16] the reason of these troubles - the anomaly depends on frequency. At low frequencies an increase of ϵ is observed, at high- a small decrease of permittivity if one compares it with the value extrapolated from the non-critical region (Fig- 2).

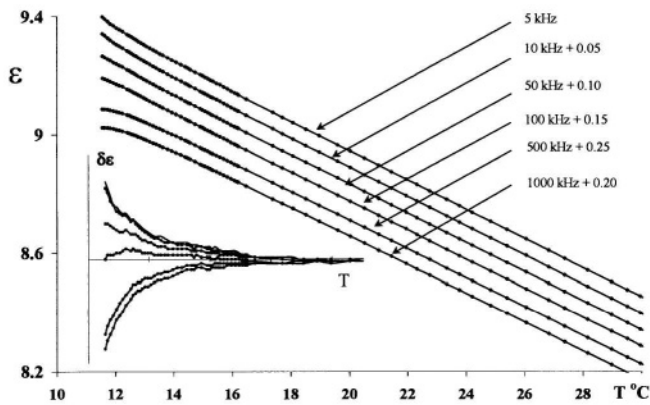


Figure 2. Electric permittivity in ethanol + dodecane mixture obtained for different frequencies in function of temperature at critical concentration of ethanol + dodecane mixture [18]

The insert in Fig. 2 presents the difference ($\delta\epsilon$) between experimentally obtained permittivity and the value extrapolated from the high temperature region. The frequency region where the dispersion is observed excluded any structural relaxation in simple liquids. The relaxation frequency strongly depends on conductivity [12] but seems to not depend on temperature. The relaxation frequency could be roughly estimated by simple expression:

$$f_r = \frac{\sigma_B}{2\pi\epsilon_0\epsilon_B} \quad (1)$$

where ϵ_B and σ_B are the permittivity and conductivity of a medium respectively. The explanation of the observed effect is based on the assumption that fluctuations can be described as real inhomogeneity. Figure 3 presents a system with large and long-living

concentration fluctuations. Here fluctuations are treated as droplets immersed in the bulk medium

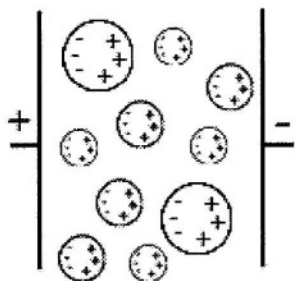


Figure 3. Inhomogeneous system under influence of external electric field

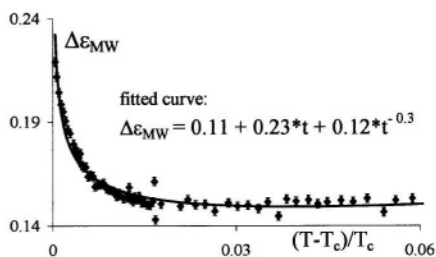


Figure 4. The dependence of $\Delta\epsilon_{MW}$ versus reduced temperature in ethanol + dodecane system [18]

Electric permittivities and conductivities of “droplets” and “bulk” are different that results from the differences in concentrations of the polar component inside and outside fluctuations. Movement of ions in the external electric field results in polarisation of droplets. Analysing this picture it is possible to adopt the classical Maxwell-Wagner (MW) [44] model for description of the critical system [12,17,18,22]. The Maxwell-Wagner increment is defined as a difference between low-frequency and high-frequency permittivities. Simple approximation leads to the conclusion that the temperature dependence of MW increment can be estimated as follows:

$$\Delta\epsilon_{MW} \approx \eta \cdot \xi = C \cdot t^{\beta-\nu} \quad (2)$$

where β is the order parameter critical exponent, ν is the correlation length exponent and C - the critical amplitude. Assuming the universal values of critical exponents, the predicted exponent of the Maxwell-Wagner effect is -0.3 . Figure 4 presents the temperature dependence of MW increment in an ethanol - dodecane mixture [18]. It is evident that even at non-critical conditions considerable differences between low and high frequency permittivities exist. It probably reflects the electrode polarization effect that was assumed to be a non-critical contribution to the observed increment. However, some influence of critical heterogeneity on the electrode polarization phenomena, and on structure of the double layer and the kinetics of electrochemical reactions could be expected. Neither experiments nor theoretical expectations concerning this interesting, and probably technologically important effect, were published so far. In the performed approximation the non-critical component of $\Delta\epsilon_{MW}$ was approximated by a linear dependence. The predicted critical exponent describes fairly well the experimental dependence.

What is the expected influence of ionic species on Maxwell-Wagner dispersion? The macroscopic polarization of inhomogeneous system reflects formation of “macro-dipoles” as a result of movement of ions inside fluctuations treated as “droplets”. The increase of the mean concentration of ions should increase their concentration inside fluctuations and enhance the discussed effect. Following this idea it was compared permittivities in pure critical mixtures and that doped by tetramethyloammonium

chloride (TMAC) (Figure 5a,b) [53]. Both in pure and in doped mixtures the increase of the derivative $|d\epsilon/dT|$ at low frequencies and the decrease at high frequencies were observed.

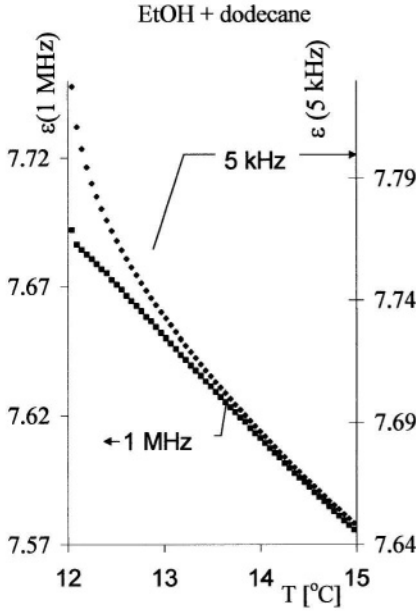


Figure 5a. Electric permittivity versus temperature in the "pure" system [53]

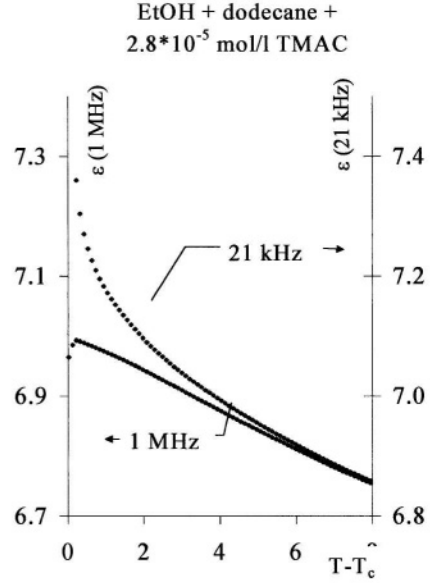


Figure 5b. Electric permittivity versus temperature in the system doped by ions [53]

The differences between low and high frequency permittivity anomalies (compare Figs 5a and 5b) and, consequently, the MW increment in the doped mixture (Fig. 6) strongly increases.

According to theoretical expectations [45,46] when correction to scaling is omitted, the predicted temperature dependence of electric permittivity is:

$$\epsilon \cong \epsilon_c + \epsilon_1 \cdot t + \epsilon_2 \cdot t^{1-\alpha} \quad (3)$$

where t is the reduced temperature, α is the specific heat exponent.

It should be taken into account that only the maximum of the coexistence curve is the second order phase transition and only in that case equation 4 is correct. The transitions on side-wings of the coexistence curve are the first order ones. It is impossible, from the experimental point of view, to obtain precisely the critical point conditions and any experimental attempt approaches the critical point only. Consequently, the experimentally obtained phase transition temperature is usually not critical, but bimodal temperature. In order to obtain simple scaling of experimental data, instead of the critical temperature, the spinodal temperature, and appropriate spinodal reduced

temperature for close-critical systems have to be used [47,48]. Consequently, an important conclusion arises: the critical temperature should be treated as a variable and it should be always obtained in

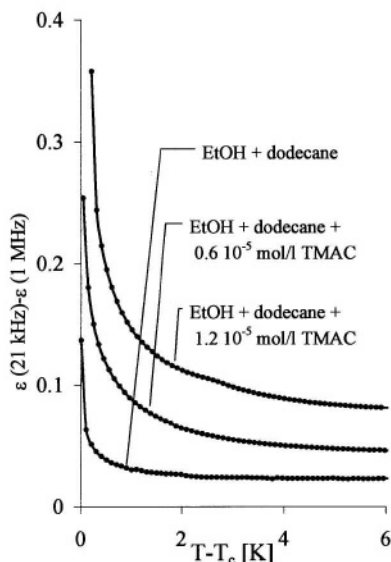


Figure 6. The Maxwell – Wagner increment for permittivity obtained in the pure and in the doped ethanol + dodecane mixture [53]

a fitting routine. Fitting of the function (3) requires to adjust many parameters to the smooth $\varepsilon(T)$ dependence that has to result in strong correlation between fitted parameters. Nevertheless, it was proved [18,23] that the critical exponent is consistent with the Ising 3D model. The equation (3) describes an “inherent” anomaly of electric permittivity observed at sufficiently high frequencies. For low frequencies an additional term related to MW dispersion has to be included:

$$\varepsilon \cong \varepsilon_c + \varepsilon_1 \cdot t + \varepsilon_2 \cdot t^{1-\alpha} + C \cdot t^{\beta-\nu} \quad (4)$$

The generalized equation is appropriate for description of $\varepsilon(T)$ both at low and at high frequencies [22] and especially in doped mixtures. This equation was used to approximate the $\varepsilon(T)$ data obtained for ethanol - dodecane -TMAC system. The critical amplitude increases with the increase of salt concentration, and, in doped mixtures, the temperature region where the Maxwell-Wagner dispersion is observed is much wider.

3. Electric conductivity.

Another parameter that is usually measured in dielectric experiment is conductivity. In simple liquids conductivity decreases with the decrease of temperature (mobility of ions decreases). Critical properties of electric conductivity can be correctly measured

only in liquids containing ions being a result of auto-dissociation of components [18] and/or ionic additives [22]. In critical mixtures the decrease in the vicinity of critical point is much stronger (Figs.7 a,b) than that in non-critical region.

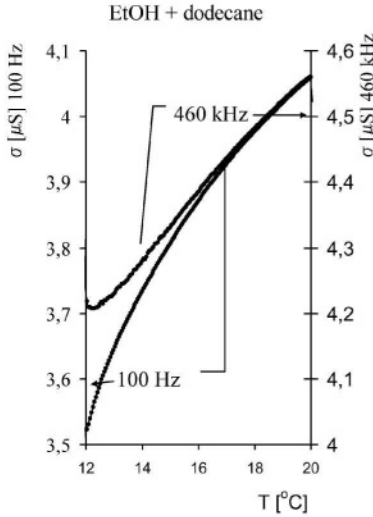


Figure 7a The temperature dependence of electric conductivity in pure system [53]

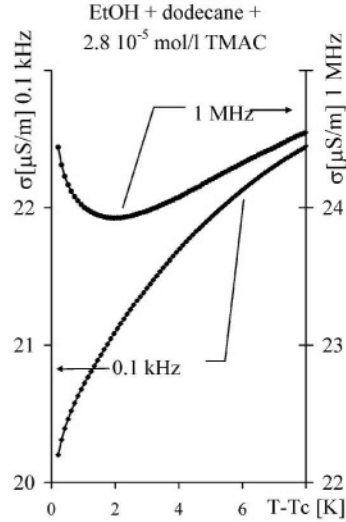


Figure 7b The temperature dependence of electric conductivity in doped system [53]

It was found that the anomaly at low frequencies is stronger than that at high ones. The differences in critical behaviors at low and high frequencies result from low frequency dispersion located in the same interval as the MW permittivity dispersion. The discussed previously “pseudo-heterogeneity” allows to understand the differences in critical behaviors of conductivity at low and high frequencies. Some ions are trapped in alcohol-rich fluctuations and do not take part in global current flow, resulting in low frequency conductivity decrease. Movement of ions inside fluctuations is restricted to the diameter of heterogeneity. At high frequencies and close to the critical temperature, when the “diameter” of fluctuations (treated as droplets) is large, even “trapped ions” take part in conduction - and, consequently, conductivity measured in high frequencies (1 MHz in the data presented in Figs 7a/b) increases. Application of Maxwell-Wagner model allows to predict that the conductivity increment, defined as a difference between high and low frequency conductivity, should be described by the exponent of the order parameter β :

$$\Delta\sigma_{MW} = \sigma_h - \sigma_l \approx D \cdot t^\beta \quad (5)$$

An example of approximation of experimental data is presented in Figure 8a. In the fitting a linear, non-critical term was included. In a system doped by ionic ingredients the amplitude of the $\Delta\sigma_{MW}$ increases considerably (Fig 8b). Following the macroscopic

model adopted to explain the conductivity anomaly it could be concluded that an “inherent” anomaly of conductivity should be observed at low frequencies, whereas at

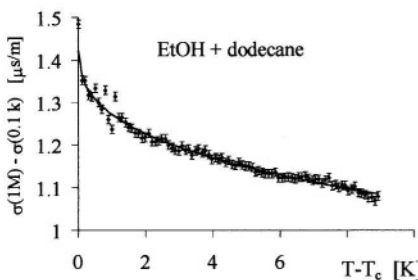


Figure 8a Maxwell – Wagner increment for conductivity obtained in pure system [53]
 $\Delta\sigma_{MW} = 1.45 - 0.2t - 1.1t^{0.325}$

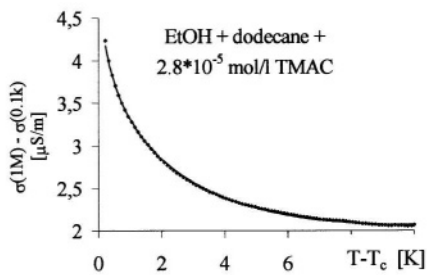


Figure 8b Maxwell – Wagner increment for conductivity obtained in doped system [53]
 $\Delta\sigma_{MW} = 5.7 - 51.9t - 16.2t^{0.325}$

high frequency the MW dispersion term has to be included. The generalized temperature dependence of conductivity, applicable both at low and at high frequencies, has the form:

$$\sigma = \sigma_c + \sigma_1 \cdot t + \sigma_2 \cdot t^\varphi + D \cdot t^\beta \quad (6)$$

In equation 6 the background term is approximated by a linear temperature dependence and Wegner correction to scaling is omitted. The equation contains many adjustable parameters, however both in pure alcohol-hydrocarbon mixture [18] as well as in doped ones [22] the exponent $\varphi = 1 - \alpha = 0.89$ was found to be the best. Theoretical expectations do not predict definitely the critical exponent φ . Stein and Allen [24] took into account that resistivity ($1/\sigma$) is proportional to viscosity and should be described by this same critical exponent. Shaw and Goldburg [25], adapting the percolation approach, predicted $\varphi = 2\beta = 0.65$. Ramakrishnan et al. [26] considered scattering of ions by the concentration fluctuations and found for resistivity an exponent equal to $\varphi = \nu = 0.63$ (ν is the correlation length exponent). Jasnov, Goldburg and Semura, on the base of proton hopping model, predicted an exponent equal to $(1 - \alpha)$ [49]. The same exponent was predicted by Wheeler [50] who considered the anomaly of dissociation constant.

4. Non-linear dielectric effect

Non-linear dielectric effect (NDE) consists in measurements of the difference between permittivity obtained in high (ϵ^E) and low (ϵ^0) intensity electric fields. According to Debye-Langevin theory for liquids containing dipolar, rigid, non-interacting molecules, the NDE increment ($\Delta\epsilon_{NDE} = \epsilon^E - \epsilon^0$) is negative and proportional to the square of electric field intensity (when higher order expansion terms of Debye-Langevin function are neglected). Usually, the NDE increment is small and not easy to

determine. However, in the vicinity of critical mixing point very strong increase of the NDE increment is observed (Fig. 9).

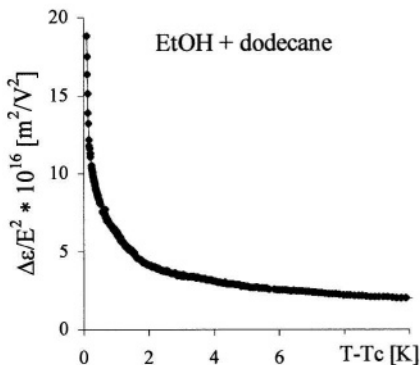


Figure 9. The temperature dependence of non-linear dielectric increment in pure critical system [33]

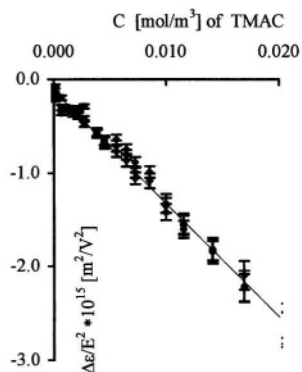


Figure 10. The dependence of NDE increment versus salt concentration in non-critical ethanol + p-xylene mixture [53]

Amplitude of the NDE anomaly increases proportionally to the difference between permittivities of the components of binary mixture [30]. The reason of the observed anomalous increase of NDE increment is an “elongation” or an “extension” of polar component rich fluctuations in the direction of the strong electric field. It results in anisotropy of polarizability (Kerr effect) and in increase of macroscopic permittivity measured in the direction of the strong electric field. The anomaly of NDE increment can be described by the equation:

$$\frac{\Delta \epsilon_{NDE}}{E^2} = (a + bt)_B + c \cdot t^\psi \quad (7)$$

where $(a + bt)_B$ is the background contribution. The droplet model [51] predicts the critical exponent ψ equal to -0.56, however Rzoska and coworkers [52] motivate that the exponent should have the value of -0.3. Experimental investigations give exponents between -0.56 and -0.3.

What is the influence of ions on NDE increment in the vicinity of critical mixing point? To answer this question, at first the influence of ions on NDE increment in non-critical systems should be recognized. To the best knowledge of the authors, neither experiments nor theoretical expectations concerning this effect have been published so far. Measurements in conducting systems are not easy because of strong heating effect what disturbs considerably the obtained NDE increment. To overcome these troubles, very short pulses of strong field have to be applied [54] and at larger concentration of ions “single shot” measurements are necessary. Figure 10 presents the NDE increment obtained in non-critical ethanol - p-xylene doped by TMAC. The increment decreases linearly with the increase of salt concentration. Figure 11 presents the temperature

dependence of NDE increment in the vicinity of critical mixing point in pure ethanol + dodecane mixture and in the mixture doped by TMAC.

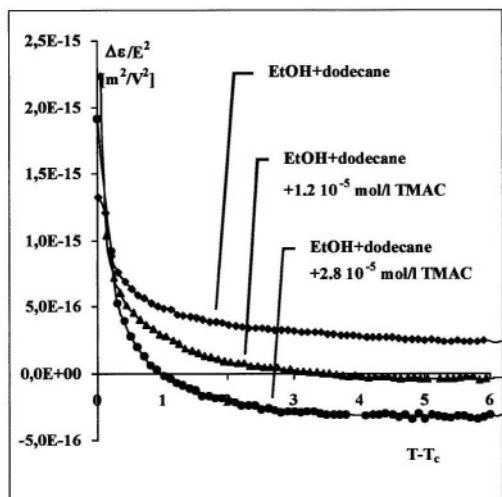


Figure 11 Comparison of critical anomalies of NDE increments in pure and in doped critical mixtures [53]

In non-critical region, “normal” decrease of NDE increment is observed. Close to T_c the increment increases strongly and both for pure system and for doped ones the NDE increment has a large positive value. Results of the fitting of equation 6 to the experimental points is presented below:

$$\Delta \varepsilon / E^2 \cdot 10^{16} (0 \text{ mol} / \text{dm}^3) = 1.76 - 30.3t + 0.14t^{-0.56} \quad T_c = 13.38^\circ \text{C}$$

$$\Delta \varepsilon / E^2 \cdot 10^{16} (1.2 \cdot 10^{-5} \text{ mol} / \text{dm}^3) = -2.14 - 2.14t + 0.19t^{-0.56} \quad T_c = 13.45^\circ \text{C}$$

$$\Delta \varepsilon / E^2 \cdot 10^{16} (2.8 \cdot 10^{-5} \text{ mol} / \text{dm}^3) = -6.89 - 59.5t + 0.27t^{-0.56} \quad T_c = 13.39^\circ \text{C}$$

The critical exponent was supposed to be consistent with the value predicted by the droplet model. The influence of ionic ingredients on critical anomaly of the NDE effect is evident. With an increase of salt concentration, the temperature range where critical anomaly is observed increases, also the critical amplitudes goes up.

Unfortunately in spite of strong critical anomaly, the critical exponent is uncertain because of relatively large experimental error of NDE experiments. Figures 12 a/b present the results of fitting equation (6) using the critical exponent $\psi = -0.56$ (droplet model) and $\psi = -0.3$ (Rzoska model). The critical exponent consistent with the droplet model seems to be better, but the experimental error do not allow to discriminate definitely between exponents -0.56 and -0.3 .

Formal similarities between NDE anomaly and that observed in permittivity Maxwell-Wagner increment, especially in mixtures doped by ions, tend to ask question on a relationship between these two effects. Qualitative similarities are strong (compare Figs

6 and 12). In both cases an addition of ionic species increases considerably the critical anomaly, both of them could be approximated by the same exponent. However, it has to be stressed that in the case of MW effect only movement of ions should be considered,

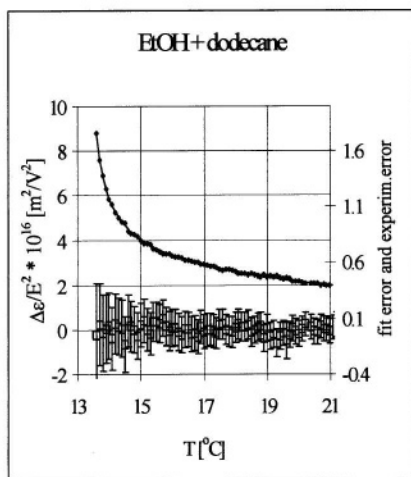


Figure 12a Approximation of the experimental data obtained in ethanol + dodecane mixture by the exponent $\psi = -0.56$, (mean error = $3.5 \cdot 10^{-18}$)

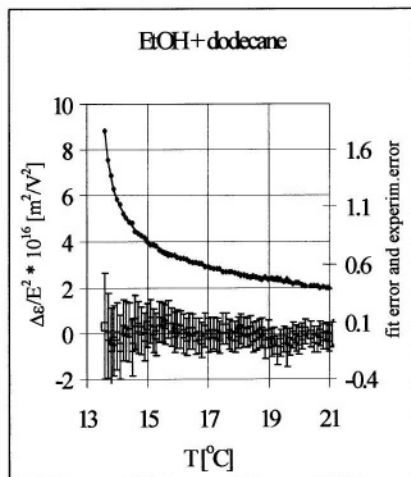


Figure 12b. Approximation of the experimental data obtained in ethanol + dodecane mixture by the exponent $\psi = -0.3$ (mean error = $7 \cdot 10^{-18}$)

whereas in the case of NDE both the effects - movement and elongation of inhomogeneities should be taken into account.

5. Conclusions

In binary mixtures doped by small amounts of ions, critical anomalies observed in dielectric measurements are similar to those in pure systems, but, considerable increase of critical amplitudes of the low-frequency Maxwell-Wagner dispersion of permittivity and conductivity were observed. Doped critical mixtures are especially convenient for investigation of conductivity anomaly and allow to observe new interesting effects. In doped non-critical mixtures, the NDE effect was found to decrease with addition of ions. In doped critical mixtures, in spite of a decrease of the NDE increment in the pre-critical region, that in the vicinity of critical point is still positive and large. Critical amplitude of the NDE anomaly increases with the increase of the salts concentration.

6. References

- Weingartner H., Weigand, S. and Schroer, W. (1992) Near-critical light scattering of an ionic fluid with liquid-liquid phase transition, *J. Chem. Phys.*, **96**, 848-851.
- Prafulla, B.V., Narayanan, T., and Kumar, A. (1992) Double-critical-point phenomena in three-component liquid mixtures: light scattering investigation, *Phys. Rev. A*, **46**, 7456-7465.
- Fusenig, S. and Woermann, D., (1993) Static light scattering experiments with 2-butoxyethanol/water mixtures of near critical composition in the vicinity of the lower critical point, *Ber. Bunsenges. Phys. Chem.*, **97**, 577-582.
- Bonetti, M., Bagnuls, C. and Bervillier, C. (1997) Measurement and analysis of the scattered light in the critical ionic solution of ethylammonium nitrate in n-octanol, *J. Chem. Phys.*, **107**, 550-561.
- Durr, U., Mirzaev, S.Z. and Kaatz, U. (2000) Concentration fluctuations in ethanol/ dodecane mixtures. A light- scattering and ultrasonic spectroscopy study, *J. Phys. Chem.*, **104**, 8855-8862.
- Gopal, E.S.R. (1981) Critical point phenomena heat capacities and the renormalization group theory of fluctuations, *Bull. Mater. Sci.*, **3**, 91-99.
- Flewelling, A.C., DeFonseka, R.J., Khaleeli, N., Partee, J. and Jacobs, D.T. (1996) Heat capacity anomaly near the lower critical consolute point of triethylamine-water, *J. Chem. Phys.*, **104**, 8048-8057.
- Rebillot, P.F. and Jacobs, D.T. (1998) Heat capacity anomaly near the critical point of aniline-cyclohexane, *J. Chem. Phys.*, **109**, 4009-4014.
- Heimburg, T. Mirzaev, S.Z. and Kaatz, U. (2000) Heat capacity behaviour in the critical region of the ionic binary mixture ethylammonium nitrate-n-octanol, *Phys. Rev. E*, **62**, 4963-4967.
- Garland, C.W., and Sanchez, G. (1983) Ultrasonic study of critical behaviour in the binary liquid 3-methylpentane + nitroethane, *J. Chem. Phys.*, **79**, 3090-3099.
- Fast, S.J. and Yun, S.S. (1985) Critical behaviour of the ultrasonic attenuation for the binary mixture: triethylamine and water, *J. Chem. Phys.*, **83**, 5888-5891.
- Thoen, J., Kindt, R. and Van Dael, W. (1980) Measurements of the temperature and frequency dependence of the dielectric constant near the consolute point of benzonitrile-isooctane, *Phys. Lett.*, **76A**, 445-448.
- Merabet, M. and Bose, T.K. (1982) Dielectric constant anomaly near the consolute point of a binary mixture: nitrobenzene - isooctane, *Phys. Rev. A*, **25**, 2281-2288.
- Cohn, R.H. and Greer, S.C. (1986) Dielectric constant near the liquid-liquid critical point in perfluorocyclohexane + carbon tetrachloride, *J. Phys. Chem.*, **90**, 4163-4166.
- Kindt R., Thoen, J. and Van Dael, W. (1988) Dielectric study of the two-phase region of binary liquid mixtures near the consolute point, *Int. J. Thermoph.*, **9**, 749-759.
- Orzechowski, K. (1988) Measurement of dielectric permittivity near the consolute critical point of methanol-cyclohexane mixture, *Ber. Bunsenges. Phys. Chem.*, **92**, 931-934.
- Thoen, J., Kindt, R., Van Dael, W., Merabet, W. and Bose, T.K. (1989) Low-frequency dielectric dispersion and electric conductivity near the consolute point in some binary liquid mixtures, *Physica A*, **156**, 92-113.
- Orzechowski, K. (1994) Electric properties of an ethanol-dodecane mixture near the upper critical solution point, *J. Chem. Soc. Faraday Trans.*, **90**, 2757-2763.
- Hamelin, J., Gopal, B.R., Bose, T.K. and Thoen, J. (1995) Intrinsic dielectric constant anomaly in critical liquid mixtures, *Phys. Rev. Lett.*, **74**, 2733-2736.
- Paluch, M., Haldas, P., Rzoska, S.J. and Schimpel, T. (1996) Electric permittivity in the one- and two-phase region of 1-nitropropane-hexadecane near-critical solution, *Chem. Phys.*, **213**, 483-488.
- Hamelin, J., Bose, T.K. and Thoen, J. (1996) Critical behaviour of the dielectric constant in the triethylamine-water binary liquid mixture: Evidence of an intrinsic effect, *Phys. Rev. E*, **53**, 779-784.
- Orzechowski, K., (1997) Dielectric properties of methanol + hexane critical mixtures without and with ionic additives, *J. Mol. Liquid*, **73,74**, 291-303.
- Rzoska, S.J., Drozd-Rzoska, A., Ziolo, J., Haldas, P. and Jadzyn, P. (2001) Critical anomaly of dielectric permittivity for the temperature and pressure path on approaching the critical consolute point, *Phys. Rev. E*, **64**, 6406, 1104+.
- Stein, G.F. Allen, G.F. (1973) Electrical resistance of the system isobutyric acid-water near the critical point, *J. Chem. Phys.*, **59**, 6079-6087.
- Shaw, C-H. and Goldberg, W.I. (1976) Electrical conductivity of binary mixtures near the critical point, *J. Chem. Phys.*, **65**, 4906-4912.
- Ramakrishnan, J., Nagarajan, N., Kumar, A., Gopal, E.S.R., Chandrasekhar, P. and Ananthakrishna, G. (1978) Critical behaviour of electrical resistivity in polar + non-polar binary liquid systems, *J. Chem. Phys.*, **68**, 4098-4104.

27. Gunasekharan, M.K., Guha, S., Vani, V. and Gopal, E.S.R. (1985) Effect of interfacial polarisation on the critical behaviour of electrical resistivity and dielectric constant in polar+non-polar binary liquid mixtures, *Ber. Bunsenges. Phys. Chem...* **89**, 1279-1285.
28. Hamelin, J., Bose, T.K. and Thoen, J. (1990) Dielectric constant and the electric conductivity near the consolute point of the critical binary liquid mixture nitroethane-3-methylpentane, *Phys. Rev. A*, **42**, 4735-4742.
29. Oleinikova, and Bonetti, M. (1999) Evidence of a critical anomaly of the electrical conductivity in highly concentrated nonaqueous ionic mixtures, *Phys. Rev. Lett.*, **83**, 2985-2988.
30. W. Pyżuk, W. and Zboiński, K. (1977) Nonlinear dielectric effect near the critical point of binary mixtures, *Chem. Phys. Lett.*, **52**, 577-579.
31. Chrapeć, J., Rzoska, S.J. and Zioto, J. (1988) Properties of the nonlinear dielectric effect in the critical nitrobenzene in n-alkane solutions in a broad range of temperatures, *Chem. Phys.*, **122**, 471-477.
32. Chrapeć, J. and Rzoska, S.J. (1989) Nonlinear dielectric effect investigation in the immediate vicinity of the critical point, *Phys. Lett. A*, **139**, 343-346.
33. Orzechowski, K. (1991) Nonlinear dielectric effect in ethanol-dodecane critical mixture, *Physica B*, **172**, 339-345.
34. Rzoska, S.J. and Zioto, J. (1993) Experimental studies on the temperature behaviour of the nonlinear dielectric effect in critical binary solution, *Phys. Rev. E*, **47**, 1445-1447.
35. Rzoska, S.J. (1993) Kerr effect and the nonlinear dielectric effect on approaching the critical consolute point, *Phys. Rev. E*, **48**, 1136-1141.
36. Zioto, J. and Rzoska, S.J. (1999) Classical-nonclassical crossover between behaviour of critical and noncritical liquid binary solutions in strong electric field, *Phys. Rev. E*, **60**, 4983-4985.
37. Orzechowski, K. (1999) Electric field effect on the upper critical solution temperature, *Chem. Phys.*, **204**, 275-281.
38. Ripley, B.D. and McIntosh, R. (1961) The complex dielectric constant of solutions of trimethylpentane and nitrobenzene near the consolute temperature, *Can. J. Chem.* **39**, 526-534.
39. Lubezky, I. and McIntosh, R. (1974) Dielectric behaviours of the aniline-cyclohexane system in the consolute region, *Can. J. Chem.*, **52**, 3176-3180.
40. Givon, M. Pelach, I. and Efron, U. (1974) Behaviour of the dielectric constant of a binary liquid mixture near the critical point, *Phys. Lett. A*, **48**, 1-2.
41. Hollecker, M., Goulon, J., Thiebaut, J.M. and Rivail, J.L. (1975) Dielectric behaviour of a molecular liquid mixture in the one-phase precritical region, *Chem. Phys.*, **11**, 99-105.
42. Halliwell, R., Hutchinson, D.A. and McIntosh, R. (1976) A re-examination of nitrobenzene-2,2,4-trimethyl pentane system in the consolute region and of the thermodynamical considerations concerning the value of permittivity at the consolute point, *Can. J. Chem.*, **54**, 1139-1145.
43. Konecki, M. (1978) Electric permittivity near the critical point of binary mixtures, *Chem. Phys. Lett.*, **57**, 90-92.
44. Wagner, K.W. (1914) Erklärung der dielektrischen Nachwirkungsvorgänge auf Grund Maxwellscher Vorstellungen, *Arch. Elektrotechn.*, **II Bd. 9. Heft.**, 371-387.
45. Sengers, J.V., Bedeaux, D. Mazur, P. and Greer, S.C. (1980) Behaviour of the dielectric constant of fluids near a critical point, *Physica*, **104A**, 573-593.
46. Mistura, L. (1973) Behaviour of the dielectric constant near a critical point in fluid systems, *J. Chem. Phys.*, **59**, 4563-4564.
47. Chu, B., Schoenes, F.J., Fisher, M.E., (1969) Light scattering and pseudospinodal curves in the critical region, *Phys. Rev.*, **195**, 219-226.
48. Chrapeć, J., Rzoska, S.J. and Zioto, J. (1987) Pseudospinodal curve for binary solutions determined from the nonlinear dielectric effect, *Chem. Phys.*, **111**, 155-160.
49. Jasnov, D., Goldburg, W.J. And Semura, J.S. (1974) Resistance anomaly in a weak acid near the critical point, *Phys. Rev. A*, **9**, 355-359.
50. Wheeler, J.C., 1984, Singularity in the degree of dissociation of isobutyric acid, water solutions at the critical solution point, *Phys. Rev. A*, **30**, 648649.
51. Goulon, J., Greffe, J-L., Oxtoby, D.W. (1979) Droplet model for the analysis of the dielectric properties of critical binary mixtures, *J. Chem. Phys.*, **70**, 4742-4750.
52. Rzoska, S.J., Drozd-Rzoska, A., Górný, M., and Zioto, J., (1995) Time-scale dependence of the critical exponent for the nonlinear dielectric effect in critical binary solution, *Phys. Rev. E*, **52**, 6325-6328.
53. Kosmowska, M. and Orzechowski, K. to be published.
54. Kosmowska, M. and Orzechowski, K (2003) *Pol. J. Chem.* in press.

NONLINEAR DIELECTRIC EFFECT BEHAVIOR IN A CRITICAL AND NEAR-CRITICAL BINARY MIXTURE.

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Abstract. Experimental results are presented of the nonlinear dielectric effect (*NDE*) studies in the homogeneous phase of critical and near-critical binary mixtures. Both the stationary *NDE* and the related dynamic properties are discussed. In a critical mixture the *NDE* stationary response is described by a critical exponent $\psi \approx 0.4$ near the critical consolute temperature (T_C) and $\psi \approx 0.6$ remote from T_C . For the non-critical mixture the exponent describing the temperature behavior near T_C decreases down to $\psi \approx 0.1$. The temperature behavior of the *NDE* decay after switching off a strong electric field is described by the exponent $\gamma \approx 1.3$ for a critical mixture and $\gamma \rightarrow 1$ for a non-critical mixture. The possible explanation of the observed phenomena is proposed. It assumes the appearance of a quasi-nematic structure induced the external field, leading to the appearance of mean-field properties in the vicinity of T_C . The possible relationship with the behavior observed in a critical mixture under shear-flow, for instance when testing the anomaly of shear viscosity, is also shown.

In 1936 Arkadiusz Piekara reported results of studies of a strong electric field induced changes of dielectric permittivity in homogeneous nitrobenzene – hexane critical mixture. The measure of the mentioned nonlinearity, called nonlinear dielectric effect (*NDE*) is defined by: He noted, that “*a very strong increase towards positive values of NDE*” occurs [1, 2]. Despite numerous experimental results confirming this finding, the first successful parameterizations of experimental data were carried out by Pyżuk and Zboiński in 1978 [3], namely:

$$\varepsilon_{NDE} = \varepsilon_{NDE}^{bckg} + \varepsilon_{NDE}^{critical} = \varepsilon_{NDE}^{bckg} + A(T - T_C)^{-\psi}$$

where the index “bckg” denotes a non-critical, molecular, background effect, index “critical” is for the fluctuation-related pretransitional anomaly, T_C denotes the critical consolute temperature.

They obtained $\psi \approx 0.5$ A year later Malecki and Ziolo reported $\psi \approx 0.34$ [4].

In 1979 Goulon, Greffe and Oxtoby [5] associated the *NDE* anomaly with the elongation of fluctuations – droplets in a strong electric field. The derived a relation analogous to equation (1) with the universal critical exponent:

$$\psi = \gamma - 2\beta \approx 1.23 - 0.65 \approx 0.6 \quad (2)$$

where $\gamma \approx 1.23$ is related to the critical anomaly of susceptibility (compressibility) and $\beta \approx 0.325$ is critical exponent for the order parameter.

The same value of the exponent ψ was suggested for *NDE* and the electrooptical Kerr effect (*EKE*) [5]. In the eighties the same dependence was obtained for the improved droplet model by Pyžuk [6] and next by Hoyer and Stell [7]. The latter based on the microscopic analysis of the strong field induced distortion of the correlation function. Finally, in 1992 Onuki and Doi (OD) [8] obtained the same *NDE/EKE* critical exponent $\psi = \gamma - 2\beta \approx 0.6$ due to the analysis of the uniaxiality of the structure factor caused by dipolar interactions induced by a strong electric field. Despite the fact that critical anomalies of *NDE* and *EKE* are strong, experimental results remain puzzling for decades [2]. Only in the late eighties it was shown that that $\psi_{NDE} \approx 0.37$ for $T \rightarrow T_C$ and $\psi_{NDE} \approx 0.4$ [9-11] when data at some distance from T_C are considered. As for the *EKE* it was found that the exponent ψ_{EKE} spanned continuously from 0.65 to 0.88 (Pyžuk et al. [12], Degiorgio et al. [13, 14]). Only in 1993, for a selected critical mixture with a very small difference between dielectric permittivities of solution's components, $\psi_{EKE} \approx 0.6$ was obtained [15]. Hence [15, 16]:

$$\text{Experiment: } \psi_{EKE}(0.6 - 0.85) > \psi_{theoret.}(\approx 0.6) \geq \psi_{NDE}(\approx 0.4) \quad (3)$$

$$\text{Theories: } \psi_{EKE} = \psi_{NDE} = \psi_{theoret.} \quad (4)$$

In 1993 it was shown [16] that surprisingly, both above equations may be valid. The GGO droplet model relates both *NDE* and *EKE* critical anomalies with the elongation of critical fluctuations under a strong electric field. However, in ref. [16] it was suggested that an additional factor is also important: the correlation length may exhibit a semi-classical anisotropy:

$$\xi(E=0) = \xi_0 \theta^{-0.63} \mapsto \xi(E) = (\xi_{||}, \xi_{\perp}, \xi_{\perp})_{E \gg 0} \quad (5)$$

where $\theta = T - T_C$ or $\theta = (T - T_C)/T_C$. Components of the correlation length show non-classical $\xi_{||} \propto \theta^{-0.63}$ and mean-field (classical) $\xi_{\perp} \propto \theta^{-0.5}$ critical properties.

The application of the extended GGO model [5, 6] and relation (5) gave [16]:

$$\varepsilon_{NDE}^{crit.} \propto \xi^{-d} \chi^2 \propto \langle \Delta M^2 \rangle \chi \quad (6)$$

where $\langle \Delta M^2 \rangle \propto \theta^{2\beta}$, with non-classical exponent $\beta \approx 0.325$, denotes the mean square of the order parameter fluctuations. The semi-classical properties of the correlation length resulted in the classical behavior of the susceptibility (compressibility), i.e. $\gamma \rightarrow 1$ [16].

This gave: $\psi_{NDE} \approx 0.37$ for $T \rightarrow T_C$ and $\psi_{NDE} \approx 0.4$ when correction-to-scaling at final distances from T_C are considered [16]. The same reasoning enabled explanation the explanation of experimental values of the critical exponents for the electrooptical Kerr effect (*EKE*): $0.6 < \psi_{EKE} < 0.85$ [15, 16]. Different experimental values of ψ_{NDE} and ψ_{EKE} was related to the difference between definitions of *EKE* and *NDE*. The significant influence of the way of measurements on obtained values of ψ_{EKE} was also pointed [15, 16]. The validity of the proposed explanation based not only on the

agreement between experimental and “theoretical” values of ψ_{NDE} and ψ_{EKE} critical exponents but also on the experimental dependencies of A_{NDE} and A_{EKE} pretransitional amplitudes [15, 17]. Noteworthy is another unique feature of the *nonlinear dielectric effect*. In *NDE* studies the frequency (f_m) of the weak, measuring field can be changed [18-20]. The measurement time-scale ($\sim 1/f_m$) and the relevant system time-scale associated with the decay time of critical fluctuations (τ) can be correlated. Both $1/f_m < \tau$ and $1/f_m > \tau$ regimes are accessible for experimental values of f_m [18]. Hence, one may expect that near T_C ($1/f_m < \tau$) the *NDE* registers the response from a single average fluctuation whereas remote from T_C ($1/f_m > \tau$) an additional averaging of several fluctuations in takes place. This factor influences the value of the critical exponent. It is semi-classical near T_C and non-classical remote from T_C [18]. Until the late nineties *NDE* tests were conducted for measurement frequencies about few MHz [2]. Therefore, analysis limited to the vicinity of T_C gave $\psi_{NDE} \approx 0.4$ [9-11 and refs therein]. Only recently, tests within the kHz domain and the scan of frequencies start to be possible. In first studies of this type for $f_m \approx 300\text{kHz}$ the value of $\psi_{NDE} \approx 0.6$ for $T - T_C > 3\text{K}$ was registered [18].

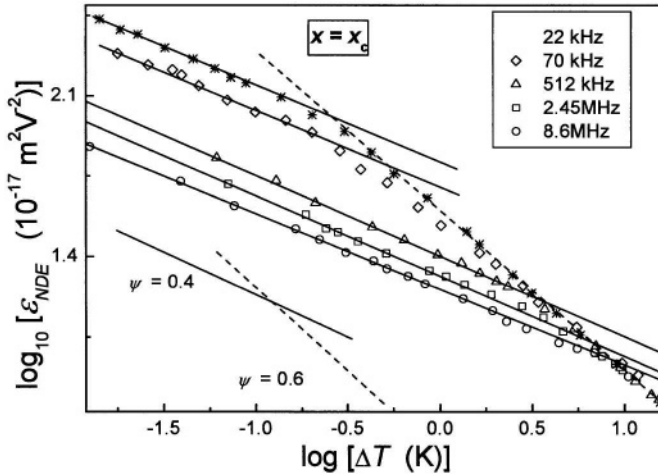


Figure 1 The critical part of *NDE* pretransitional effect in nitrobenzene – hexane critical solution, in a log-log scale showing values of critical exponents. The figure present data from ref. [18] and results of novel measurements for the lowest *NDE* measurement frequency $f = 22\text{ kHz}$ ever applied.

Fig. 1 and Fig. 2 present *NDE* pretransitional effects in nitrobenzene – dodecane mixture of critical and non-critical concentration. It contains results for $f_m = 22\text{ kHz}$, the lowest ever *NDE* measurement frequency applied. For this frequency the semi-classical region described by exponents $\beta \approx 0.33$ and $\gamma \approx 1$ leading to $\psi_{NDE} \approx 0.4$

shrinks to $T - T_C \approx 0.3K$ (!). For any frequency $\psi_{NDE} \approx 0.6$ and hence $\beta \approx 0.33$ and $\gamma \approx 1.23$, remote from T_C . For this domain the pretransitional behavior is totally non-classical. The pretransitional behavior in the non-critical mixture was analyzed using the pseudospinodal hypothesis:

$$\varepsilon_{NDE}^{critical} = A(T - T_{Sp})^{-\psi_{NDE}} \quad (7)$$

where $T > T_{Binodal} = T_{Sp} + \Delta T$, T_{Sp} is the extrapolated pseudospinodal temperature, basing on data in the thermodynamically stable region, above the coexistence curve dissolution temperature $T_{Binodal}$.

The most striking feature of the “non-critical” anomaly is the decreases of ψ_{NDE} down to almost 0.1 on approaching the singularity temperature T_{Sp}

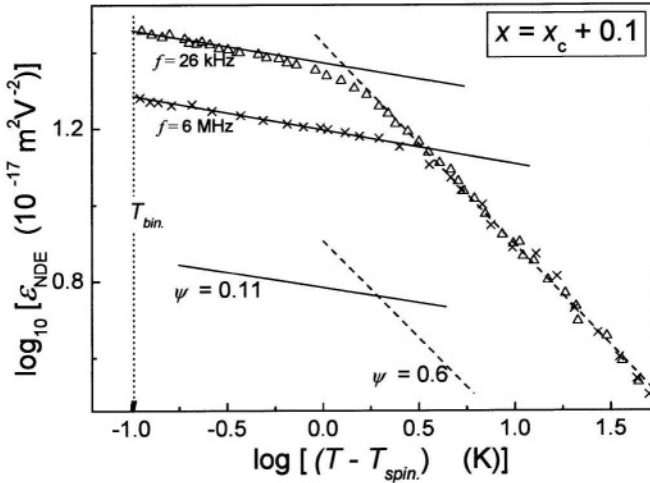


Figure 2 The critical part of the NDE pretransitional effect in nitrobenzene – hexane near-critical solution. The log – log scale was plotted basing on the pseudospinodal hypothesis: $T_{spin.} = T_{bin.} - \Delta T$.

Studies were carried out in the homogeneous for $T > T_{spin.}$, i. e. above the temperature of the separation of phase (binodal temperature). Applied frequencies of the weak measuring field are given in figure

In the NDE experiments the influence of the decay time of critical fluctuations on results can be also detected from a time-domain scanning of the deformation of NDE response after switching off a strong electric field. In practice, such behavior is reduced to $T - T_C < 0.2K$ in temperature studies [21-24]. More favorite is the isothermal, pressure approaching to the critical consolute point in which such deformation may occur already for $P_C - P \approx 40MPa$ [23].

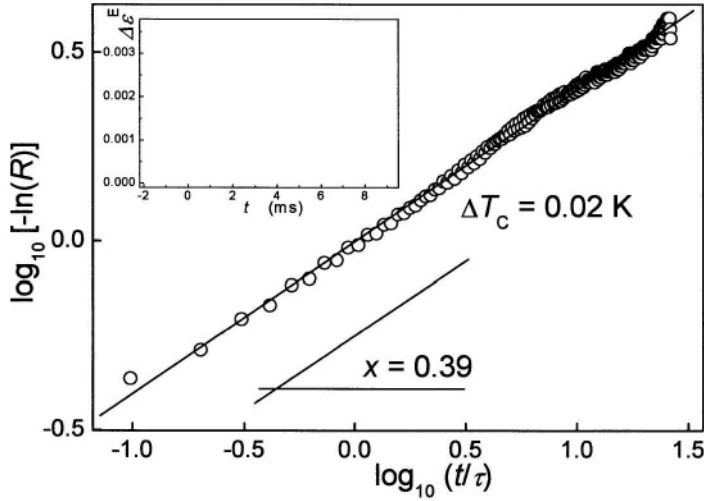


Figure 3 NDE decay after switching off a strong electric field in nitrobenzene – dodecane critical solutions. The inset shows experimentally observed “nonlinear” changes of dielectric permittivity for NDE measured in the DC-mode, i.e. strong, steady electric field is switched-off. In this case $U = 500$ V for $d = 0.5$ gap of the measurement capacitor. This way of measurement reduces the influence of heating effects associated with ionic contaminations. The main part of the shows the stretched exponential behavior of experimental data from the inset.

As shown in refs. [21-24] the NDE decay may be described by the stretched – exponential response function:

$$R(t) = \frac{\varepsilon_{NDE}(t)}{\varepsilon_{NDE}(\Delta t_D \gg \tau)} \quad (8)$$

where t is the elapsed time after switching-off the strong electric field, Δt_D described the length of the DC pulse. The dynamic droplet model predicted the stretched-exponential (SE) decay [25]:

$$R(t) = \exp\left[-\left(\frac{t}{\tau}\right)^x\right] \quad , \quad x = \frac{2-\eta}{5-\eta} \quad \text{and} \quad t/\tau > 1 \quad (9)$$

where $\eta \approx 0.04$ is the critical exponent for the correlation function.

The less phenomenological OD model gave [8]:

$$R(t) = \frac{4}{\pi} \int_0^x dy \left(\frac{y^2}{1+y^2} \right) \exp\left[-2K(y) \frac{t}{\tau_{OD}}\right] \quad (10)$$

where $K(y)$ is the Kawasaki function.

For early stages of the decay function takes the von-Schweindler form [8]:

$$\tau_{OD} \approx 1 - 2.29(t/\tau_{OD}) \quad \text{for} \quad (t/\tau_{OD}) \ll 1 \quad (11)$$

The validity of the relations (10) – (13) was shown for time-resolved *NDE* [21-24] and *EKE* [21, 25] studies. However, there are significant discrepancy between experiment and theory in this case. The dynamic droplet model [14, 25] and the OD [8] model also predicted:

$$\tau \propto \theta^y = \theta^{-(z+z_\eta)y} = \theta^{-3.06 \times 0.63} \approx \theta^{-1.9} \quad (12)$$

where $z = 3$ is the dynamic critical exponent and $z_\eta \approx 0.064$ is the viscosity exponent.

However, experiments yielded [21-25 and refs. therein]: $y = 1.1 - 1.3$

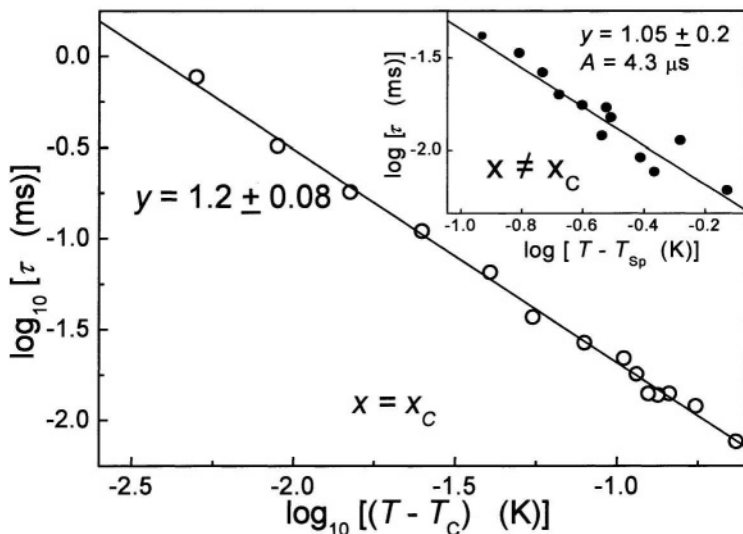


Figure 4 The temperature dependence of *NDE* decay times in a critical and non-critical nitrobenzene – dodecane solution.

Fig. 3 presents the validity of the mentioned universality of the *SE* behavior in a critical mixture. The inset presents the form of the *NDE* response due to the application of a pulse of a strong electric field, which was the base of the plot in the main part. The temperature evolution of the *NDE* decay times, i.e. relaxation times of critical fluctuations, are presented in Fig. 4. For the critical mixture $y \approx 1.3$ and for the non-critical ones $y \approx 1.1$. Worth recalling is the fact that existing theoretical models predict $y \approx 1.9$ for a critical mixture [8, 14, 25]. There are no theoretical predictions for non-critical mixtures. The possible explanation of the discrepancy between theory and experiment may be associated with the fact that in nitrobenzene – *n*-alkane critical mixture the nitrobenzene-rich ($\epsilon_{rich} > \epsilon$) and nitrobenzene-poor ($\epsilon_{poor} < \epsilon$, ϵ is the average permittivity of the mixture) pretransitional fluctuations occur. One may expect

that the nitrobenzene “rich” fluctuations will expand along the direction of E and the “poor” fluctuations will shrink. Hence, the critical fluctuation under a strong electric field induces a complex liquid “structure” composed of prolate (*rod-like*) and oblate (*disk-like*) fluctuations, as shown in Fig. 5.

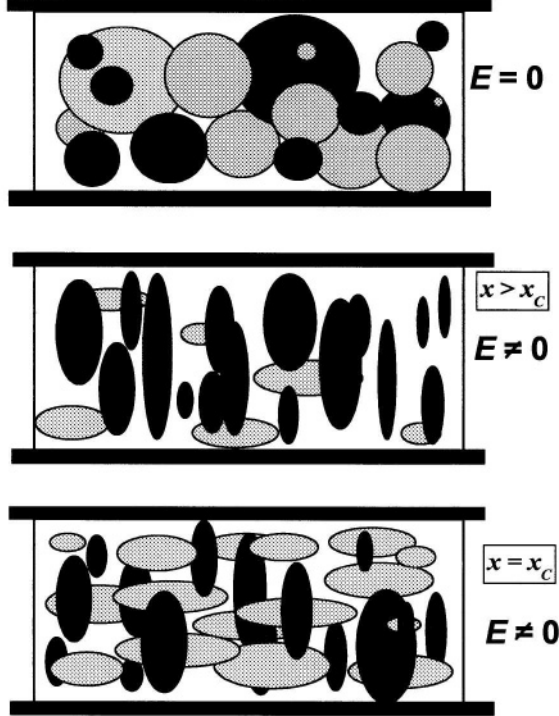


Figure 5 The assumed picture of critical an near-critical mixture under strong external electric field

However, the oblate deformation was never found in experiments on liquid droplets immersed in another liquid (for instance oil in water). Only the prolate deformation was observed [26-28]. The lack of the disc-like deformation, despite the basic electrostatics-based analysis [29], was explained as the consequence of the instability of the oblate form [28]. However, this factor may not be of vital importance for naturally unstable, short-lived critical fluctuations. Hence, taking into account the semi-classical behavior fluctuations one may expect [24]:

$$(\xi_{long}, \xi_{short}, \xi_{short}) \text{ for } \varepsilon_{rich} > \varepsilon_{mixt.} \text{ (prolate, rod-like)} \quad (13)$$

$$(\xi_{short}, \xi_{long}, \xi_{long}) \text{ for } \varepsilon_{rich} < \varepsilon_{mixt.} \text{ (oblate, disc-like)} \quad (14)$$

with: $\xi_{long} \propto \theta^{-0.63}$ (non-classical) and $\xi_{short} \propto \theta^{-0.5}$ (classical)

Based on this the evolution of the decay time may average from oblate and prolate quasi-nematic structures:

$$y = 1/2[(z + z_\eta)\nu_{short} + (z + z_\eta)\nu_{long}] \approx 1.3 \quad (15)$$

where $z_\eta = 0.064$ is the dynamic exponent for viscosity and the diffusion coefficient.

For the non-critical mixture one type of fluctuations dominates. In such a case:

$$y(x \neq x_C) \rightarrow y = (z + z_\eta)\nu_{short} \approx 1.1 \quad (16)$$

Values of the exponent y resulting from the above relations are in fair agreement with experimental result (see above and refs. [21-25]).

The same reasoning may explain the small value of the exponent ψ_{NDE} for a non-critical mixture (Fig. 2). When moving always from the critical concentration the excess number of prolate or oblate fluctuations increase. This excess of one-type fluctuations is associated with totally classical pretransitional effect. Hence, for a non-critical mixture:

$$\psi_{NDE}(x \neq x_C) \rightarrow \psi_{NDE} = \gamma - 2\beta \approx 1 - 2 \times 0.5 = 0 \quad (17)$$

Worth recalling here is the fact that in a critical nitrobenzene – hexane mixture under flow, where shear induced elongation for all fluctuation, classical exponents $\gamma = 1$ and $\beta = 1/2$ were obtained [30]. Remote from T_C , for the weak shear rate $S\tau < 1$, Beysens et al [30] obtained the non-classical behavior with $\gamma = 1.23$.

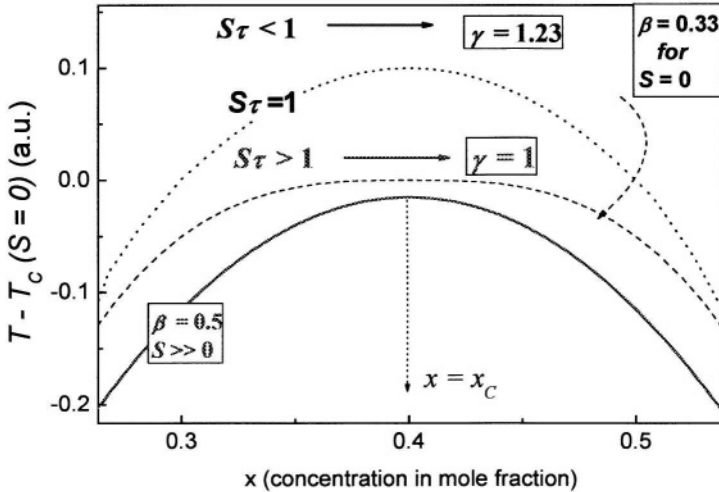


Figure 6 Schematic plot of results of results obtained in a critical mixture under shear flow [30]. Exponent γ was determined from light scattering studies and the exponent β from miscibility observations. The dashed coexistence curve is for the non-sheared mixture ($S = 0$). Solid curve shows the binodal under shear flow. The dotted curve at the top part of the figure shows the position where the condition $S\tau = 1$ occurs.

In the opinion of the authors the appearance of mean-field, classical, behavior near the critical consolute point may be concluded also for the critical anomaly of shear viscosity $\eta(T)$, at least when tests are carried out in the capillary viscometer. Generally, the following relation is predicted for the shear viscosity in the homogeneous phase of a critical mixture [31]:

$$\eta(\xi) = \eta_B (\Lambda \xi_0)^{z_\eta} t^{-z_\eta \nu} = \eta_B A_\eta t^{-\phi} \quad (18)$$

where Λ is the Debye cutoff number, $\xi = \xi_0 t^{-\nu}$ is the correlation length, and ξ_0 is the correlation length amplitude. A_η and $\nu \approx 0.63$ are the critical amplitude and the critical exponent, respectively. z_η is the universal critical exponent. The exponent: $z_\eta = \phi/\nu$.

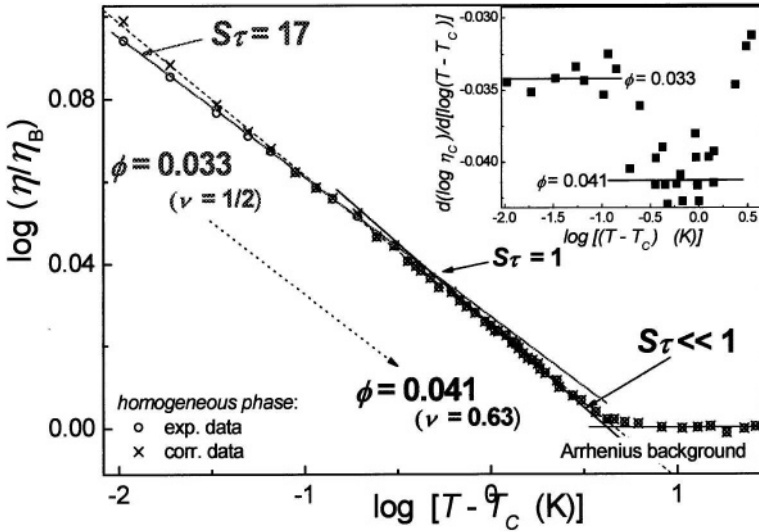


Figure 7 Critical anomaly of the shear viscosity in the homogeneous phase of nitrobenzene – decane critical mixture. The dashed curve and shows the analysis employing shear-rate corrected data (crosses). Open circles are for “direct” experimental data. Separate analysis of these data near T_C and remote from T_C gave different values of the critical exponents, as shown in the figure. The shift of the values of the shear-rate coefficient on approaching T_C is also shown. The inset presents the novel derivative analysis of the “direct” experimental data from the main part of the figure.

Existing analysis suggest that experimental $\eta(T)$ data can follow the above relation only if the experimental values are transformed to reduce shear rate coefficient S_τ on approaching T_C [31 and refs. therein]. Results of such analysis are shown by “cross-

point” in Fig. 7. The same Figure presents also “rough”, non-transformed data, as shown in Fig. 7, following ref. [31]. Assuming the significance of the quasi-nematic picture also for the shear viscosity anomaly and taking $\eta \propto (\xi_{\perp})^{z_{\eta}}$ one can obtain in the vicinity of T_C [31]:

$$z_{\eta} = \phi/\nu_{class.} \approx 0.033/0.5 = 0.066 \pm 0.002, \quad \nu_{\perp} = 0.5 \quad (19)$$

for $T \rightarrow T_C$.

On moving away from T_C the order parameter fluctuations are less affected by the shear and their elongation decreases ($S\tau < 1$) [31]:

$$z_{\eta} = \phi/\nu_{non-class.} \approx 0.041/0.63 = 0.065 \pm 0.002, \quad \nu_{\perp} = \nu \approx 0.63, \quad (20)$$

for $T > T_C + 1K$

The obtained values of z_{η} is the approximately the same near and remote from T_C . The discussed behavior is clearly visible for the derivative analysis of the data from the main plot, presented in the inset in Fig. 7.

Results presented above conclude existing experimental facts for the nonlinear dielectric effect in homogeneous critical mixtures. A comprehensive explanation of observed phenomena is also proposed. It bases on the possible appearance of quasi-nematic structure with semi-classical critical properties under strong electric field. Noteworthy is the similarity of the *NDE* behavior in the homogeneous phase, particularly for a non-critical mixture, with the *NDE* anomaly in isotropic phase of nematogens, with naturally elongated rod-like molecules [31-34]. In both case the susceptibility exponent $\gamma = 1$ and the decay exponent $y = 1$. Pretransitional anomalies of *NDE* and *EKE* are naturally associated with a strong electric field. Hence, worth mentioning is also the question of the strong electric field induced shift of the critical consolute temperature T_C . All existing experimental data shows a small decrease of $T_C(E)$ in comparison with $T_C(E=0)$, i.e. the give: $dT_C/dE^2 < 0$. However, the most complete theoretical analysis gave a clear opposite prediction, i.e. $dT_C/dE^2 > 0$ [35, 36 and refs. therein]. Such prediction can be associated with the increase of the volume of the critical fluctuation and hence correlation length due to the electrostriction as one may conclude from refs. [35, 36]. The discussed above elongation of fluctuation and the appearance of the quasi-nematic structure causes the decrease of the correlation length what is correlated with $dT_C/dE^2 < 0$, in agreement with experimental observations. It is noteworthy that the downward shift of T_C was also obtained in critical mixtures under shear flow (see Fig. 6). Hence, also here the picture proposed above is an agreement with experimental results. It is noteworthy is also the negligible influence of the electrostriction-related effect in comparison with the elongation of critical fluctuations on *NDE* and *EKE* “static” critical exponent clearly shown within the droplet model [5, 6].

The anisotropy induced under strong external field (strong electric field, shear flow) may result in the appearance of mean-field properties near T_C and non-classical remote from T_C . This sequence is reversed, in comparison with an “ordinary”, non-disturbed (isotropic) critical mixture, i.e. for $E \rightarrow 0$ or $S\tau \rightarrow 0$.

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References

1. Piekara A. (1936) Saturation electrique et point critique de dissolution (presente par Aime Cotton)", *C. R. Acad. Sci. Paris* **203**, 1058-1059.
2. Chełkowski A (1993) *Fizyka Dielektryków* (in Polish), PWN-Warsaw.
3. Pyżuk W. and Zboiński K. (1977) Nonlinear dielectric effect near the critical point of binary mixture, *Chem. Phys. Lett.* **52**, 577-579.
4. Małecki J. and Ziolo J. (1978) Nonlinear dielectric effect study of pretransitional effects above the phase transition temperature, *Chem. Phys.* **35**, 187-191.
5. Goulon J., Greffe J.-L., Oxtoby D. W. (1979) Droplet model for the analysis of the dielectric properties of critical binary mixtures, *J. Chem. Phys.* **70**, 4742-4750.
6. W. Pyżuk (1986) Effects induced by strong electric fields in critical solutions", *Habilitation thesis*, Warsaw University Press.
7. Hoyer J. S. and Stell G. (1984) Kerr effect I. Field effect on correlation in polarizable fluids", *J. Chem. Phys.* **81**, 3200-3220.
8. Onuki A. and Doi M. (1992) Electric birefringence and dichroism in critical binary mixtures, *Europhys. Lett.* **17**, 63-68.
9. Rzoska S. J., Chrapeć J. and Ziolo J. (1986) Nonlinear dielectric effect in the vicinity of the critical point of binary and doped critical solutions", *Physica A* **139**, 569-584.
10. Chrapeć J. and Rzoska S. J. (1989) Nonlinear dielectric effect investigation in the immediate vicinity of the critical point, *Phys. Lett. A*, **139**, 343-346.
11. Chrapeć J., Rzoska S. J. and Ziolo J. (1988) Properties of the nonlinear dielectric effect in critical nitrobenzene in n-alkane solutions in a broad range of temperatures, *Chem. Phys.* **122**, 471-477.
12. Pyżuk W. (1992) The critical exponent for the Kerr effect in binary liquids, *Europhys. Lett.* **17**, 339-342.
13. Degiorgio V. and Piazza R., Electric birefringence of critical micellar solutions" (1985) *Phys. Rev. Lett.* **55**, 288-291
14. Bellini T. and Degiorgio V. (1989) Electric birefringence of a binary liquid mixture near the critical consolute point, *Phys. Rev. B* **39**, 7263-7265.
15. Rzoska S. J., Degiorgio V. and Giardini M. (1994) Relationship between dielectric properties and critical behaviour of the electric birefringence on binary liquid mixtures, *Phys. Rev. E* **49**, 5234-5237.
16. Rzoska S. J. (1993) Kerr effect and nonlinear dielectric effect on approaching the critical consolute point, *Phys. Rev. E* **48**, 1136-1143.
17. Rzoska S. J. and Ziolo J. (1993) Experimental studies of the nonlinear dielectric effect in critical solutions", *Phys. Rev. E* **47**, 1445-1448.
18. Rzoska S. J. Drozd – Rzoska A., Górny M. and Ziolo J. (1995) Time-scale dependence of the critical exponent for the nonlinear dielectric effect, *Phys. Rev. E* **52**, 6325-6328.
19. M. Górny, J. Ziolo and S. J. Rzoska, (1996) A new application of nonlinear dielectric effect for studying relaxation processes in liquids, *Rev. Sci. Instrum.* **67**, 4290-4293.
20. Górny M. and Rzoska S. J. (2004) Experimental solutions for nonlinear dielectric effect measurements in complex liquids, *this volume*.
21. Rzoska S. J., Degiorgio V., Bellini T. and Piazza R. (1994) Relaxation of the electric birefringence near a critical consolute point", *Phys. Rev. E* **49**, 3093-3096.
22. Rzoska S. J., Górny M. and Ziolo J. (1991) Stretched-exponential relaxation of the nonlinear dielectric effect in a critical solution, *Phys. Rev. A* **43**, 1100-1102.
23. Rzoska S. J., Ziolo J., Drozd – Rzoska A. (1997) Stretched-relaxation after switching-off a strong electric field in a critical solution under high pressure", *Phys. Rev. E* **56**, 2578-2581.
24. Rzoska S. J., Drozd-Rzoska A., Ziolo J. (2000) Dynamics of critical fluctuations in a binary mixture of limited miscibility under strong electric field, *Phys. Rev. E* **61**, 960-964.
25. Piazza R., Bellini T., and Degiorgio V., Goldstein R. E., Leibler S., and Lipowsky R. (1988) Stretched-exponential relaxation of birefringence in a critical binary mixture, *Phys. Rev. B* **38**, 7223-7226.
26. C. O'Konsky and H. C. Thatcher (1953) The distortion of aerosol droplets by an electric field, *J. Phys. Chem.* **57**, 955-958.

27. Garton G. C. and Krasucki Z. (1964) Bubbles in insulating liquids: stability in an electric field, *Proc. R. Soc. London*, **280**, 211-226.
28. Scaife B.K.P. (1989) *Principles of Dielectrics*", Claredon Press., Oxford.
29. Stratton J. A. (1941) *Electromagnetic Theory*, McGraw-Hill, New York and London.
30. Beysens D., Gbadamasi M. , and Moncef- Bouanz B. (1982) New developments of binary fluids under shear flow", *Phys. Rev. A* **28**, 2491 – 2509.
31. Drozd-Rzoska A. (2000) Shear viscosity studies above and below the critical consolute point in a nitrobenzene - decane mixture, *Phys. Rev. E* **62**, 8071-8078.
32. Drozd-Rzoska A. (1999) Quasicritical behavior of dielectric permittivity in the isotropic phase of n-hexyl- cyanobiphenyl in a large range of temperatures and pressures, *Phys. Rev. E* **59**, 5556.
33. Drozd-Rzoska A. (1998) Influence of measurement frequency on the pretransitional behaviour of non-linear dielectric effect in the isotropic phase of liquid crystalline materials, *Liquid Crystals* **24**, 835 -841.
34. Drozd-Rzoska A. and Rzoska S. J. (2002) Complex dynamics of the isotropic 4-cyano-4-n-pentylbiphenyl (SCB) in linear and nonlinear dielectric relaxation studies, *Phys. Rev. E* **65**, 041701.
35. Orzechowski K. (1999) Electric-Field Effect on the Upper Critical Solution Temperature, *Chem. Phys.* **240**, 275-281.
36. Onuki A. (1995) Electric-Field Effects in Fluids Near the Critical-Point, *Europhys. Lett.* **29**, 611-616.

ELECTRIC FIELD EFFECTS NEAR CRITICAL POINTS

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Abstract. We present a general Ginzburg-Landau theory of electrostatic interactions and electric field effects for the order parameter, the polarization, and the charge density. Electric field effects are then investigated in fluids near the critical points and liquid crystals near the isotropic-nematic phase transition. We also examine the liquid-liquid phase transition in polar binary mixtures with a small fraction of ions. Some new predictions are given together with a short review.

1 Introduction

Electric field effects in near-critical fluids have been investigated by many authors [1-19]. Examples are weak critical singularity in the macroscopic dielectric constant and the refractive index, nonlinear dielectric effects, and electric birefringence (Kerr effect). In near-critical fluids the order parameter ψ (density or concentration) exhibits large fluctuations and the local dielectric constant ε becomes strongly inhomogeneous. Similar effects have also been studied in liquid crystals, where the local dielectric tensor depends on the orientation tensor Q_{ij} or the director $\mathbf{n}$ [20, 21].

We here summarize theoretical results for near-critical fluids. Usually, the order parameter ψ has been taken to be $n/n_c - 1$ for pure (one-component) fluids and to $c - c_c$ for binary fluid mixtures, where n is the density and c is the molar concentration or volume fraction of one component. The quantities with the subscript c will represent the critical values. To be precise, however, there is a mapping relationship between fluids and Ising systems in describing the critical phenomena [22]. The number density in fluids may be expressed as

$$n(\mathbf{r}) = n_0 + \alpha_1 \psi(\mathbf{r}) + \beta_1 \psi(\mathbf{r})^2, \quad (1.1)$$

in terms of the spin ψ (=the true order parameter) in the corresponding Ising system. Although not well justified, we expand ε in powers of ψ in a local form as

$$\varepsilon(\mathbf{r}) = \varepsilon_0 + \varepsilon_1 \psi(\mathbf{r}) + \frac{1}{2} \varepsilon_2 \psi(\mathbf{r})^2 + \cdots, \quad (1.2)$$

where ε_1 and ε_2 are constants independent of the reduced temperature $\tau = T/T_c - 1$. The quantity ψ^2 corresponds to the energy density in Ising systems and the average $\langle \psi^2 \rangle$ over the thermal fluctuations contains a term proportional to $|\tau|^{1-\alpha}$ on the critical isochore above T_c and on the coexistence curve below T_c [22]. Therefore, the weak singularity ($\propto |\tau|^{1-\alpha}$) appears in the so-called coexistence curve diameter for $\beta_1 \neq 0$ below T_c and in the thermal average $\langle \varepsilon \rangle$ for $\varepsilon_2 \neq 0$ above T_c .

Regarding the expansion (1.2) we make two remarks. (i) For nonpolar pure fluids the overall density-dependence of ε may well be approximated by the Clausius-Mossotti relation $(\varepsilon - 1)/(\varepsilon + 2) = \alpha_m n/3$, where α_m is the molecular polarizability. Using this relation and assuming $\beta_1 = 0$ in (1.1) we have $\varepsilon_1 = (\varepsilon_0 - 1)(\varepsilon_0 + 2)/3$ and $\varepsilon_2 = 2\varepsilon_1^2/(2 + \varepsilon_0) > 0$. However, dielectric formulas like Clausius-Mossotti are valid only in the long wavelength limit where the electric field fluctuations are neglected (in text books) or averaged out [3, 4]. Thus estimation of ε_2 from Clausius-Mossotti is not justified when we use (1.2) to derive dielectric anomaly due to the small-scale critical fluctuations. Notice that (1.1) itself gives rise to a contribution ($= 2\beta_1\varepsilon_1/\alpha_1$) to ε_2 from the linear dependence $\varepsilon = \varepsilon_c + \varepsilon_1(n/n_c - 1)$. (ii) For binary mixtures A+B, ε_1 should be of order $\varepsilon_A - \varepsilon_B$, where ε_A and ε_B are the dielectric constants of the two components, so ε_1 can be 10-100 in polar binary mixtures (where at least one component is polar). Electric field effects are much stronger in polar binary mixtures than in nonpolar fluids.

Once we assume (1.2), it is straightforward to solve the Maxwell equations within the fluid if the deviation $\delta\varepsilon = \varepsilon - \langle \varepsilon \rangle$ is treated as a small perturbation. Hereafter $\langle \dots \rangle$ represents the average over the fluctuations of ψ . The macroscopic static dielectric tensor $\overset{\leftrightarrow}{\varepsilon}_{\text{eff}}$ is obtained from the relation $\langle \mathbf{D} \rangle = \overset{\leftrightarrow}{\varepsilon}_{\text{eff}} \cdot \langle \mathbf{E} \rangle$ between the average electric induction $\langle \mathbf{D} \rangle$ and the average electric field $\langle \mathbf{E} \rangle$. To leading order, the fluctuation contribution $\Delta \overset{\leftrightarrow}{\varepsilon}_{\text{eff}}$ in the long wavelength limit can be expressed in terms of the structure factor $I(\mathbf{q}) = \langle |\psi_{\mathbf{q}}|^2 \rangle$ [3, 23]. The contribution from the long wavelength fluctuations with $q < \Lambda$ is written as

$$\Delta \overset{\leftrightarrow}{\varepsilon}_{\text{eff}}^< = \int_{\mathbf{q}} I(\mathbf{q}) \left(\frac{1}{2} \varepsilon_2 \overset{\leftrightarrow}{I} - \frac{1}{\varepsilon_0} \varepsilon_1^2 \hat{\mathbf{q}} \hat{\mathbf{q}} \right), \quad (1.3)$$

where $\int_{\mathbf{q}} = (2\pi)^{-3} \int d\mathbf{q}$, $\overset{\leftrightarrow}{I} = \{\delta_{ij}\}$ is the unit tensor, and $\hat{\mathbf{q}} = q^{-1}\mathbf{q}$. The upper cutoff wave number Λ in (1.3) is smaller than the inverse particle size. Note that $I(\mathbf{q})$ is uniaxial at small q in the direction of electric field, but it is nearly isotropic at large q . Thus the contribution $\Delta \overset{\leftrightarrow}{\varepsilon}_{\text{eff}}^>$ from the short wavelength fluctuations with $q > \Lambda$ is proportional to the unit tensor and may be included into ε_0 in (1.2).

We may also calculate an electromagnetic wave within near-critical fluids [3, 23]. Let $\mathbf{k}$ be its wave vector. The average electric field $\langle \mathbf{E} \rangle$ is nearly perpendicular to $\mathbf{k}$, oscillates with frequency ω , and obeys

$$\omega^2 \left[\langle \varepsilon(\omega) \rangle + \Delta \overset{\leftrightarrow}{\varepsilon}(\mathbf{k}, \omega) \right] \cdot \langle \mathbf{E} \rangle = c^2 k^2 \langle \mathbf{E} \rangle, \quad (1.4)$$

where $\varepsilon(\omega) = \varepsilon_0(\omega) + \varepsilon_1(\omega)\psi + \dots$ is the dielectric constant at frequency $\omega (\cong ck/\varepsilon_0(\omega)^{1/2})$ dependent on ψ as in (1.2). The fluctuation contribution to the dielectric tensor for the electromagnetic waves is written as [3, 23, 24]

$$\Delta_{\vec{\varepsilon}}^{\leftrightarrow}(\mathbf{k}, \omega) = \frac{\varepsilon_1(\omega)^2}{\varepsilon_0(\omega)} \int_{\mathbf{q}} \frac{I(\mathbf{k} - \mathbf{q})}{q^2 - k^2 - i0} (k^2 \vec{I}_{\perp} - \mathbf{q}_{\perp} \mathbf{q}_{\perp}), \quad (1.5)$$

where $\mathbf{q}_{\perp} = \mathbf{q} - k^{-2}(\mathbf{q} \cdot \mathbf{k})\mathbf{k}$ and $\vec{I}_{\perp} = \vec{I} - k^{-2}\mathbf{k}\mathbf{k}$ are perpendicular to $\mathbf{k}$, and $+i0$ represents a small imaginary part arising from the causality law. The imaginary part gives rise to damping and can be calculated using the formula $1/(x - i0) = \text{vp}(1/x) + i\pi\delta(x)$ with vp representing taking the Cauchy principal value. Then $\Delta_{\vec{\varepsilon}}^{\leftrightarrow}(\mathbf{k}, \omega)$ has two eigenvalues $\Delta_{\alpha}(\omega)$ ($\alpha = 1, 2$) in the plane perpendicular to $\mathbf{k}$. The dispersion relations for the two polarizations are written as

$$k = c^{-1}\omega[\langle\varepsilon(\omega)\rangle + \Delta_{\pm}(\omega)]^{1/2}. \quad (1.6)$$

In particular, if we apply an electric field along the z axis and send a laser beam along the x axis, we have $\Delta\varepsilon_{yz} = \Delta\varepsilon_{zy} = 0$. The principal polarization is then either along the z axis ($\alpha = 1$) or along the y axis ($\alpha = 2$). The turbidity $\mathcal{T}_{\alpha}$ is written as

$$\mathcal{T}_{\alpha} = \frac{k}{\varepsilon_0(\omega)} \text{Im}\Delta_{\alpha}(\omega) = \frac{\omega^4}{16\pi^2 c^4} \varepsilon_1(\omega)^2 \int d\Omega I(\mathbf{k} - k\hat{\mathbf{q}})(1 - \hat{q}_{\alpha}^2), \quad (1.7)$$

where $\hat{q}_1 = \hat{q}_z$, $\hat{q}_2 = \hat{q}_y$, and $d\Omega$ represents integration over the direction $\hat{\mathbf{q}}$. The Ornstein-Zernike intensity gives the famous turbidity expression. Generally, when $I(\mathbf{q})$ depends on $\hat{\mathbf{q}}$, the difference $\Delta_1 - \Delta_2$ becomes nonvanishing. Its real and imaginary parts can be measured as (form) birefringence and dichroism, respectively. In near-critical fluids under shear flow, both these effects exhibit strong critical divergence [25]. In polymer science, birefringence in shear flow arising from the above origin is called form birefringence [24], whereas alignment of optically anisotropic particles gives rise to anisotropy in $\langle\varepsilon_{ij}\rangle$ leading to intrinsic birefringence. Form dichroism is maximum when the scattering objects have sizes of the order of the laser wavelength and, for shear flow, it has been used to detect anisotropy of the particle pair correlations in colloidal suspensions [26] and polymer solutions [27]. In Ref.[23] an experimental setup to measure dichroism was illustrated.

In Section 3 we will examine the effects mentioned above using (1.3) and (1.5).

2 Ginzburg-Landau free energy in electric field

Phase transitions occur in various systems in electric field. To treat such problems we need to construct a Ginzburg-Landau free energy including electric field under each given boundary condition. However, there seems to be no clear-cut argument on its form in the literature. We will give such a general theory in which the gross

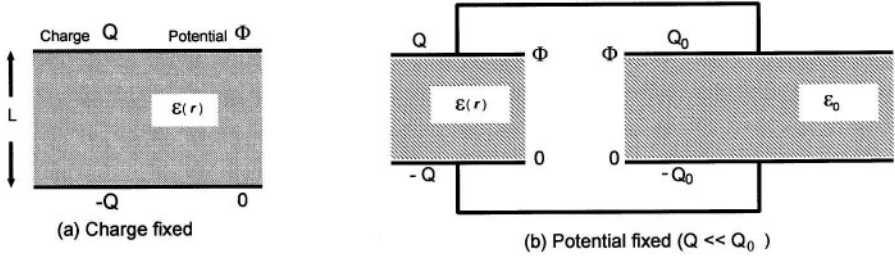


Figure 1: (a) System of a capacitor and a dielectric material with inhomogeneous dielectric constant $\epsilon(\mathbf{r})$ at fixed capacitor charge Q . The potential difference Φ is a fluctuating quantity dependent on $\epsilon(\mathbf{r})$. (b) Two capacitors connected in parallel with charges Q and Q_0 . The smaller one contains an inhomogeneous dielectric material, and the larger one a homogeneous dielectric material. In the limit $Q/Q_0 \rightarrow 0$, the potential difference Φ becomes fixed, while Q is a fluctuating quantity.

variables are the order parameter ψ , the polarization $\mathbf{p}$, and the charge density ρ . They are coarse-grained variables with their microscopic space variations being smoothed out. Since the electromagnetic field is determined for instantaneous values of the gross variables, we will suppress their time dependence.

2.1 Dielectrics under given capacitor charge

The first typical experimental geometry is shown in Fig.1a, where we insert our system between two parallel metallic plates with area S and separation distance L . We assume $S^{1/2} \gg L$ and neglect the effects of edge fields. Generalization to other geometries is straightforward. The z axis is taken perpendicularly to the plates. Let the average surface charge density of the upper plate be σ_{ex} and that of the lower plate be $-\sigma_{\text{ex}}$. The total charge on the upper plate is

$$Q = S\sigma_{\text{ex}}. \quad (2.1)$$

The Ginzburg-Landau free energy functional F consists of a chemical part $F_{\text{ch}}\{\psi, \mathbf{p}, \rho\}$ and an electrostatic part $F_{\text{st}}\{\mathbf{p}, \rho, Q\}$ as

$$F = F_{\text{ch}}\{\psi, \mathbf{p}, \rho\} + F_{\text{st}}\{\mathbf{p}, \rho, Q\}, \quad (2.2)$$

where ψ represents a set of variables including the order parameter. In ferroelectric systems $\mathbf{p}$ is the order parameter. The equilibrium distribution of the gross variables is given by $\text{const.} \exp(-F/k_B T)$ at each fixed Q . We determine F_{st} as follows.

If infinitesimal deviations $\delta \mathbf{p}$, $\delta \rho$, and δQ are superimposed on $\mathbf{p}$, ρ , and Q , the incremental change of F_{st} should be given by the work done by the electric field,

$$\begin{aligned} \delta F_{\text{st}} &= F_{\text{st}}\{\mathbf{p} + \delta \mathbf{p}, \rho + \delta \rho, Q + \delta Q\} - F_{\text{st}}\{\mathbf{p}, \rho, Q\} \\ &= \int d\mathbf{r} [-\mathbf{E} \cdot \delta \mathbf{p} + \phi \delta \rho] + \Phi \delta Q, \end{aligned} \quad (2.3)$$

where the space integral is within the system between the plates, $\mathbf{E} = -\nabla \phi$ is the electric field vector, and Φ is the potential difference between the two plates. The electric potential ϕ may be set equal to 0 at the lower plate and Φ at the upper plate. The electric induction $\mathbf{D} = \mathbf{E} + 4\pi \mathbf{P}$ satisfies

$$\nabla \cdot \mathbf{D} = -\nabla^2 \phi + 4\pi \nabla \cdot \mathbf{p} = 4\pi \rho, \quad (2.4)$$

in the bulk region. The potential ϕ satisfies

$$-\nabla^2 \phi = 4\pi \rho_{\text{eff}}, \quad (2.5)$$

where

$$\rho_{\text{eff}}(\mathbf{r}) = \rho(\mathbf{r}) - \nabla \cdot \mathbf{p}(\mathbf{r}) \quad (2.6)$$

is the effective charge density. The boundary conditions at $z = 0$ and L are

$$E_x = E_y = 0, \quad D_z = -4\pi \sigma_{\text{ex}}. \quad (2.7)$$

With these relations of electrostatics we can integrate (2.3) formally as

$$F_{\text{st}} = \frac{1}{8\pi} \int d\mathbf{r} \mathbf{E}^2. \quad (2.8)$$

In fact (2.8) leads to the second line of (2.3) if use is made of $\delta(\mathbf{E}^2) = -2\nabla \phi \cdot \delta \mathbf{D} - 8\pi \mathbf{E} \cdot \delta \mathbf{p} = -2\nabla(\phi \delta \mathbf{D}) + 8\pi(\phi \delta \rho - \mathbf{E} \cdot \delta \mathbf{p})$.

To explicitly express F_{st} in terms of the gross variables, we first assume that all the quantities depend only on z and $\mathbf{p}$ is along the z axis, for simplicity [28]. If we define $w(z) = \int_0^z dz' \rho(z')$, we obtain

$$\phi(z) = 4\pi \int_0^z dz' [p_z(z') + \sigma_{\text{ex}} - w(z')]. \quad (2.9)$$

From the overall charge neutrality condition we require $w(L) = 0$, so (2.7) is satisfied and

$$F_{\text{st}} = \frac{S}{8\pi} \int_0^L dz E_z(z)^2 = 2\pi S \int_0^L dz [p_z(z) + \sigma_{\text{ex}} - w(z)]^2. \quad (2.10)$$

For general inhomogeneous $\mathbf{p}$ and ρ , we define the lateral averages,

$$\bar{p}(z) = \frac{1}{S} \int d\mathbf{r}_{\perp} \mathbf{p}(\mathbf{r}), \quad \bar{\rho}(z) = \frac{1}{S} \int d\mathbf{r}_{\perp} \rho(\mathbf{r}), \quad (2.11)$$

where $\mathbf{r}_\perp = (x, y)$ is the lateral position vector. We may assume $\bar{p}_x = \bar{p}_y = 0$ from the geometrical symmetry in the limit $S^{1/2}/L \rightarrow \infty$. The effective charge density ρ_{eff} is divided into the lateral average $\bar{\rho} - d\bar{p}_z/dz$ and the inhomogeneous part,

$$\rho_{\text{inh}}(\mathbf{r}) = [\rho(\mathbf{r}) - \bar{\rho}(z)] - \nabla \cdot [\mathbf{p}(\mathbf{r}) - \bar{\mathbf{p}}(z)]. \quad (2.12)$$

The electric potential is expressed as

$$\phi(\mathbf{r}) = 4\pi \int_0^z dz' [\bar{p}_z(z') + \sigma_{\text{ex}} - w(z')] + 4\pi \int d\mathbf{r}' G(\mathbf{r}, \mathbf{r}') \rho_{\text{inh}}(\mathbf{r}'). \quad (2.13)$$

The first term is of the same form as (2.9) and

$$\bar{w}(z) = \int_0^z dz' \bar{\rho}(z'), \quad (2.14)$$

which vanishes at $z = 0$ and L . The Green function $G(\mathbf{r}, \mathbf{r}') = G(\mathbf{r}', \mathbf{r})$ satisfies

$$\nabla^2 G(\mathbf{r}, \mathbf{r}') = -\delta(\mathbf{r} - \mathbf{r}') \quad (2.15)$$

and vanishes as $\mathbf{r}$ and $\mathbf{r}'$ approach the surfaces of the conductors as

$$\lim_{z \rightarrow 0, L} G(\mathbf{r}, \mathbf{r}') = \lim_{z' \rightarrow 0, L} G(\mathbf{r}, \mathbf{r}') = 0. \quad (2.16)$$

Then we have $F_x = E_y = 0$ at $z = 0$ and L . The potential difference Φ is written as

$$\begin{aligned} \Phi &= 4\pi \int_0^L dz [\bar{p}_z(z) + \sigma_{\text{ex}} - \bar{w}(z)] \\ &= 4\pi L \langle p_z + \sigma_{\text{ex}} + z\rho \rangle_s, \end{aligned} \quad (2.17)$$

where $\langle \dots \rangle_s = \int d\mathbf{r}(\dots)/SL$ represents the space average and use has been made of $\langle \rho \rangle_s = 0$. This relation may also be written as

$$\Phi/4\pi L - \langle p_z \rangle_s = Q/S - \langle (L/2 - z)\rho \rangle_s, \quad (2.18)$$

which relates the mean electric field $-\Phi/L$ and the capacitor charge Q . The second term on the right hand side becomes important when the charge is accumulated near the capacitor plates in electric field.

Because we are taking the limit $S^{1/2}/L \rightarrow \infty$, the translational invariance $G(\mathbf{r}, \mathbf{r}') = G(\mathbf{r}_\perp - \mathbf{r}'_\perp, z, z')$ holds in the xy plane. The Fourier transformation $G_k(z, z')$ in the xy plane satisfies $(-\nabla_z^2 + k^2)G_k(z, z') = \delta(z - z')$ and becomes [8]

$$\begin{aligned} G_k(z, z') &= G_k(z', z) = \frac{1}{2k} e^{-k|z-z'|} - \frac{1}{2k \sinh(kL)} \\ &\times \left[\sinh(kz) e^{-k(L-z')} + \sinh(kL - kz) e^{-kz'} \right]. \end{aligned} \quad (2.19)$$

In particular, in the long wavelength limit $k \rightarrow 0$, we have

$$G_0(z, z') = \lim_{k \rightarrow 0} G_k(z, z') = \frac{1}{2}[z + z' - |z - z'|] - zz'/L. \quad (2.20)$$

From (2.17) and (2.20), as it should be the case, the potential ϕ is also expressed as

$$\phi(\mathbf{r}) = \Phi z/L + 4\pi \int d\mathbf{r}' G(\mathbf{r}, \mathbf{r}') \rho_{\text{eff}}(\mathbf{r}'). \quad (2.21)$$

The electrostatic energy is written in terms of ρ_{inh} as

$$F_{\text{st}} = 2\pi S \int_0^L dz \left[\bar{p}_z(z) + \sigma_{\text{ex}} - w(z) \right]^2 + 2\pi \int d\mathbf{r} \int d\mathbf{r}' \rho_{\text{inh}}(\mathbf{r}) G(\mathbf{r}, \mathbf{r}') \rho_{\text{inh}}(\mathbf{r}'). \quad (2.22)$$

With the aid of (2.17) and (2.20), F_{st} in terms of ρ_{eff} reads

$$F_{\text{st}} = \frac{S}{8\pi L} \Phi^2 + 2\pi \int d\mathbf{r} \int d\mathbf{r}' \rho_{\text{eff}}(\mathbf{r}) G(\mathbf{r}, \mathbf{r}') \rho_{\text{eff}}(\mathbf{r}'). \quad (2.23)$$

2.2 Dielectrics under given capacitor potential

In the previous case, the capacitor charge Q is a control parameter and the potential difference Φ is a fluctuating quantity. We may also control Φ by using (i) a battery at a fixed potential difference connected to the capacitor or (ii) another large capacitor connected in parallel to the capacitor containing a dielectric material as in Fig.1b. We examine the well-defined case (ii). The area S_0 and the charge Q_0 of the large capacitor are much larger than S and Q , respectively, so the large capacitor acts as a charge reservoir. We are supposing an experiment in which the total charge $Q_{\text{tot}} = Q_0 + Q$ is fixed and the potential difference is commonly given by $\Phi = Q_0/C_0$, where C_0 is the capacitance of the large capacitor. Obviously, in the limit $Q/Q_0 \sim S/S_0 \rightarrow 0$, the deviation of Φ from the upper bound $\Phi_{\text{tot}} = Q_{\text{tot}}/C_0$ becomes negligible. Because the electrostatic energy of the large capacitor is given by $E_0 = Q_0^2/2C_0 = (Q_{\text{tot}}^2/2C_0)(1 - Q/Q_{\text{tot}})^2$, we obtain

$$E_0 \cong (Q_{\text{tot}}^2/2C_0) - \Phi Q, \quad (2.24)$$

where the first term is constant and a term of order $(Q/Q_{\text{tot}})^2$ is neglected. Therefore, for the total system including the two capacitors, the potential difference Φ is a control parameter and the appropriate free energy functional is given by the Legendre transformation [1],

$$G = F - \Phi Q. \quad (2.25)$$

If Φ is fixed, Q is a fluctuating quantity determined by (2.18). The equilibrium distribution of the gross variables is given by $\text{const.} \exp(-G/k_B T)$ at each fixed Φ .

2.3 Dielectrics in vacuum and dipolar ferromagnets

There is another typical case, in which a sample of dielectrics is placed in vacuum. There is no polarization and charge immediately outside the sample, but there can be an applied electric field created by capacitor plates far from the sample. As far as I am aware, simulations of phase transitions in dipolar particle systems have been performed under this boundary condition [29], where the particles are assumed to interact via the dipolar potential $\propto \delta_{ij}/r^3 - 3x_i x_j/r^5$ even close to the surface. In ferromagnetic systems there is no magnetic charge and this boundary condition is always assumed [30].

We assume no free charge ($\rho = 0$) and apply an electric field E_{ex} along the z axis. The electrostatic potential is given by

$$\begin{aligned}\phi(\mathbf{r}) &= -E_{\text{ex}}z + \int d\mathbf{r}' G_0(\mathbf{r}, \mathbf{r}') \rho_{\text{eff}}(\mathbf{r}') + \int da G_0(\mathbf{r}, \mathbf{r}_a) \sigma_{\text{eff}}(\mathbf{r}_a) \\ &= -E_{\text{ex}}z + \int d\mathbf{r}' \mathbf{p}(\mathbf{r}') \cdot \nabla' G_0(\mathbf{r} - \mathbf{r}').\end{aligned}\quad (2.26)$$

In the first line $\rho_{\text{eff}} = -\nabla \cdot \mathbf{p}$ is the effective charge as given in (2.6), $\sigma_{\text{eff}} = \mathbf{p} \cdot \mathbf{n}$ is the effective surface charge with $\mathbf{n}$ being the outward normal unit vector at the surface, and $\mathbf{r}_a$ represents the surface point. In the second line the space integral is within the sample and $\nabla' = \partial/\partial \mathbf{r}'$. Since there is no capacitor charge in contact with the system, G_0 is of the usual Coulombic form,

$$G_0(\mathbf{r} - \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'|. \quad (2.27)$$

The total free energy consists of the chemical part and electrostatic part as $F = F_{\text{ch}}\{\psi, \mathbf{p}\} + F_{\text{st}}\{\mathbf{p}\}$. The latter is the usual dipolar interaction,

$$F_{\text{st}} = - \int d\mathbf{r} E_{\text{ex}} p_z + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \sum_{ij} p_i(\mathbf{r}) p_j(\mathbf{r}') [-\nabla_i \nabla_j G_0(\mathbf{r} - \mathbf{r}')], \quad (2.28)$$

which satisfies $\delta F_{\text{st}}/\delta \mathbf{p} = -\mathbf{E}$ in (2.3). Here $-\nabla_i \nabla_j G_0(\mathbf{r}) = \delta_{ij}/r^3 - 3x_i x_j/r^5$, as ought to be the case. In the ferromagnetic case, $\mathbf{p}$ and E_{ex} correspond to the magnetization and the applied magnetic field, respectively [1].

The above electrostatic (magnetic) energy (2.28) depends on the sample shape due to the depolarization (demagnetization) effect, so the phase transition to a ferroelectric (ferromagnetic) phase becomes shape-dependent [29]. As is well known, if the dielectric constant ε is uniform in the sample, the field inside is given by $E_{\text{ex}}/\varepsilon$ for a thin plate and $3E_{\text{ex}}/(2 + \varepsilon)$ for a sphere along the z axis.

3 Near-critical fluids without ions

As an application of the general scheme in Section 2, we consider a near-critical fluid in the geometry of Fig.1a. We will use the results already presented in Section 1.

3.1 General relations in the charge-free case

In the absence of free charges ($\rho = 0$), F_{ch} in (2.2) is written as

$$F_{\text{ch}}\{\psi, \mathbf{p}\} = F_0\{\psi\} + \int d\mathbf{r} \frac{1}{2\chi} \mathbf{p}^2, \quad (3.1)$$

where χ represents the electric susceptibility. The first term is the usual free energy functional for the order parameter ψ . Close to the critical point it is of the form,

$$F_0\{\psi\} = k_B T_c \int d\mathbf{r} \left[\frac{a_0}{2} \tau \psi^2 + \frac{u_0}{4} \psi^4 + \frac{K_0}{2} |\nabla \psi|^2 \right], \quad (3.2)$$

where a_0 , u_0 and K_0 are positive constants, and τ is the reduced temperature. The term $\propto \int d\mathbf{r} \psi$ is not written (because ψ is a conserved variable). Use of (2.3) gives

$$\delta F = \delta F_0 + \int d\mathbf{r} \left[(\chi^{-1} \mathbf{p} - \mathbf{E}) \cdot \delta \mathbf{p} - \frac{1}{2\chi^2} \mathbf{p}^2 \delta \chi \right] + \Phi \delta Q. \quad (3.3)$$

Thus F is minimized for

$$\mathbf{p} = \chi \mathbf{E}, \quad \mathbf{D} = \varepsilon \mathbf{E}. \quad (3.4)$$

The static dielectric constant is

$$\varepsilon = 1 + 4\pi\chi \quad (3.5)$$

and depends locally on the order parameter ψ as in (1.2). In usual fluids $\mathbf{p}$ rapidly relaxes to $\chi \mathbf{E}$ on a microscopic time scale, so (3.4) may be assumed even in nonequilibrium. Then $\mathbf{p}$ is determined by ψ and Q . The charge-free condition within the fluid $\nabla \cdot \mathbf{D} = 0$ is written as

$$\nabla \cdot (\varepsilon \nabla \phi) = 0. \quad (3.6)$$

From the general expressions (2.8) and (3.1) with the aid of (3.4) we obtain

$$F = F_0\{\psi\} + \frac{1}{8\pi} \int d\mathbf{r} \mathbf{E} \cdot \mathbf{D} = F_0\{\psi\} + \frac{1}{2} \Phi Q. \quad (3.7)$$

The expression in terms of Q also follows directly from integration of $\delta F = \Phi \delta Q$ at fixed ψ , where the factor 1/2 arises because the ratio Φ/Q is a functional of ψ only and is independent of Q from (3.4). On the other hand, in the fixed-potential case in the geometry of Fig.1b, the free energy functional G in (2.25) is written as

$$G = F_0\{\psi\} - \frac{1}{8\pi} \int d\mathbf{r} \mathbf{E} \cdot \mathbf{D} = F_0\{\psi\} - \frac{1}{2} \Phi Q. \quad (3.8)$$

The electrostatic parts $\Delta F = F - F_0$ and $\Delta G = G - F_0$ are functionals of $\varepsilon(\mathbf{r})$ at fixed Q and Φ , respectively. The functional derivative of ΔF at fixed Q and that of ΔG at fixed Φ with respect to ε are both of the same form,

$$\left(\frac{\delta}{\delta \varepsilon} \Delta F \right)_Q = \left(\frac{\delta}{\delta \varepsilon} \Delta G \right)_\Phi = -\frac{1}{8\pi} |\mathbf{E}|^2, \quad (3.9)$$

because $\int d\mathbf{r} \mathbf{E} \cdot \delta \mathbf{D} = -\int d\mathbf{r} \nabla \phi \cdot \delta \mathbf{D} = 0$ at fixed Q and $\int d\mathbf{r} \mathbf{D} \cdot \delta \mathbf{E} = 0$ at fixed Φ . These relations directly follow from (3.3) under $\mathbf{p} = \chi \mathbf{E}$. Even if a sample is placed in vacuum, $(\delta \Delta F / \delta \varepsilon)_{E_0}$ assumes the same form. To derive (3.9) more evidently, we may assume that $\varepsilon = \varepsilon(z)$ is a function of z only. Then we explicitly obtain $\Delta F = 2\pi Q^2 \int_0^L dz \varepsilon(z)^{-1}$ and $\Delta G = -(8\pi)^{-1} S \Phi^2 / \int_0^L dz \varepsilon(z)^{-1}$ to confirm (3.9).

3.2 Landau expansion and critical behavior

We assume that a constant electric field $\mathbf{E}_0 = (0, 0, -E_0)$ is applied in the negative z direction. Then $\varepsilon_2 E_0^2 / 4\pi k_B T_c (= A_0 \tau_c$ in (3.19)) and $(\varepsilon_1^2 / \varepsilon_0) E_0^2 / 4\pi k_B T_c (= g_e$ in (3.16)) are two relevant parameters representing the influence of electric field. We assume that they are *independent* of the upper cut-off Λ of the coarse-graining, while the coefficients in F_0 in (3.2) depend on Λ [22]. This causes some delicate issues. Theory should be made such that the observable quantities are independent of Λ .

We expand the electrostatic free energy with respect to the order parameter ψ . In the following we assume the fixed charge condition, but the same expressions follow in the fixed potential condition owing to (3.9). Let the electric field be written as $\mathbf{E} = \mathbf{E}_0 - \nabla \delta \phi$, where $\delta \phi$ is the deviation of the electric potential induced by $\delta \varepsilon = \varepsilon - \langle \varepsilon \rangle$. Then (3.9) is expanded as

$$\left(\frac{\delta}{\delta \varepsilon} \Delta F \right)_Q = -\frac{1}{8\pi} E_0^2 + \frac{1}{4\pi} \mathbf{E}_0 \cdot \nabla \delta \phi + \dots \quad (3.10)$$

To first order in $\delta \varepsilon$ the charge-free condition (3.6) becomes $\langle \varepsilon \rangle \nabla^2 \delta \phi = \mathbf{E}_0 \cdot \nabla \delta \varepsilon$. Using the Green function $G(\mathbf{r}, \mathbf{r}')$ in (2.15) and $\langle \varepsilon \rangle \cong \varepsilon_0$, we obtain

$$\delta \phi(\mathbf{r}) = -\frac{1}{4\pi \varepsilon_0} \int d\mathbf{r}' G(\mathbf{r}, \mathbf{r}') \mathbf{E}_0 \cdot \nabla' \delta \varepsilon(\mathbf{r}'). \quad (3.11)$$

The electrostatic free energy $\Delta F = F - F_0$ is composed of two parts up to order $O(\delta \varepsilon^2)$. The first part is

$$F_{e0} = -\frac{1}{8\pi} \int d\mathbf{r} E_0^2 \varepsilon = -\frac{1}{8\pi} \int d\mathbf{r} E_0^2 \left(\varepsilon_0 + \varepsilon_1 \psi + \frac{1}{2} \varepsilon_2 \psi^2 \right). \quad (3.12)$$

The linear term ($\propto \int d\mathbf{r} \psi$) is irrelevant for fluids and the bilinear term ($\propto \int d\mathbf{r} \psi^2$) gives rise to a shift of the critical temperature as will be shown in (3.19) and (3.22). The second part is a dipolar interaction arising from the second term in (3.10),

$$F_{\text{dip}} = \frac{1}{8\pi} A_s E_0^2 \int d\mathbf{r} \int d\mathbf{r}' [\nabla_z \psi(\mathbf{r})] G(\mathbf{r}, \mathbf{r}') [\nabla_z \psi(\mathbf{r}')], \quad (3.13)$$

where $\nabla_z = \partial / \partial z$. The coefficient A_s is defined by

$$A_s = \varepsilon_1^2 / \varepsilon \cong \varepsilon_1^2 / \varepsilon_0. \quad (3.14)$$

which is small for pure fluids ($= (\varepsilon_0 - 1)^2(\varepsilon_0 + 2)^2/9\varepsilon_0$ from Clausius-Mossotti), but can be 10 – 100 for polar binary mixtures. The F_{dip} is positive-definite for the fluctuations varying along $\mathbf{E}_0$ but vanishes for those varying perpendicularly to $\mathbf{E}_0$. Thus F_{dip} produces no shift of T_c in the mean-field theory, but it suppresses the fluctuations leading to a fluctuation contribution to the shift as in (3.23) below.

Far from the capacitor plates we may set $G(\mathbf{r}, \mathbf{r}') = 1/4\pi|\mathbf{r} - \mathbf{r}'|$. Picking up only the Fourier components $\psi_{\mathbf{q}} = \int d\mathbf{r} \psi(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}}$ with $qL \gg 1$, we obtain

$$F_{\text{dip}} = \frac{1}{2} k_B T_c g_e \int_{\mathbf{q}} \hat{q}_z^2 |\psi_{\mathbf{q}}|^2, \quad (3.15)$$

where $\hat{q}_z = q_z/q$. The strength of the interaction is given by

$$g_e = (4\pi k_B T_c)^{-1} A_s E_0^2. \quad (3.16)$$

A similar dipolar interaction is well-known for uniaxial ferromagnets [30, 33]. At the critical density (or composition) in one-phase states, the structure factor $I(\mathbf{q})$ in the presence of F_{dip} becomes uniaxial as

$$I(\mathbf{q}) = [a_0(\tau - \tau_c) + g_e \hat{q}_z^2 + K_0 q^2]^{-1}, \quad (3.17)$$

where τ_c is a shift induced by electric field. For $g_e \hat{q}_z^2 > a_0 \tau_c$, the intensity decreases with increasing electric field even if $\tau_c > 0$.

(i) *Weak field regime*: If g_e is smaller than $a_0 \tau = \hat{\chi}^{-1}$, the electric field is weak and the structure factor may be expanded as

$$I(\mathbf{q}) = I_0(q) + I_0(q)^2 (a_0 \tau_c - g_e \hat{q}_z^2) + \dots, \quad (3.18)$$

where $I_0(q) = \hat{\chi}/(1 + q^2 \xi^2)$ is the intensity at zero electric field with $\hat{\chi} = I(0)$. The *apparent* shift arises from the bilinear term ($\propto \psi^2$) in F_{c0} in (3.12):

$$a_0 \tau_c = \varepsilon_2 E_0^2 / 4\pi k_B T_c = \varepsilon_2 g_e / A_s. \quad (3.19)$$

Note that $a_0 \tau_c$ and hence (3.18) are independent of Λ . The usual critical behavior at long wavelengths $q\xi < 1$ follows for $\Lambda\xi \sim 1$, where $\xi = \xi_{+0} \tau^{-\nu}$ is the correlation length. The asymptotic scaling relations are $\hat{\chi} = \Gamma \tau^{-\gamma}$ (or $a_0 = \Gamma^{-1} \tau^{\gamma-1}$) and $K_0 = \hat{\chi}^{-1} \xi^2 = \Gamma^{-1} \xi_{+0}^2 \tau^{-\nu\eta}$, where Γ is a constant, and $\gamma \cong 1.24$, $\nu \cong 0.625$, and $\eta = 0.03 - 0.05$ are the usual critical exponents.

(ii) *Strong field regime*: The electric field is strong for $\tau - \tau_c < \tau_e$. The crossover reduced temperature τ_e and the characteristic wave number k_e are written as

$$\tau_e = (\Gamma g_e)^{1/\gamma}, \quad k_e = \xi_{+0}^{-1} (\Gamma g_e)^{\nu/\gamma}. \quad (3.20)$$

As a rough estimate, we set $\Gamma \sim \xi_{+0}^3$, $\xi_{+0} \sim 2.5 \times 10^{-8} \text{ cm}$, and $T_c \sim 300 \text{ K}$ to obtain $\tau_e \sim 10^{-6} A_s^{0.8} E_0^{1.6}$ with E_0 in units of 10^4 V/cm . There is no experimental

report in this regime. According to the renormalization group theory in the presence of the uniaxial dipolar interaction (3.15) (which treats $F_0 + F_{\text{dip}}$) [33], there is no renormalization of the coefficient g_e and the dipolar interaction strongly suppresses the fluctuations with wave numbers smaller than k_e in the temperature range $\tau - \tau_c < \tau_e$ resulting in mean field critical behavior for $d \geq d_c = 3$. For these fluctuations we may set $\Lambda \sim k_e$ to obtain the renormalized coefficients,

$$a_0 = \Gamma^{-1} \tau_e^{\gamma-1}, \quad K_0 = \Gamma^{-1} \xi_{+0}^2 \tau_e^{-\nu\eta}, \quad u_0 = g^* K_0^2 k_e' / K_d, \quad (3.21)$$

where $K_d = (2\pi)^{-d} 2\pi^{d/2} / \Gamma(d/2)$, $\epsilon = 4 - d$, and $g^* = \epsilon/9 + O(\epsilon^2)$ is the fixed point value of the coupling constant $g = K_d u_0 / K_0^2 \Lambda^\epsilon$ [22]. The shift τ_c in (3.17) in strong field consists of two terms as $\tau_c = \tau_{c1} + \tau_{c2}$. The origin of τ_{c1} is the same as that of τ_c in (3.19). Here using (3.20) and (3.21) we obtain

$$\tau_{c1} = \varepsilon_2 E_0^2 / 4\pi a_0 k_B T = (\varepsilon_2 / A_s) \tau_e. \quad (3.22)$$

The τ_{c2} arises from the quartic term ($\propto u_0$) in F_0 in (3.2):

$$\tau_{c2} = -\frac{3}{a_0} u_0 \int_{\mathbf{q}} \left[\frac{1}{g_e \hat{q}_z^2 + K_0 q^2} - \frac{1}{K_0 q^2} \right] = 3g^* C_d \tau_e, \quad (3.23)$$

where $C_d = K_d^{-1} \int_{\mathbf{q}} \ell_z^2 / \ell^2 (\ell^4 + \ell_z^2)$ ($= \pi/4$ at $d = 3$). The τ_{c2} is a positive fluctuation contribution meaningful only in strong field. (A similar shift was calculated for near-critical fluids in shear flow [22].) Therefore both τ_{c1} and τ_{c2} are of order τ_e . We also consider the correlation function $g(\mathbf{r}) = \int_{\mathbf{q}} I(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}}$ in strong field. From (3.17) and (3.21) the scaling form $g(\mathbf{r}) = G(x/\xi_\perp, y/\xi_\perp, z/\xi_\parallel) / K_0 \xi_\parallel$ holds with

$$\xi_\perp = k_e^{-1} [\tau_e / (\tau - \tau_c)]^{1/2}, \quad \xi_\parallel = k_e \xi_\perp^2 = k_e^{-1} \tau_e / (\tau - \tau_c) > \xi_\perp. \quad (3.24)$$

Here $G(0, 0, Z) \sim Z^{-3}$ for $Z \gg 1$. The large-scale critical fluctuations ($\gg k_e^{-1}$) are elongated along the z axis, as expected in experimental papers [13].

We now comment on previous work.

(i) If a_0 is treated as a constant, $T_c \tau_{c1}$ is the mean field shift in Landau-Lifshitz's book for pure fluids [1]. The same shift was later proposed for binary mixtures [7]. (ii) Debye and Kleboth [2] derived a reverse shift ($\Delta T_c = -T_c \tau_{c1}$) neglecting the inhomogeneity of $\mathbf{E}$ and setting $\mathbf{E} = \mathbf{E}_0$ in (3.7). The dipolar interaction was nonexistent, leading to the normalized turbidity change $\mathcal{T}(E_0)/\mathcal{T}(0) - 1 \cong \hat{\chi} a_0 \tau_c$ for $k\xi \ll 1$, where $\mathcal{T}(E_0)$ is the turbidity in electric field (see (1.7)). They found turbidity decreases in nitrobenzene+ 2,2,4-trimethylpentane to obtain $\tau_c = -0.5 \times 10^{-4}$ at $E_0 = 45 \text{ kV/cm}$ in agreement with their theory, where Hildebrand's theory gave $a_0 = (4.3 \text{ \AA})^{-3}$ and data of $\varepsilon(\phi)$ as a function of the volume fraction ϕ of nitrobenzene gave $\partial^2 \varepsilon / \partial \phi^2 = 28.7$. (Notice that their $|\tau_c|$ is of order τ_e in (3.20) if $A_s \sim 10$.) Subsequent light scattering experiments detected similar suppression in a

near-critical binary mixture [31] and in a polymer solution [32]. In our theory (3.18) and (3.19) hold in weak field, so for $k\xi \ll 1$ we have

$$\mathcal{T}(E_0)/\mathcal{T}(0) - 1 \cong \hat{\chi}(a_0\tau_c - g_e/5) \quad \text{or} \quad \hat{\chi}(a_0\tau_c - 2g_e/5) \quad (3.25)$$

for the polarization along the z or y axis. Thus we predict that the turbidity decreases for $g_e/5 > a_0\tau_c$ or for $A_s > 5\varepsilon_2$ for any polarization. Here we expect that A_s is considerably larger than $|\varepsilon_2|$ in polar mixtures (see the end of Subsection 3.3 also). Complex effects also arise from a small amount of ions which are present in most binary mixtures (see Section 4).

3.3 Macroscopic dielectric constant

We calculate the macroscopic dielectric constant $\varepsilon_{\text{eff}} = 4\pi\langle Q \rangle / SE_0 = \langle D_z \rangle / E_0$ in the absence of charges. From the charge-free condition $\nabla \cdot \langle \mathbf{D} \rangle = \nabla_z \langle D_z \rangle = 0$, $\langle D_z \rangle$ is homogeneous in the fluid as

$$\langle D_z \rangle = \langle \varepsilon \rangle E_0 - \langle \delta\varepsilon \nabla_z \delta\phi \rangle = \text{const.} \quad (3.26)$$

Far from the boundary surfaces, by setting $M = \langle \psi \rangle$, we obtain

$$\varepsilon_{\text{eff}} = \varepsilon_0 + \varepsilon_1 M + \frac{1}{2}\varepsilon_2 M^2 + \int_{\mathbf{q}} \left[\frac{1}{2}\varepsilon_2 - A_s \hat{q}_z^2 \right] I(\mathbf{q}), \quad (3.27)$$

where the last term is the zz component of the tensor in (1.3).

(i) *Linear response:* The linear dielectric constant $\varepsilon_{\text{eff}}(0)$ is defined in the limit $E_0 \rightarrow 0$, where $\hat{q}_z^2$ in (3.27) may be replaced by $1/3$. Because $a_0\psi^2$ corresponds to the energy density in the corresponding Ising model (see the sentences below (1.2)), the renormalization group theory gives $\langle a_0\psi^2 \rangle = \text{const.} - A\tau^{1-\alpha}/(1-\alpha) + \dots$ with $\alpha \cong 0.11$ (the specific-heat critical exponent) and $A = R_\xi^d/(\alpha\xi_{+0}^d)$ at the critical density or composition above T_c [22]. In terms of this A , the specific heat C_V for pure fluids and C_{pc} for binary mixtures per unit volume grow as $-k_B\partial\langle a_0\psi^2 \rangle/\partial\tau \cong k_B A\tau^{-\alpha}$. The $R_\xi^d = \alpha A\xi_{+0}^d (\cong K_d/4)$ is a universal number (the two-scale-factor universality). It follows that $\varepsilon_{\text{eff}}(0)$ should exhibit weakly singular behavior [4-6, 8],

$$\varepsilon_{\text{eff}}(0) = \varepsilon_c + D_1\tau^{1-\alpha} + D_2\tau + \dots \quad (3.28)$$

In our theory $D_1 = (A_s - 3\varepsilon_2/2)A/3a_0$ depends on the arbitrary cut-off Λ since $a_0 \propto \Lambda^{(\gamma-1)/\nu}$ for $\Lambda \gg \xi^{-1}$, indicating inadequacy of our theory at short wavelengths. To calculate D_1 correctly we need to interpolate the renormalization group theory to a microscopic theory [34]. On the other hand, the refractive index $n(\omega) = \varepsilon(\omega)^{1/2}$ at optical frequency has also been predicted to be of the form of (3.28) [4, 6]. However, despite a number of experiments, unambiguous detection of the weak singularity in these quantities has been difficult for both pure fluids and binary mixtures [10].

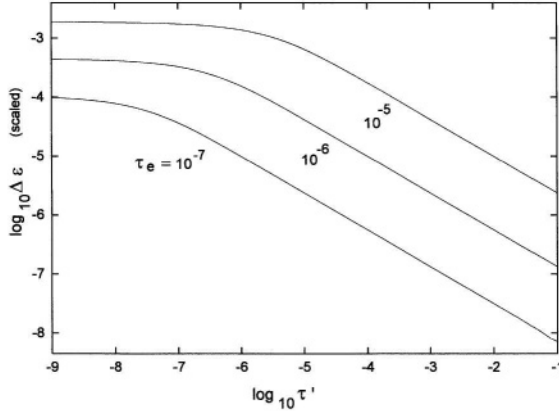


Figure 2: Nonlinear dielectric constant $\Delta\epsilon_{\text{eff}}(\tau, E_0)$ (divided by a constant B_0) vs reduced temperature $\tau' = \tau - \tau_c > 0$ in applied electric field E_0 for $\tau_e = 10^{-5}, 10^{-6}$, and 10^{-7} , where $\tau_e \propto E_0^{1.6}$ from (3.20).

(i) *Nonlinear response:* The nonlinear dielectric constant $\Delta\epsilon_{\text{eff}} = \epsilon_{\text{eff}}(E_0) - \epsilon_{\text{eff}}(0)$ has been observed to become positive and grow near the critical point in polar binary mixtures [12-15]. Because small-scale fluctuations are insensitive to electric field, such critical anomaly arises from nonlinear effects at long wavelengths ($q \lesssim \xi^{-1}$ for weak field and $q \lesssim k_e$ for strong field). Its calculation is therefore much easier than that of $\epsilon_{\text{eff}}(0)$. Use of the structure factor (3.17) yields

$$\Delta\epsilon_{\text{eff}} \cong \frac{1}{16\pi}(2A_s/5 - \epsilon_2 + \epsilon_2^2/A_s)K_0^{-2}g_e\xi \quad (\tau \gg \tau_e) \quad (3.29)$$

$$\cong \frac{1}{16\pi}(A_s - \epsilon_2)K_0^{-1}k_e \quad (0 < \tau' \lesssim \tau_e), \quad (3.30)$$

In the first line we have $K_0 \propto \xi^\eta$ and $\Delta\epsilon_{\text{eff}} \propto E_0^2 \xi^{1-2\eta}$, while in the second line $K_0 \propto k_e^{-\eta}$ and $\Delta\epsilon_{\text{eff}} \propto E_0^{(1+\eta)/(2-\eta)}$. Here we set $\tau' = \tau - \tau_c > 0$. Then $\tau' \cong \tau$ for weak field. If $\Delta\epsilon_{\text{eff}}$ is positive for any τ' , we need to require $A_s > \epsilon_2$. Previously we calculated (3.29) without the terms involving ϵ_2 [8]. For general τ'/τ_e we find the scaling,

$$\Delta\epsilon_{\text{eff}} = B_0 \tau_e^{\nu(1+\eta)} F_{\text{non}}(k_e \xi), \quad (3.31)$$

where B_0 is a constant, $F_{\text{non}}(x) \sim x^{1-2\eta}$ for $x \ll 1$, and $F_{\text{non}}(x) \rightarrow 1$ for $x \gg 1$. Here $x = k_e \xi \cong (\tau_e/\tau')^\nu$. If we neglect the contributions involving ϵ_2 and set $\eta = 0$, $F_{\text{non}}(x)$ is calculated in a universal form,

$$F_{\text{non}}(x) = \left(\frac{1}{x} + \frac{1}{2x^3}\right)\sqrt{1+x^2} - \frac{1}{2x^4} \ln(x + \sqrt{1+x^2}) - \frac{4}{3x}. \quad (3.32)$$

In Fig.2 we plot $\Delta\epsilon_{\text{eff}}/B_0 = \tau_e^\nu F_{\text{non}}(k_e \xi)$ vs τ' by neglecting η . For weak field $\tau_e \ll \tau$, we predict $\Delta\epsilon_{\text{eff}} \propto \tau^{-2\nu_{\text{non}}} E_0^2$ at the critical density or composition, where

$z_{\text{non}} = \nu(1 - 2\eta) = \gamma - 2\beta \cong 0.58$ using $\gamma + 2\beta = 2 - \alpha = 3\nu$ [4, 5, 8]. For strong field $\tau_e \gtrsim \tau'$, $\Delta\varepsilon_{\text{eff}}$ should saturate into (3.30).

In the experiments, z_{non} was around 0.4 and the coefficient $\Delta\varepsilon_{\text{eff}}/[\tau^{-z_{\text{non}}} E_0^2]$ was proportional to $(\varepsilon_A - \varepsilon_B)^4/\varepsilon^2$ for various binary mixtures [13, 14]. The latter aspect is in accord with (3.29) if $\varepsilon_1 \sim \varepsilon_A - \varepsilon_B$ and $A_s - 5(\varepsilon_2 - \varepsilon_2^2/A_s)/2 \sim A_s$. We also note that a weak tendency of saturation of $\Delta\varepsilon_{\text{eff}}$ was detected at $\tau = 3 \times 10^{-4}$ with increasing E_0 above 60 kV/cm, but it was attributed to a negative critical temperature shift [15]. These results and Debye-Kleboth's data suggest that $|\varepsilon_2|$ is considerably smaller than A_s at least in polar mixtures.

3.4 Critical electrostriction

We consider equilibrium of pure fluids in which $\langle \mathbf{E} \rangle = \mathbf{E}_0(\mathbf{r})$ varies slowly in space. In equilibrium the chemical potential defined by the following is homogeneous [1],

$$\mu(\tau, M, E_0) = \langle \delta F / \delta n \rangle = \mu(\tau, M, 0) - \frac{1}{8\pi n_c} \varepsilon_1 E_0^2 = \text{const.} \quad (3.33)$$

Here we set $\psi = (n - n_c)/n_c$. When $\mathbf{E}_0$ varies slowly compared with the correlation length, an inhomogeneous average density variation is induced as

$$\langle \delta n \rangle(\mathbf{r}) \cong n_c K_T \varepsilon_1 E_0(\mathbf{r})^2 / 8\pi, \quad (3.34)$$

where $K_T = (\partial n / \partial \mu)_T / n^2 \sim \tau^{-\gamma} / k_B T_c n_c$ is the isothermal compressibility. Experimentally, the above relation was confirmed optically for SF_6 around a wire conductor [35], and was used to determine $\mu(T, M)$ for ^3He in a cell within which a parallel-plate capacitor was immersed [36].

This problem should be of great importance on smaller scales particularly in near-critical polar binary mixtures. For example, let us consider a spherical particle with charge Ze and radius R placed at the origin of the reference frame. The fluid is in a one-phase state and is at the critical density or composition far from the particle, so $\tau > 0$. In the Ginzburg-Landau scheme (3.2) and (3.9) yield

$$(a_0\tau + u_0\psi^2 - K_0\nabla^2)\psi = h(r)\xi_{+0}^{-3} \cong A_0\xi_{+0}r^{-4}, \quad (3.35)$$

where $A_0 = \varepsilon_1 Z^2 e^2 / 8\pi \varepsilon_0^2 k_B T \xi_{+0}$. The $h(r) = A_0(\xi_{+0}/r)^4$ is a dimensionless space-dependent ordering field. We may assume $\varepsilon_1 > 0$ and $A_0 > 0$. For polar binary mixtures and/or for colloidal particles with $Z \gg 1$, A_0 can well exceed 1 (see Section 4). In the space region, where $\xi < (\partial \ln h(r) / \partial r)^{-1} \sim r$, the usual scaling relations hold locally at each point and the renormalization yields the coefficients a_0 , u_0 , and K_0 dependent on τ and $h(r)$ [22]. However, $\xi < r$ is violated at small r for $\xi > R$, where the gradient term in (3.35) ($\propto \nabla^2 \psi$) is indispensable. The linear relation $\psi \cong \Gamma \xi_{+0}^{-3} \tau^{-\gamma} h(r)$ given in (3.34) holds for $h(r) < \tau^{\beta\delta}$ and $r > \xi$, where the former condition is rewritten as $r > \xi_{+0} A_0^{1/4} \tau^{-\beta\delta/4}$. As $\tau \rightarrow 0$, the profile $\psi(r)$ becomes very complicated depending on A_0 , ξ/R , and the boundary condition at $r = R$. Detailed discussions will appear shortly.

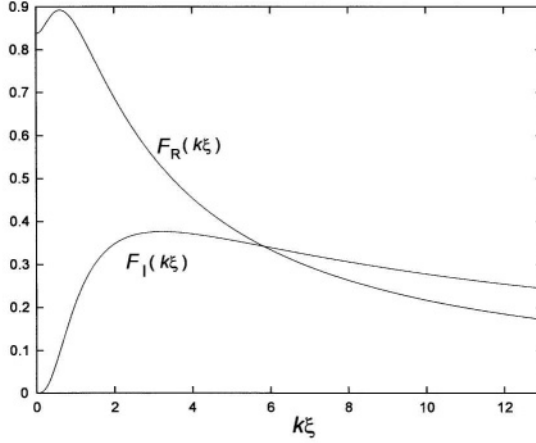


Figure 3: Two scaling functions corresponding to form birefringence and dichroism [8]. The k is the wave number of probing light and ξ is the correlation length.

3.5 Electric birefringence and dichroism

The anisotropy of the structure factor in (3.17) has not yet been measured in near-critical fluids, but it gives rise to critical anomaly in electric birefringence (Kerr effect) [16-19] and dichroism. These effects can be sensitively detected even in the weak field regime $\tau_e \ll \tau$ and even for not large ε_1 using high-sensitivity optical techniques. We assume that a laser beam with optical frequency ω is passing through a near-critical fluid along the x axis, while an electric field E_0 is applied along the z axis. In (1.5) we have $\Delta\varepsilon_{yz} = 0$ and the difference $\Delta n = (\Delta\varepsilon_{zz} - \Delta\varepsilon_{yy})/2n(\omega)$ is written as [23, 24]

$$\Delta n = \frac{A_{\text{op}}}{2n(\omega)} \int_{\mathbf{q}} \frac{q_y^2 - q_z^2}{q^2 - k^2 - i0} I(\mathbf{k} - \mathbf{q}), \quad (3.36)$$

where $k = \omega/n(\omega)$ is the laser wave number in the fluid and

$$A_{\text{op}} = (\partial\varepsilon(\omega)/\partial\psi)^2/\varepsilon(\omega). \quad (3.37)$$

Here A_{op} is different from the static coefficient A_s in (3.14). In fact $A_{\text{op}} \ll A_s$ for polar fluid mixtures where $\varepsilon(0) \gg \varepsilon(\omega)$ at optical frequency ω [40]. When $\tau \gg \tau_c$, substitution of (3.18) into (3.36) gives the steady state result,

$$\Delta n = \frac{A_{\text{op}}}{32\pi^2 n(\omega)} K_0^{-2} g_e \xi \left[F_R(k\xi) + i F_I(k\xi) \right], \quad (3.38)$$

where the two scaling functions are plotted in Fig.3 and are given by

$$\begin{aligned} F_R(x) &= \frac{\pi}{4x^2} \left(1 + \frac{1}{4x^2} \right) \left[\left(\frac{3}{2x} + 2x \right) \tan^{-1}(2x) - 3 \right], \\ F_I(x) &= \frac{\pi}{4x} \left[\left(1 + \frac{1}{x^2} + \frac{3}{16x^2} \right) \ln(1 + 4x^2) - \frac{3}{4x^2} - \frac{5}{2} \right]. \end{aligned} \quad (3.39)$$

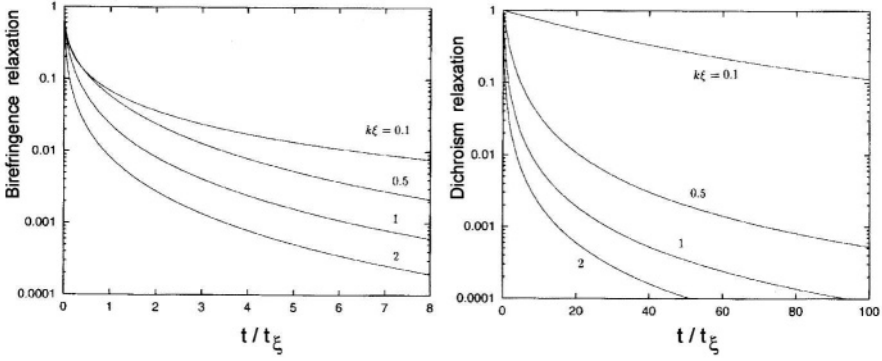


Figure 4: Normalized birefringence $\text{Re}\Delta n(t)/\text{Re}\Delta n(0)$ and dichroism $\text{Im}\Delta n(t)/\text{Im}\Delta n(0)$ vs t/t_ξ on semilogarithmic scales for $k\xi = 0.1, 0.5, 1$, and 2 .

For $x \ll 1$ we have $F_R(x) \cong 4\pi/15$ and $F_I(x) \cong \pi x^3/3$. In the long wavelength limit ($k\xi \ll 1$), we find $\Delta\varepsilon_{\text{eff}}/n(\omega)\Delta n = 3(A_s - 5\varepsilon_2/6)/A_{\text{op}}$ from (3.29) and (3.38), so $\Delta\varepsilon_{\text{eff}}$ and $\lim_{k\xi \rightarrow 0} \Delta n$ should have the same critical behavior. Experimentally, however, $\Delta n \propto \tau^{-z_{\text{op}}}$ with $z_{\text{op}} \cong 0.65 - 0.85 > z_{\text{non}}$ was obtained [14, 18].

In transient electric birefringence, applied electric field is switched off (at $t = 0$) and the subsequent relaxation $\Delta n(t)$ (for $t > 0$) is measured. For near-critical binary mixtures, this experiment has been carried out by applying a rectangular pulse of electric field [16-19]. If the pulse duration time Δt is much longer than the relaxation time t_ξ of the critical fluctuations, the fluid can reach a steady state while the field is applied. Here $t_\xi = 6\pi\bar{\eta}\xi^3/k_B T_c$ with $\bar{\eta}$ being the shear viscosity. A remarkable finding is that $\Delta n(t)$ follows a stretched exponential relaxation at short times. We hereafter explain our theory for weak field $\tau_c \ll \tau$ [8].

We assume that the relaxation of the structure factor obeys

$$I(\mathbf{q}, t) = I_0(q) - I_0(q)^2 g_e \hat{q}_z^2 \exp(-2\Gamma_q t) + \dots, \quad (3.40)$$

where $\Gamma_q = t_\xi^{-1} K_0(q\xi)$ is the relaxation rate with $K_0(x) = (3/4)[1 + x^2 + (x^3 - x^{-1})\tan^{-1}x]$ being the Kawasaki function [22]. Thus $\Gamma_q = Dq^2$ for $q\xi \ll 1$ with the diffusion constant $D = k_B T_c / 6\pi\eta\xi$. Here we neglect the term proportional to τ_c in (3.18) because it does not contribute to Δn . We substitute (3.40) into (3.36) to obtain $\Delta n(t)$ as a function of $k\xi$ and t/t_ξ , where the initial value $\Delta n(0)$ is given by (3.38). In Fig.4 we plot its normalized real and imaginary parts for various $k\xi$. The imaginary part decays slower than the real part. In the limit $k\xi \rightarrow 0$, it becomes real and is of the form,

$$\lim_{k\xi \rightarrow 0} \frac{\Delta n(t)}{\Delta n(0)} = G(t/t_\xi) = \frac{4}{\pi} \int_0^\infty dy \frac{y^2}{(1+y^2)^2} \exp[-2K_0(y)t/t_\xi], \quad (3.41)$$

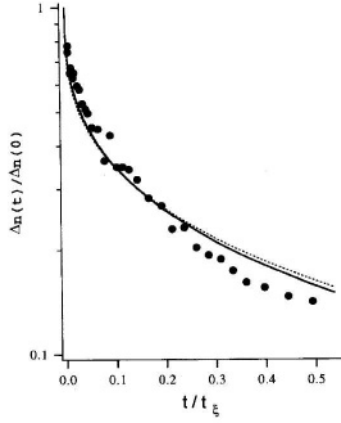


Figure 5: Comparison of the theoretical decay function (bold line) defined by (3.41) and data (dots) taken from Ref.[18]. The stretched exponential function $\exp(-2.3x^{1/3})$ (dotted line) is a good approximation in the initial relaxation.

where the scaling function $G(x)$ behaves as

$$\begin{aligned} G(x) &\cong 1 - 2.3x^{1/3} \cong \exp(-2.3x^{1/3}) & (x \ll 1) \\ &\cong 0.2x^{-3/2} & (x \gg 1). \end{aligned} \quad (3.42)$$

In Fig.5 data on butoxyetbaranol + water [18] are compared with (3.41) for $t < t_\xi$. The agreement is excellent. It demonstrates that the theoretical $G(t)$ is nearly stretched-exponential for $G(t) \gtrsim 0.1$ or for $t/t_\xi \lesssim 0.5$. As another theory, Piazza *et al.* [17] derived a stretched exponential decay of $\Delta n(t)$ on the basis of a phenomenological picture on the distribution of large clusters.

Let us consider the case $k\xi \ll 1$, where (3.41) is a good approximation for $t \lesssim 1/Dk^2$. At $t \sim 1/Dk^2$, $G(t/t_\xi)$ becomes a very small number of order $0.2(k\xi)^3$. In the later time region $t \gtrsim (Dk^2)^{-1}$, (3.41) cannot be used and the fluctuations with wave numbers of order $(Dt)^{-1/2}$ give rise to the following birefringence signal,

$$\frac{\text{Re}\Delta n(t)}{\text{Re}\Delta n(0)} \cong 0.2(t/t_\xi)^{-3/2}(Dk^2t)^{-1}. \quad (3.43)$$

Data of birefringence relaxation in Ref.[19] indicated that the decay becomes faster than predicted by (3.41) at long times. The same tendency can be seen in Fig.4. In future such data should be compared with the theoretical curves for finite $k\xi$. We note that transient electric dichroism has not yet been measured for near-critical fluids, but was measured for a polymer solution[27].

3.6 Interface instability induced by electric field

An interface between two immiscible fluids becomes unstable against surface undulations in perpendicularly applied electric field. This is because the electrostatic energy is higher for perpendicular field than for parallel field. In classic papers [37] the instability on an interface between conducting and nonconducting fluids (such as Hg and air) was treated. In helium systems, where an interface can be charged with ions, the critical field is much decreased and intriguing surface patterns have been observed [38].

We will derive this instability in the simplest manner [39]. Let a planar interface be placed at $z = z_0$ in a near-critical fluid without ions in weak field, $\tau < 0$ and $|\tau| \gg \tau_e$. If the interface is displaced by a small height $\zeta(x, y)$, we may set $\partial\psi/\partial z = \Delta\psi\delta(z - z_0 - \zeta)$ in (3.13), where $\Delta\psi$ is the order parameter difference between the two phases. This means that the effective surface charge density is given by $-\epsilon_1\Delta\psi E_0$. If z_0 is far from the boundaries, we obtain

$$F_{\text{dip}} = \frac{1}{8\pi} C_e \int d\mathbf{r}_\perp \int d\mathbf{r}'_\perp [|\zeta(\mathbf{r}_\perp) - \zeta(\mathbf{r}'_\perp)|^2 + |\mathbf{r}_\perp - \mathbf{r}'_\perp|^2]^{-1/2}, \quad (3.44)$$

where $\mathbf{r}_\perp = (x, y)$, $\mathbf{r}'_\perp = (x', y')$, and

$$C_e = A_s E_0^2 (\Delta\psi)^2 / 4\pi. \quad (3.45)$$

We expand the integrand of (3.44) in powers of $[\zeta(\mathbf{r}_\perp) - \zeta(\mathbf{r}'_\perp)]^2$. The first correction is negative and bilinear in ζ . In terms of the Fourier transformation $\zeta_{\mathbf{k}}$ we have

$$\begin{aligned} \Delta F_{\text{dip}} &= -\frac{1}{16\pi} C_e \int d\mathbf{r}_\perp \int d\mathbf{r}'_\perp \frac{1}{|\mathbf{r}_\perp - \mathbf{r}'_\perp|^3} [\zeta(\mathbf{r}_\perp) - \zeta(\mathbf{r}'_\perp)]^2 \\ &= -\frac{1}{2} C_e \int_{\mathbf{k}} k |\zeta_{\mathbf{k}}|^2, \end{aligned} \quad (3.46)$$

where $\mathbf{k}$ is the two-dimensional wave vector with $k = |\mathbf{k}|$ and $\int_{\mathbf{k}} = (2\pi)^{-2} \int d\mathbf{k}$. We have used the formula $\int d\mathbf{r}_\perp [1 - \exp(i\mathbf{k} \cdot \mathbf{r}_\perp)] / r_\perp^{3/2} = 4\pi k$. Including gravity we write the total free energy change due to the surface deformation as

$$\Delta F_{\text{surface}} = \frac{1}{2} \int_{\mathbf{k}} [\sigma k^2 + g\Delta\rho - C_e k] |\zeta_{\mathbf{k}}|^2, \quad (3.47)$$

where σ is the surface tension, g is the gravitational acceleration, and $\Delta\rho$ is the mass density difference between the two phases. The coefficient in front of $|\zeta_{\mathbf{k}}|^2$ is minimum at $k = (C_e/2\sigma)^{1/2}$ and an instability is triggered for $C_e > 2(\sigma g \Delta\rho)^{1/2}$. For polar mixtures this criterion is typically $E_0 > |\tau|^{1/2-3\beta/4} \text{kV/cm}$ on earth.

4 Near-critical fluids with ions

We will discuss the effects of ions doped in binary mixtures. It has long been known that even a small fraction of ions (salt) with $c \ll 1$ dramatically changes the liquid-liquid phase behavior in polar binary mixtures, where c is the mass or mole fraction

of ions. For small c , the UCST coexistence curve shifts upward as

$$(\Delta T)_c = A_1 c + O(c^2) \quad (4.1)$$

with large positive coefficient A_1 , expanding the region of demixing. For example, $A_1/T_c \sim 10$ with $T_c \sim 300\text{K}$ when NaCl was added to cyclohexane+methyl alcohol [41] and to triethylamine+water [42]. Similar large impurity effects were observed when water was added to methanol+cyclohexane [43]. In some polar mixtures, even if they are miscible at all T at atmosphere pressure without salt, addition of a small amount of salt gives rise to reentrant phase separation behavior [44, 45].

We consider two species of ions with charges, Ze and $-e$, at very low densities, $n_1(\mathbf{r})$ and $n_2(\mathbf{r})$, in a near-critical binary mixture. The average densities are written as $\langle n_1 \rangle_s = \bar{n}$ and $\langle n_2 \rangle_s = Z\bar{n}$, where $\langle \cdots \rangle_s$ denotes taking the space average. The charge neutrality condition yields $Z\langle n_1 \rangle_s = \langle n_2 \rangle_s$. The Debye wave number κ and the Bjerrum length $\ell_B (= 7\text{\AA}$ for water at 300K) are defined by

$$\kappa = [4\pi(Z^2 + Z)\bar{n}e^2/\varepsilon k_B T]^{1/2}, \quad \ell_B = e^2/\varepsilon k_B T. \quad (4.2)$$

4.1 Ginzburg-Landau theory

We set $\mathbf{p} = \chi(\psi)\mathbf{E}$ from the beginning. Then the electric potential ϕ satisfies $-\nabla \cdot \varepsilon \nabla \phi = 4\pi\rho$ with $\varepsilon = 1 + 4\pi\chi$ and $\rho = e(Zn_1 - n_2)$. We assume that the free energy F in (2.2) in the fixed charge condition is of the form,

$$F = F_0\{\psi\} + k_B T \int d\mathbf{r} \left[n_1 \ln n_1 + n_2 \ln n_2 + (w_1 n_1 + w_2 n_2)\psi \right] + \frac{1}{8\pi} \int d\mathbf{r} \varepsilon \mathbf{E}^2, \quad (4.3)$$

where the first term depends only on ψ and is given by (3.2), and the terms proportional to w_1 and w_2 arise from an energy decrease due to microscopic polarization of the fluid around individual ions. In the neighborhood of an ion of species α ($\alpha = 1, 2$), the electric field and the polarization are given by $\mathbf{E}_{\text{ind}} = -\nabla(Z_\alpha e/\varepsilon r)$ and $\mathbf{p}_{\text{ind}} = \chi \mathbf{E}_{\text{ind}}$ in terms of the local χ and ε , where we write $Z_1 = Z$ and $Z_2 = -1$. The resultant electrostatic energy density is localized near the ion ($\propto r^{-4}$) and its space integral is $\int d\mathbf{r} \varepsilon \mathbf{E}_{\text{ind}}^2/8\pi = Z_\alpha^2 e^2/2\varepsilon r_\alpha$, where r_α is the lower cutoff representing an effective radius of an ion of species α . Here the screening length is assumed to be much longer than r_α . Due to the polarization, the decrease of the electrostatic energy is given by

$$\Delta E_\alpha = (1/\varepsilon - 1)Z_\alpha^2 e^2/2r_\alpha. \quad (4.4)$$

Neglecting ψ -dependence of r_α we estimate w_α as

$$w_\alpha = (k_B T)^{-1} \frac{\partial}{\partial \psi} (\Delta E_\alpha) = -\varepsilon_1 Z_\alpha^2 \ell_B / 2\varepsilon_0 r_\alpha. \quad (4.5)$$

The last term in (4.3) is the electrostatic free energy ΔF arising from slowly-varying fluctuations and depends on the boundary condition. As a clear illustration, if all the quantities are functions of z only in the charge-fixed condition, we have

$$\Delta F = 2\pi S \int_0^L dz [\sigma_{\text{ex}} - w(z)]^2 / \varepsilon(z), \quad (4.6)$$

where σ_{ex} is the capacitor charge density and $w(z) = \int_0^z dz' \rho(z')$. Though neglected here, electrostriction should also be investigated around charged particles (see Subsection 3.4), which can well produce a shift of the critical composition.

In this model the chemical potentials $\mu_\alpha = \delta F / \delta n_\alpha$ of the ions are given by

$$\mu_\alpha = k_B T (\ln n_\alpha + 1 + w_\alpha \psi) + Z_\alpha e \phi. \quad (4.7)$$

In equilibrium μ_α become homogeneous, leading to ion distributions,

$$\begin{aligned} n_\alpha(\mathbf{r}) &= n_{\alpha 0} \exp[-w_\alpha \psi(\mathbf{r}) - Z_\alpha e \phi(\mathbf{r}) / k_B T] \\ &\cong n_{\alpha 0} [1 - w_\alpha \psi(\mathbf{r}) - Z_\alpha e \phi(\mathbf{r}) / k_B T]. \end{aligned} \quad (4.8)$$

The second line holds when the exponents in the first line are small. Let us use the second line to derive Debye-Hückel-type relations. Then $n_{\alpha 0} \cong \langle n_\alpha \rangle_s [1 + w_\alpha \langle \psi \rangle_s + Z_\alpha e \langle \phi \rangle_s / k_B T]$. The potential ϕ satisfies

$$\varepsilon_0 (\kappa^2 - \nabla^2) \phi = \varepsilon_1 \nabla \psi \cdot \nabla \phi + 4\pi e [Z n_{10} - n_{20} - Z n (w_1 - w_2) \psi]. \quad (4.9)$$

The right hand side consists of new contributions dependent on ψ , where the first term is important in the presence of applied field. We here notice the following.

- (i) In applied electric field we can examine the ions distribution accumulated near the boundaries using (2.4) and (4.8) (or (4.9)).
- (ii) When $w_1 \neq w_2$, charge distributions arise around domains or wetting layers. Let the interface thickness ($\sim \xi$) be shorter than the Debye length κ^{-1} . For a spherical domain with radius R , for example, the electric potential $\phi(r)$ is a function of the distance r from the center of the sphere and then

$$\Delta \phi = \phi(0) - \phi(\infty) = [1 - e^{-\kappa R} (1 + \kappa R)] \Phi_{\text{sat}}. \quad (4.10)$$

For $\kappa R \gg 1$, $\Delta \phi$ saturates into

$$\Phi_{\text{sat}} = -[k_B T / e(Z + 1)] (w_1 - w_2) \Delta \psi, \quad (4.11)$$

where $\Delta \psi$ is the difference of ψ between the two phases. For $\kappa R \ll 1$ we find $\Delta \phi \cong (\kappa R)^2 \Phi_{\text{sat}}$. The same potential difference Φ_{sat} arises across a planar interface. For example, if $w_1 - w_2 \sim 3$, $Z = 1$, and $\Delta \psi \sim 10^{-1}$, we have $|\Phi_{\text{sat}}| \sim 10^{-2} \text{V}$.

- (iii) In slow relaxation of $\delta \psi$, the deviations $\delta \mu_\alpha = k_B T (\delta n_\alpha / \langle n_\alpha \rangle_s + w_\alpha \delta \psi) + Z_\alpha e \delta \phi$ should quickly relax to zero. Then the deviations δn_α are written in terms of $\delta \psi$ as

$$\delta n_1 + \delta n_2 = -\bar{n} (w_1 + Z w_2) \delta \psi, \quad (4.12)$$

$$(\kappa^2 - \nabla^2) \rho = \left[Z e \bar{n} (w_1 - w_2) \nabla^2 + \frac{1}{4\pi} \varepsilon_1 \kappa^2 \mathbf{E}_0 \cdot \nabla \right] \delta \psi, \quad (4.13)$$

where we allow the presence of electric field E_0 to derive (4.22) below.

4.2 Ion effects on phase transition

We consider small fluctuations in a one-phase state without electric field ($E_0 = 0$). The fluctuation contributions to F in the bilinear order are written as

$$\begin{aligned} \frac{\delta F}{k_B T} &= \int_{\mathbf{q}} \left[\frac{1}{2} (a_0 \tau + C_0 q^2) |\psi_{\mathbf{q}}|^2 + \sum_{\alpha=1,2} \left(\frac{|n_{\alpha} \mathbf{q}|^2}{2 \langle n_{\alpha} \rangle_s} + w_{\alpha} n_{\alpha} \mathbf{q} \psi_{\mathbf{q}}^* \right) + \frac{2\pi}{k_B T \varepsilon_0 q^2} |\rho_{\mathbf{q}}|^2 \right] \\ &= \frac{1}{2} \int_{\mathbf{q}} \left[a_0 \tau + C_0 q^2 - \frac{\bar{n} (w_1 + Z w_2)^2}{1 + Z} - \frac{Z n (w_1 - w_2)^2}{(1 + Z)(q^2 + \kappa^2)} q^2 \right] |\psi_{\mathbf{q}}|^2. \end{aligned} \quad (4.14)$$

In the first line $n_{\alpha} \mathbf{q}$ and $\rho_{\mathbf{q}}$ are the Fourier transformations of $\delta n_{\alpha} = n_{\alpha} - \langle n_{\alpha} \rangle_s$ and the charge density $\rho = e(Z n_1 - n_2)$. In the second line we have expressed $n_{\alpha} \mathbf{q}$ in terms of $\psi_{\mathbf{q}}$ using (4.12) and (4.13) and minimized the first line. We introduce a parameter,

$$\gamma_p = |w_1 - w_2| / [(1 + Z)(4\pi C_0 \ell_B)^{1/2}]. \quad (4.15)$$

This number is independent of the ion density and represents the strength of asymmetry in the ion-induced polarization between the two components. The structure factor at $E_0 = 0$ in the mean field theory is written as

$$1/I_0(q) = a_0(\tau - \tau_{\text{ion}}) + C_0 q^2 [1 - \gamma_p^2 \kappa^2 / (q^2 + \kappa^2)], \quad (4.16)$$

where

$$\tau_{\text{ion}} = (w_1 + Z w_2)^2 n / (1 + Z) a_0. \quad (4.17)$$

We draw the following conclusions.

(i) If $\gamma_p < 1$, $I_0(q)$ is maximum at $q = 0$ and the critical temperature shift due to ions is given by $T_c \tau_{\text{ion}}$ in the form of (4.1). As a rough estimate for $Z = 1$, we set $a_0^{-1} \bar{n} \sim \xi_{+0}^3 \bar{n} \sim c$, where c is the mass or mole fraction. Then $\tau_{\text{ion}} \sim (w_1 + w_2)^2 c$. If $|w_1 + w_2| \sim 3$, this result is consistent with the experiments [41, 42]. In future experiments let $1/C_0 I_0(q)$ vs q^2 be plotted; then, the slope is $1 - \gamma_p^2$ for $q \ll \kappa$ and is 1 for $q \gg \kappa$. This changeover is detectable unless $\gamma_p \ll 1$.

(ii) The case $\gamma_p = 1$ corresponds to a so-called Lifshitz point [46], where $1/I(q) - 1/I(0) \propto q^4 / (q^2 + \kappa^2)$.

(iii) If $\gamma_p > 1$, the structure factor attains a maximum at an intermediate wave number q_m given by

$$q_m = (\gamma_p - 1)^{1/2} \kappa \propto \bar{n}^{1/2}. \quad (4.18)$$

The maximum structure factor $I_0(q_m)$ diverges as $\tau \rightarrow \tau'_{\text{ion}}$, where

$$\tau'_{\text{ion}} = \tau_{\text{ion}} + (\gamma_p - 1)^2 \xi_{+0}^2 \kappa^2, \quad (4.19)$$

with the aid of $C_0 = a_0 \xi_{+0}^2$. A charge-density-wave phase should be realized for $\tau < \tau'_{\text{ion}}$. It is remarkable that this mesoscopic phase appears however small $\bar{n}$ is (as long as $\gamma_p > 1$ and $q_m L \gg 1$, L being the system length). Here relevant is the

coupling of the order parameter and the charge density in the form $\propto \psi \rho$ in the free energy density, which generally exists in ionic systems. This possibility of a mesoscopic phase was already predicted for electrolytes [47], but has not yet been confirmed in experiments. However, we note that γ_p increases with increasing Z . As an extreme case, we may consider charged colloids with $Z \gg 1$ and radius r_1 in a near-critical polar mixture, where w_1 grows as Z^2 from (4.5) and

$$\gamma_p \cong (\varepsilon_1/4\varepsilon_0)(\ell_B/\pi C_0)^{1/2}Z/r_1. \quad (4.20)$$

If $Z\xi_{+0}/r_1$ can be made considerably larger than 1, γ_p should eventually exceed 1.

4.3 Nonlinear effects under electric field

In most of the previous experiments, a pulse of strong electric field has been applied. For example, the field strength was $E_0 = 10^4 \text{ V/cm}$ and the pulse duration time was $\Delta t = 1 \text{ ms}$ at $T \sim 300 \text{ K}$ [13, 15]. Let us set $Z = 1$. As can be seen from the general relation (2.18), we can neglect ion accumulation at the capacitor plates if

$$\sigma_{\text{ex}} = \varepsilon E_0/4\pi \gg e\bar{n}v_{\text{dri}}\Delta t \quad \text{or} \quad \Delta t \ll t_{\text{dri}}. \quad (4.21)$$

Here $v_{\text{dri}} = \zeta^{-1}eE_0$ is the drift velocity, ζ is the friction coefficient related to the diffusion constant by $D_i = k_B T/\zeta$, and $t_{\text{dri}} = (\kappa^2 D_i)^{-1}$ is the drift time. For $\Delta t > t_{\text{dri}}$ the electric field far from the boundaries are shielded if $\sigma_{\text{ex}} < e\bar{n}L$. Typical experimental values are $D_i \sim 10^{-6} \text{ cm}^2/\text{s}$, $\zeta \sim 10^{-8} \text{ g/s}$, $\varepsilon \sim 50$, and $E_0 = 10^4 \text{ V/cm}$, leading to $v_{\text{dri}} \sim 1 \text{ cm/s}$. Then the condition (4.21) becomes $\bar{n}\Delta t \ll 10^{12} \text{ cm}^{-3}\text{s}$ and can well hold in experiments [48]. Under this condition and in a one-phase state, the bulk region remains homogeneous and the electric field is not yet shielded. If we are interested in slow motions of ψ , we may assume (4.12) and (4.13) to obtain the decay rate of $\psi_{\mathbf{q}}$ in the form $\Gamma_{\mathbf{q}} = L_0 q^2/I(\mathbf{q})$ (L_0 being the kinetic coefficient) with

$$I(\mathbf{q})^{-1} = I_0(q)^{-1} + [-\varepsilon_2 + A_s q_z^2/(q^2 + \kappa^2)](E_0^2/4\pi k_B T), \quad (4.22)$$

where $I_0(q)$ is given by (4.16). If the pulse duration time Δt is much longer than the relaxation time $1/\Gamma_{\mathbf{q}}$, the structure factor is given by $I(\mathbf{q})$. Here $\hat{q}_z^2 = q_z^2/q^2$ in (3.17) is replaced by $q_z^2/(q^2 + \kappa^2)$ in the presence of ions due to the Debye screening. Let us consider the nonlinear dielectric constant in (3.29) and the electric birefringence $\lim_{k\xi \rightarrow 0} \Delta n$ in (3.36) on the order of E_0^2 . For $\kappa\xi < 1$ the ion effect is small, but for $\kappa\xi > 1$ they should behave as

$$\Delta\varepsilon_{\text{eff}}/A_s \sim \Delta n/A_{\text{op}} \propto E_0^2 \kappa^{-1}. \quad (4.23)$$

This crossover occurs for $c \sim \bar{n}\xi_{+0}^3 > \tau^{2\nu}$ in the weak field regime $\tau \gg \tau_e$.

We also comment on the Joule heating. While the ions are drifting, the temperature increasing rate is given by

$$C \frac{d}{dt} T = 2nv_{\text{dri}}eE_0 = 2ne^2 E_0^2/\zeta = \varepsilon E_0^2/4\pi t_{\text{dri}}, \quad (4.24)$$

where C is the specific heat per unit volume at constant volume and composition. For $\Delta t > t_{dri}$ the temperature will increase by $(\Delta T)_{\text{Joule}} \sim \varepsilon E_0^2 / 4\pi C$. By setting $C \sim k_B \xi_{+0}^{-3}$, we obtain $d\tau/dt \sim 10^{-19} \bar{n} \sim 10^{-6} t_{dri}^{-1} \text{ s}^{-1}$ at $E_0 = 10^4 \text{ V/cm}$. The heating is negligible for very small $\bar{n}\Delta t$ or for not very small τ .

As other nonlinear problems involving ions, we mention transient relaxation of the charge distribution after application of dc field, response to oscillating field, and effects of charges on wetting layers and interfaces between the two phases.

5 Liquid crystals in electric field

In liquid crystals near the isotropic-nematic transition, the order parameter is the symmetric, traceless, orientation tensor $\psi = \{Q_{ij}\}$ (which should be distinguished from the electric charge Q on a capacitor plate). The polarization and the electric induction are written as $\mathbf{p} = \vec{\chi} \cdot \mathbf{E}$ and $\mathbf{D} = \vec{\epsilon} \cdot \mathbf{E}$, respectively, where the polarizability tensor $\vec{\chi}$ depends on Q_{ij} and the local dielectric tensor $\vec{\epsilon} = 1 + 4\pi \vec{\chi}$ reads

$$\varepsilon_{ij} = \varepsilon_0 \delta_{ij} + \varepsilon_1 Q_{ij} + \varepsilon_{21} Q^2 \delta_{ij} + \varepsilon_{22} (Q^2)_{ij} + \dots, \quad (5.1)$$

where $Q^2 = \sum_{ij} Q_{ij}^2$ hereafter. In the nematic phase we may set $Q_{ij} = S(n_i n_j - \delta_{ij}/3)$ in terms of the amplitude S and the director $\mathbf{n}$. Then,

$$\varepsilon_{ij} = \varepsilon'_0(S) \delta_{ij} + \varepsilon'_1(S) n_i n_j, \quad (5.2)$$

where $\varepsilon'_0 = \varepsilon_0 + S^2(2\varepsilon_{21}/3 + \varepsilon_{22}/9)$ and $\varepsilon'_1 = \varepsilon_1 S + \varepsilon_{22} S^2/3$. These relations are analogous to (1.2) for near-critical fluids. An important difference is that the tensor $\{Q_{ij}\}$ is not conserved and its average is sensitive to applied electric field, while the average order parameter in near-critical fluids is fixed or conserved. Here we will examine the effects of the field-induced dipolar interaction.

5.1 Pretransitional growth

If we assume no mobile charges inside the fluid, the free energy functional is given by $F = F_0 + \int d\mathbf{r} \mathbf{E} \cdot \mathbf{D} / 8\pi$ at fixed capacitor charge, where

$$F_0 = \int d\mathbf{r} \left[\frac{A(T)}{2} Q^2 + \lambda \sum_j Q_{jj} + \frac{L_1}{2} \sum_{ijk} [\nabla_k Q_{ij}]^2 + \frac{L_2}{2} \sum_{ijk} \nabla_i Q_{ij} \nabla_k Q_{kj} + \dots \right] \quad (5.3)$$

is the Ginzburg-Landau free energy for $\{Q_{ij}\}$ and λ is a space-dependent Legendre multiplier ensuring $\sum_j Q_{jj} = 0$ [20]. For weakly first order phase transition, the coefficient $A(T) = a_1(T - T_0)$ becomes small as T approaches T_0 . In F_0 the higher order terms are not written explicitly. Analogously to (3.9) we find

$$\delta F = \delta F_0 - \int d\mathbf{r} \mathbf{E} \cdot \delta \vec{\epsilon} \cdot \mathbf{E} / 8\pi. \quad (5.4)$$

Thus,

$$\frac{\delta}{\delta Q_{ij}} F = [A(T)Q_{ij} + \lambda\delta_{ij} + \dots] - \frac{\varepsilon_1}{8\pi} E_i E_j, \quad (5.5)$$

where the gradient term is omitted. At fixed capacitor potential, on the other hand, the appropriate free energy is $G = F_0 - \int d\mathbf{r} \mathbf{E} \cdot \mathbf{D}/8\pi$ but $\delta G/\delta Q_{ij}$ is of the same form as $\delta F/\delta Q_{ij}$ in (5.5). In equilibrium disordered states with $T > T_0$, we set $\langle \delta F/\delta Q_{ij} \rangle = 0$ to obtain

$$\langle Q_{ij} \rangle = \frac{\varepsilon_1}{8\pi} (E_{0i} E_{0j} - \frac{1}{3} E_0^2 \delta_{ij}) \frac{1}{A(T)} + \dots, \quad (5.6)$$

where $\mathbf{E}_0$ is the average electric field assumed to be along the z axis. On the other hand, analogously to (3.27), the macroscopic static dielectric constant is given by

$$\varepsilon_{\text{eff}} = \langle \varepsilon_{zz} \rangle - \int_{\mathbf{q}} \frac{1}{\varepsilon_0 q^2} \langle |\sum_j q_j \varepsilon_{jz}(\mathbf{q})|^2 \rangle, \quad (5.7)$$

where $\varepsilon_{ij}(\mathbf{q})$ are the Fourier transformation of $\varepsilon_{ij}(\mathbf{r})$. As $T \rightarrow T_0$, the average $\langle \varepsilon_{zz} \rangle$ yields the dominant contribution to the nonlinear dielectric constant [20],

$$\Delta \varepsilon_{\text{eff}} \cong \varepsilon_1^2 E_0^2 / 12\pi A(T), \quad (5.8)$$

in agreement with the experiments [21]. The contribution from the second term in (5.7) is smaller than that in (5.8) by $(\varepsilon_1/\varepsilon_0)^2 k_B T A(T)^{1/2} / L_1^{3/2}$ for $L_2 \sim L_1$.

The electrostatic free energy $\Delta F = F - F_0$ up to of order Q^2 is written as

$$\Delta F = -\frac{E_0^2}{8\pi} \int d\mathbf{r} \varepsilon_{zz}(\vec{Q}) + A_s \frac{E_0^2}{8\pi} \int_{\mathbf{q}} \frac{1}{q^2} |\sum_j q_j Q_{jz}(\mathbf{q})|^2, \quad (5.9)$$

where $A_s = \varepsilon_1^2/\varepsilon_0$ and the dipolar interaction, the second term, is expressed in terms of the Fourier transformations $Q_{ij}(\mathbf{q})$. The correlation functions of $Q_{ij}(\mathbf{q})$ in disordered states depend on the direction $q^{-1}\mathbf{q}$ even in the limit $q \rightarrow 0$. For simplicity, for $q_z = 0$ we obtain

$$\lim_{q \rightarrow 0} \langle Q_{iz}(\mathbf{q}) Q_{jz}(\mathbf{q})^* \rangle = \frac{k_B T}{r} \left[\delta_{ij} - \frac{q_i q_j}{q^2} \frac{r_e}{r + r_e} \right] \quad (i, j = x, y), \quad (5.10)$$

where $r = 2A(T) - (2\varepsilon_{21} + \varepsilon_{22})E_0^2/4\pi$ and $r_e = A_s E_0^2/4\pi$.

5.2 Director fluctuations in nematic states

We consider nematic states considerably below the transition, where we may neglect the fluctuations of the amplitude S [20]. If ε'_1 in (5.2) is positive, the average orientation of the director can be along the z axis from minimization of the first

term in (5.8). Then the deviation $\delta \mathbf{n}$ perpendicular to the z axis undergo large fluctuations at small wave numbers. In electric field ΔF in (5.9) becomes

$$\Delta F = \frac{1}{8\pi} E_0^2 \int_{\mathbf{q}} \left[\varepsilon'_1 |\delta \mathbf{n}(\mathbf{q})|^2 + A'_s \frac{1}{q^2} |\mathbf{q} \cdot \delta \mathbf{n}(\mathbf{q})|^2 \right], \quad (5.11)$$

where $A'_s = A_s S^2$. For general $\mathbf{q}$ we obtain the correlation functions,

$$G_{ij}(\mathbf{q}) = \langle \delta n_i(\mathbf{q}) \delta n_j(\mathbf{q})^* \rangle = k_B T \frac{\delta_{ij}}{r_2} + k_B T \frac{q_i q_j}{q_{\perp}^2} \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \quad (i, j = x, y), \quad (5.12)$$

where $q_{\perp}^2 = q_x^2 + q_y^2$, and

$$r_1 = K_3 q_z^2 + K_1 q_{\perp}^2 + \frac{1}{4\pi} \left(\varepsilon'_1 + A'_s \frac{q_{\perp}^2}{q^2} \right) E_0^2, \quad r_2 = K_3 q_z^2 + K_2 q_{\perp}^2 + \frac{1}{4\pi} \varepsilon'_1 E_0^2. \quad (5.13)$$

The K_1 , K_2 , and K_3 are the Frank constants. If $\varepsilon'_1 \gtrsim A'_s$, the correlation length ξ is of the following order,

$$\xi \sim (4\pi K / \varepsilon'_1)^{1/2} E_0^{-1}, \quad (5.14)$$

where K represents the magnitude of the Frank constants and $k_B T / K$ is a microscopic length. The scattered light intensity is proportional to the following [20],

$$\langle |\mathbf{f} \cdot \overset{\leftrightarrow}{\varepsilon}(\mathbf{q}) \cdot \mathbf{i}|^2 \rangle = k_B T \varepsilon_1'^2 \left[|\mathbf{a}|^2 / r_2 + (1/r_1 - 1/r_2) |\mathbf{q} \cdot \mathbf{a}|^2 / q_{\perp}^2 \right], \quad (5.15)$$

where $\mathbf{i}$ and $\mathbf{f}$ represent the initial and final polarizations. The vector $\mathbf{a}$ is defined by

$$a_x = i_z f_x + f_z i_x, \quad a_y = i_z f_y + f_z i_y, \quad a_z = 0. \quad (5.16)$$

If $A'_s > 0$, the intensity depends on $q^{-1} \mathbf{q}$ even in the limit $q \rightarrow 0$.

In nematic states the average $\langle \varepsilon_{ij} \rangle$ is anisotropic, leading to large *intrinsic* birefringence. We here consider *form* dichroism arising from the director fluctuations, where the laser wave vector $\mathbf{k}$ is along the x axis and the average director is along the z axis. We assume the relation $\varepsilon_{ij} = \varepsilon'_0 \delta_{ij} + \varepsilon'_1 n_i n_j$ at optical frequencies using the same notation as in (5.2). As a generalization of (1.5), the fluctuation contribution to the dielectric tensor for the electromagnetic waves is of the form,

$$\Delta \overset{\leftrightarrow}{\varepsilon} = \frac{1}{\varepsilon'_0} \int_{\mathbf{q}} \frac{1}{q^2 - k^2 - i0} \langle |\overset{\leftrightarrow}{\varepsilon}(\mathbf{k} - \mathbf{q}) \cdot (k^2 \overset{\leftrightarrow}{I} - \mathbf{q}\mathbf{q}) \cdot \overset{\leftrightarrow}{\varepsilon}(\mathbf{q} - \mathbf{k})|_{\perp} \rangle, \quad (5.17)$$

where $[\dots]_{\perp}$ denotes taking the tensor part perpendicular to $\mathbf{k}$. This expression reduces to (1.5) if $\overset{\leftrightarrow}{\varepsilon}$ is diagonal and (1.2) holds. Here $\Delta \varepsilon_{yz} = 0$ and the imaginary part of $\Delta n / n \cong (\Delta \varepsilon_{zz} - \Delta \varepsilon_{yy}) / 2\varepsilon'_0$ becomes

$$\frac{\text{Im} \Delta n}{n} = \frac{k^3}{32\pi^2} (\varepsilon'_1 / \varepsilon'_0)^2 \int d\Omega \left[G_{xx}(\ell) + \hat{q}_z^2 G_{yy}(\ell) - \sum_{i,j=x,y} \hat{q}_i \hat{q}_j G_{ij}(\ell) \right], \quad (5.18)$$

where $\ell = \mathbf{k} - k\hat{\mathbf{q}}$ and $\int d\Omega \cdots$ denotes integration over the direction $\hat{\mathbf{q}} = \mathbf{q}^{-1}\mathbf{q}$. Using (5.12) we can make the following order estimations,

$$\begin{aligned} \frac{\text{Im}\Delta n}{n} &\sim 10^{-2}(\varepsilon'_1/\varepsilon'_0)^2(k_B T/K)\xi^2 k^3 & (k\xi \ll 1) \\ &\sim 10^{-2}(\varepsilon'_1/\varepsilon'_0)^2(k_B T/K)k & (k\xi \gtrsim 1). \end{aligned} \quad (5.19)$$

The form dichroism here is much larger than that in (3.38) for near-critical fluids. As far as I am aware, there was one attempt to measure anisotropy of the turbidity in an oriented nematic state [49].

6 Concluding remarks

(i) The Ginzburg-Landau theory in Section 2 generally describes how the electrostatic interactions arise depending on the boundary condition (in the presence or absence of the capacitor plates). It can be used to investigate electric field effects at various kinds of phase transitions in fluids and solids.

(ii) A brief review has been given on the dielectric properties and the electric field effects in near-critical fluids and liquid crystals. The Debye-Kleboth experiment on the critical temperature shift was performed many years ago and they neglected the dipolar interaction in their theoretical interpretation. As regards the nonlinear dielectric constant $\Delta\varepsilon_{\text{eff}}$ and the birefringence Δn , we cannot explain their experimental exponents, $z_{\text{non}} \sim 0.4$ and $z_{\text{op}} \cong 0.65 - 0.8$, whereas the common exponent $\nu(1 - 2\eta) \cong 0.58$ has been predicted for them. To resolve these issues, scattering experiments to check the anisotropic structure factor (3.17) are most needed.

(iii) New predictions have also been made on the critical temperature shift due to electric field, the nonlinear dielectric constant, the ion effects in binary mixtures, and the fluctuation intensities and the form dichroism in liquid crystals. In particular, in near-critical polar mixtures with ions, we have examined charge distributions and potential differences around two-phase interfaces, the critical temperature shift due to ions, and the scattering intensity. The condition for a charge-density-wave phase has been examined for general multivalent ions.

(iv) Effects of oscillating electric field are also worth studying particularly for ionic systems. Appreciable critical anomaly can be seen in the frequency-dependence of the dielectric constant [48]. Large dynamic electric birefringence was observed in polyelectrolyte solutions [50]. By this method we can neglect accumulation of ions at the boundaries (but the Joule heating may not be negligible).

(v) Stronger electric field effects have been observed in polymeric systems than in low-molecular-weight fluids. As such effects, we mention field-induced anisotropy in light scattering from a polymer solution [32], lamellar alignment in diblock copolymers [51], and large dielectric response in a surfactant sponge phase [52].

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References

- [1] L.D. Landau and E.M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, 1984), Chap II.
- [2] P. Debye and K. Kleboth, J. Chem. Phys., **42**, 3155 (1965).
- [3] D. Bedeaux and P. Mazur, Physica **67**, 23 (1973).
- [4] G. Stell and J.S. Hoye, Phys. Rev. Lett. **33**, 1268 (1974); J.S. Hoye and G. Stell, J. Chem. Phys. **81**, 3200 (1984).
- [5] J. Goulon, J.L. Greffe and D.W. Oxtoby, J. Chem. Phys. **70**, 4742 (1979).
- [6] J.V. Sengers, D. Bedeaux, P. Mazur and S.C. Greer, Physica, **104A**, 573 (1980).
- [7] D. Beaglehole, J. Chem. Phys. **74**, 5251 (1981).
- [8] A. Onuki and M. Doi, Europhys. Lett. **17**, 63 (1992).
- [9] A. Onuki, Europhys. Lett. **29**, 611 (1995).
- [10] G. Zalczer and D. Beysens, J. Chem. Phys. **92**, 6747 (1990).
- [11] J. Malecki and J. Ziolo, Chem Phys. **35**, 187 (1978).
- [12] W. Pyzuk, Chem Phys. **50**, 281 (1980); Europhys. Lett. **17**, 339 (1992).
- [13] S.J. Rzoska, J. Chrapeć and J. Ziolo, Physica A **139**, 569 (1980); S.J. Rzoska, A. D. Rzoska, M. Górny and J. Ziolo, Phys. Rev. E **52**, 6325 (1995).
- [14] S.J. Rzoska, Phys. Rev. E **48**, 1136 (1993).
- [15] K. Orzechowski, Physica B **172**, 339 (1991); Chem. Phys. **240**, 275 (1999).
- [16] W. Pyzuk, H. Majgier-Baranowska, and J. Ziolo, Chem Phys. **59**, 111 (1981).
- [17] R. Piazza, T. Bellini, V. Degiorgio, R.E. Goldstein, S. Leibler and R. Lipowsky, Phys. Rev. B **38**, 7223 (1988).
- [18] T. Bellini and V. Degiorgio, Phys. Rev. B **39**, 7263 (1989).
- [19] S.J. Rzoska, V. Degiorgio, T. Bellini and R. Piazza, Phys. Rev. E **49**, 3093 (1994).
- [20] P.G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Oxford, 1993).
- [21] W. Pyzuk, I. Stomka, J. Chrapeć, S.J. Rzoska, and J. Ziolo, Chem Phys. **121**, 255 (1988); A. Drozd-Rzoska, Phys. Rev. E **59**, 5556 (1999).
- [22] A. Onuki, *Phase Transition Dynamics* (Cambridge, 2002).
- [23] A. Onuki and K. Kawasaki, Physica A **11**, 607 (1982).
- [24] A. Onuki and M. Doi, J. Chem. Phys. **85**, 1190 (1986).
- [25] Y.C. Chou and W.I. Goldburg, Phys. Rev. Lett. **47**, 1155 (1981); D. Beysens and M. Gbadamassi, Phys. Rev. Lett. **47**, 846 (1981); D. Beysens, R. Gastand and De-cruppe, Phys. Rev. A **30**, 1145 (1984).

- [26] N.J. Wagner, G.G. Fuller, and W.B. Russel, J. Chem. Phys. **89**, 1580 (1988)
- [27] D. Wirtz, D.E. Werner and G.G. Fuller, J. Chem. Phys. **101**, 1679 (1994).
- [28] R. Kretschmer and K. Binder, Phys. Rev. B **20**, 1065 (1979).
- [29] B. Groh and S. Dietrich, Phys. Rev. E **53**, 2509 (1996); **57**, 4535 (1998).
- [30] T. Garel and S. Doniach, Phys. Rev. B **26**, 325 (1982).
- [31] Y. Yoshida and A. Ikushima, J. Phys. Soc. Jpn. **45**, 1949 (1978).
- [32] D. Wirtz, K. Berend, and G.G. Fuller, Macromolecules **25**, 7234 (1992); D. Wirtz and G.G. Fuller, Phys. Rev. Lett. **71**, 2236 (1993).
- [33] A. Aharony, Phys. Rev. B **8**, 3363 (1973).
- [34] M.E. Fisher and J.S. Langer, Phys. Rev. Lett. **20**, 665 (1968).
- [35] G. Zimmerli, R.A. Wilkinson, R.A. Ferrell and M.R. Moldover, Phys. Rev. E **59**, 5862 (1999).
- [36] M. Barmartz and F. Zhong, Proceedings of the 2000 NASA/JPL Workshop on Fundamental Physics in Microgravity, Solvang, June 19-21, 2000.
- [37] J.I. Frenkel, Phys. Z. Sowjetunion **8**, 675 (1935) [Zh.Eksp.Teor.Fiz. **6**, 347 (1936)]; L. Tonks, Phys. Rev. **48**, 562 (1935); G.I. Taylor and A.D. McEwan, J. Fluid Mech. **22**, 1 (1965).
- [38] L.P. Gorkov and D.M. Chernikova, Pis'ma Zh. Eksp. Teor. Fiz. **18**, 119 (1973) [JETP Lett. **18**, 68 (1973)]; M. Wanner and P. Leiderer, Phys. Rev. Lett. **42**, 315 (1979); D. Savignac and P. Leiderer, Phys. Rev. Lett. **49**, 1869 (1992).
- [39] A. Onuki, Physica A, **217**, 38 (1995).
- [40] J.N. Israelachvili, *Intermolecular and Surface Forces* (Academic, 1985).
- [41] E.L. Eckfeldt and W.W. Lucasse, J. Phys. Chem. **47**, 164 (1943).
- [42] B.J. Hales, G.L. Bertrand, and L.G. Hepler, J. Phys. Chem. **70**, 3970 (1966).
- [43] J.L. Tveekrem and D.T. Jacobs, Phys. Rev. A **27**, 2773 (1983).
- [44] T. Narayanan and A. Kumar, Phys. Rep. **249**, 135 (1994); J. Jacobs, A. Kumar, M.A. Anisimov, A.A. Povodyrev and J.V. Sengers, Phys. Rev. E **58**, 2188 (1998).
- [45] K. Yoshida, M. Misawa, K. Maruyama, M. Imai, and M. Furusaka, J. Chem. Phys. **113**, 2343 (2000).
- [46] J.F. Joanny and L. Leibler, J. Phys. (France) **51**, 545 (1990); P.M. Chaikin and T.C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge, 1995).
- [47] V.M. Nabutovskii, N.A. Nemov, and Yu.G. Peisakhovich, Phys. Lett. A, **79**, 98 (1980); Sov. Phys. JETP **52**, 111 (1980) [Zh.Eksp.Teor.Fiz. **79**, 2196 (1980)]; Mol. Phys. **54**, 979 (1985).
- [48] K. Orzechowski, private communication and the paper in this conference.
- [49] D. Langevin and M.-A. Bouchiat, J. de Physique C1, **36**, 197 (1975).
- [50] U. Krämer and H. Hoffmann, Macromolecules, **24**, 256 (1991).
- [51] K. Amundson, E. Helfand, X. Quan, S.D. Hudson, and S.D. Smith, Macromolecules, **27**, 6559 (1994); A. Onuki and J. Fukuda, Macromolecules, **28**, 8788 (1995).
- [52] M.E. Cates, P. van der Schoot, and C.-Y.D. Lu, Europhys. Lett. **29**, 689 (1995).

CRITICAL PHENOMENA IN CONFINED BINARY LIQUID MIXTURES

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Abstract: Critical phenomena are studied in confined binary liquid mixtures. The scaling hypothesis of critical phenomena in confined one-component liquid systems is generalized for finite-size binary liquid mixtures. It gives a possibility to evaluate the susceptibility of finite-size binary liquid mixtures near the liquid-liquid and liquid-vapor critical states. An important biophysical application is discussed, namely the isomorphism of critical phenomena in confined liquid mixtures and cell-to-cell communication in synapses (synaptic transmission). Kinetic equations are derived and analyzed for a system "mediator-receptor". The corresponding correlation function and correlation length of order parameter fluctuations are found for this system with geometry of restricted cylinder. The shifts of critical parameters are analyzed on the basis of scaling hypothesis for confined systems.

1. Scaling hypothesis for finite-size binary liquid mixtures

Critical phenomena and phase transitions in finite-size systems have been actively studied in recent years. Many systems of experimental and practical interest are spatially finite-sized, such as thin surface layers, interfaces, porous media, biomembranes, vesicles, synaptic clefts [1-5].

Liquid-liquid critical state. Binary liquid mixture near the liquid-liquid critical state is isomorphous to the idealized model of incompressible binary alloy which is described by independent variables "temperature T – concentration x ". The pressure P becomes an additional natural variable for the binary liquid mixture [6].

To formulate the scaling hypothesis it is convenient to use the thermodynamics potential – the Gibbs free energy $G(T,P,x)$ per one mole, i.e. chemical potential $\mu = G/N$.

$$G(T,P,x) = \mu(T,P,x) = \mu_1(1-x) + \mu_2x = \mu_1 + \mu^*x \quad (1)$$

Here μ_1 and μ_2 are chemical potentials per one mole of a pure solvent and dissolved matter; $\mu^* = \mu_2 - \mu_1 = (\partial G / \partial x)_{T,P}$ is the difference of chemical potentials; $x = (\partial G / \partial \mu)_{T,P}$ is the concentration.

The Gibbs free energy consists of two parts $G = G_0 + G_{sing}$, where the first term (G_0) is the regular part of thermodynamics potential, which has no singularities in the critical state, while the second one (G_{sing}) is the fluctuation (singular) part which is determined by cooperation of strongly developed fluctuations of order parameter [7]. The same presentation is fully related to the chemical potential of pure solvent $\mu_1(T, P, \mu^*)$: $\mu_1 = \mu_{1pez} + \mu_{1cise}$. At the vicinity of liquid-liquid critical state of the binary mixture the order parameter is $\phi(P) = x - x_c(P)$, i.e. the deviation of concentration x from its critical value $x_c(P)$.

The generalization of the bulk scaling hypothesis for the case of binary liquid systems in confined geometry with the linear size $L \approx \xi$ gives the following expressions for the chemical potential $\mu_{1sing}(T, P, x)$ and the correlation length ξ :

$$\mu_{1cise}(T, P, x) = L^{-d} f_\mu[a\phi^{1/\beta}(P)L^{1/\nu}, bhL^{\beta\delta/\nu}], \quad (2)$$

$$\xi(T, P, x) = L f_\xi[a\phi^{1/\beta}(P)L^{1/\nu}, bhL^{\beta\delta/\nu}]. \quad (3)$$

Here d is the spatial dimension of the system, and $f_\mu(y, z)$ and $f_\xi(y, z)$ are the scaling functions with asymptotics at $L \rightarrow \infty$:

$$\begin{aligned} f_\mu(y \rightarrow \infty) &\sim y^{\beta(\delta+1)} \sim \phi^{\delta+1} \sim \tau^{2-\alpha}, \\ f_\mu(z \rightarrow \infty) &\sim z^{1+1/\delta} \sim h^{1+1/\delta}, \\ f_\xi(y \rightarrow \infty) &\sim y^{-\nu} \sim \phi^{-\nu/\beta} \sim \tau^{-\nu}, \\ f_\xi(z \rightarrow \infty) &\sim z^{-\nu/\beta\delta} \sim h^{-\nu/\beta\delta}. \end{aligned} \quad (4)$$

The limiting transition from the scaling hypothesis (2)-(3) for the finite-size binary liquid mixtures to the scaling hypothesis for the spatially infinite systems (at $L \rightarrow \infty$) near the liquid-liquid critical state could be obtained using asymptotics (4):

$$\begin{aligned} G_{cise} &\sim \mu_{1cise} \sim L^{-d} y^{\beta(\delta+1)} \sim L^{-d} \phi^{\delta+1} L^{\beta(\delta+1)/\nu} \sim \phi^{\delta+1} L^{-d + (2\beta+1)/\nu} \sim \\ &\sim \phi^{\delta+1} L^0 \sim \phi^{\delta+1} \sim \tau^{\beta(\delta+1)} \sim \tau^{2-\alpha}, \\ G_{cise} &\sim \mu_{1cise} \sim L^{-d} z^{(\delta+1)/\delta} \sim L^{-d} h^{(\delta+1)/\delta} L^{\beta(\delta+1)/\nu} \sim h^{(\delta+1)/\delta} L^0 \sim h^{(\delta+1)/\delta}, \\ \xi &\sim L y^{-\nu} \sim L \phi^{-\nu/\beta} L^{-1} \sim \phi^{-\nu/\beta} L^0 \sim \phi^{-\nu/\beta} \sim \tau^{-\nu}, \\ \xi &\sim L z^{-\nu/\beta\delta} \sim L h^{-\nu/\beta\delta} L^{-1} \sim h^{-\nu/\beta\delta} L^0 \sim h^{-\nu/\beta\delta}. \end{aligned} \quad (5)$$

Liquid-vapor critical state. The binary liquid mixture near this critical state is isomorphous to the idealized model of a lattice gas with independent “temperature T –density ρ (or volume V)”. An additional variable for binary liquid mixture can be chosen either as the concentration x (the natural “density” variable) or as the conjugated (with respect to x) variable – the difference of chemical potential $\mu^* = \mu_T - \mu_1$ [6].

The scaling hypothesis of the liquid-vapor critical state has to be formulated in terms the Helmholtz free energy $F_{sing}(T, \rho, \mu^*)$ and correlation length $\xi(T, \rho, \mu^*)$ as follows:

$$F_{sing}(T, \rho, \mu^*) = L^{-d} f_F[a\phi^{1/\beta}(\mu^*)L^{1/\nu}, bh(\mu^*)L^{\beta\delta/\nu}], \quad (6)$$

$$\xi(T, \rho, \mu^*) = L f_{\xi} [\alpha \varphi^{1/\beta}(\mu^*) L^{1/\nu}, b h(\mu^*) L^{\beta\delta/\nu}] \quad (7)$$

The order parameter of a binary liquid mixture near the liquid-vapor critical state is the difference of the mixture density and the critical density $\varphi(\mu^*) = [\rho - \rho_c(\mu^*)] / \rho_c(\mu^*)$. The conjugated field is $h = [\mu_1 - \mu_1(\rho_c(\mu^*), T)] / \mu_1(\rho_c(\mu^*), T)$.

Scaling functions of the Helmholtz free energy $f_T(y, z)$ and correlation length $f_{\xi}(y, z)$ have the same asymptotics as in previous case of the liquid-liquid critical state. It gives an opportunity to obtain the limiting transition from a finite-size binary liquid mixture to the spatially infinite one.

2. Susceptibility of finite-size binary liquid mixtures

Liquid-liquid critical state. The susceptibility χ in the liquid-liquid critical region is connected with the second derivative of the singular part of the thermodynamical potential μ_{ls} with respect to the difference of chemical potentials μ^* :

$$\chi_{P,T} = -RT_c \cdot (\partial^2 \mu_{ls} / \partial \mu^*)_{P,T}, \quad (8)$$

As μ^* determines the external field $h = [\mu^* - \mu^*(x_c, T)] / RT_c$, it gives

$$\begin{aligned} \chi &= -RT_c (\partial^2 \mu_{ls} / \partial^2 z)_{P,T} \cdot (\partial z / \partial h)^2 \cdot (\partial h / \partial \mu^*)_T^2 = \\ &= -(RT_c)^{-1} L^{-d} \cdot (\partial^2 f_{\mu}(y, z) / \partial^2 z)_y \cdot b^2 L^{2\beta\delta/\nu} = L^{\gamma/\nu} f_{\chi}(y, z), \end{aligned} \quad (9)$$

where the scaling function of the susceptibility $f_{\chi}(y, z) = -b^2 (RT_c)^{-1} (\partial^2 f_{\mu}(y, z) / \partial^2 z)_y$ has such asymptotics: $f_{\chi}(y \rightarrow \infty) \sim y^{-\gamma}$, $f_{\chi}(z \rightarrow \infty) \sim z^{-\gamma/\beta\delta}$. As a result, one can obtain the limiting transition to the spatially infinite system: $\chi(L \rightarrow \infty) \sim \tau^{-\gamma} \sim h^{-\gamma/\beta\delta}$.

Liquid-vapor critical state. The isomorphous susceptibility of finite-size binary liquid mixtures is as follows:

$$\begin{aligned} \chi_{T,\mu^*} &= \frac{RT_c}{\rho_c} \left(\frac{\partial^2 p}{\partial \mu_1^2} \right)_{T,\mu^*} = \frac{RT_c}{\rho_c} \left(\frac{\partial^2 \rho}{\partial \mu_1} \right)_{T,\mu^*} = \\ &= L^{-d} \cdot \left(\frac{\partial^2 f_p^{(1)}}{\partial z^2} \right)_y \cdot \left(\frac{\partial z}{\partial h} \right)^2 \cdot \left(\frac{\partial h}{\partial \mu_1} \right)^2 = \\ &= L^{-d} b^2 L^{2\beta\delta/\nu} (RT_c)^{-2} \cdot \left(\frac{\partial^2 f_p^{(1)}}{\partial z^2} \right)_y = L^{\gamma/\nu} f_{\chi}(y, z), \end{aligned} \quad (10)$$

where the scaling function $f_{\chi} = b^2 (RT_c)^{-2} (\partial^2 f_p^{(1)} / \partial z^2)_y$, $y = \alpha t L^{1/\nu}$, $z = b h L^{\beta\delta/\nu}$. It can be easily seen that this equation gives $\chi_{T,\mu^*}(L \rightarrow \infty) \sim \tau^{-\gamma}$, i.e. the susceptibility of the one-components liquid near the critical point.

The scaling hypothesis of finite-size binary liquid mixtures can be written near the critical state of evaporation in the following form:

$$\Delta P_{cuz} = L^{-d} f_p^{(2)}(z_1, z_2), \quad \xi = L f_{\xi}^{(2)}(z_1, z_2) \quad (11)$$

where arguments $z_1 = h_1 L^{\beta\delta/\nu}$ and $z_2 = h_2 L^{1/\nu}$ are connected with two scaling fields [8]:

$$h_1 = a_1 \Delta\mu_1 + a_2 \tau + a_3 \Delta\mu^*, \quad h_2 = b_1 \tau + b_2 \Delta\mu_1 + b_3 \Delta\mu^* \quad (12)$$

The density scaling values φ_1 and φ_2 are conjugated to these fields h_1 and h_2

$$\varphi_1 = \left(\frac{\partial \Delta P_{\text{cunz.}}}{\partial h_1} \right)_{h_2} = L^{-d+\beta\delta/\nu} \cdot \left(\frac{\partial f_p^{(2)}}{\partial z_1} \right)_{z_2} = L^{-\beta/\nu} \cdot \left(\frac{\partial f_p^{(2)}}{\partial z_1} \right)_{z_2} \quad , \quad (13)$$

$$\varphi_2 = \left(\frac{\partial \Delta P_{\text{cunz.}}}{\partial h_2} \right)_{h_1} = L^{-d+1/\nu} \cdot \left(\frac{\partial f_p^{(2)}}{\partial z_2} \right)_{z_1} = L^{(\alpha-1)/\nu} \cdot \left(\frac{\partial f_p^{(2)}}{\partial z_2} \right)_{z_1} \quad , \quad (14)$$

The first scaling density is the order parameter because $\varphi_1 \sim L^{-\beta/\nu} \sim \tau^\beta$.

It is possible to obtain the following expressions for the susceptibility of finite-size binary liquid mixtures:

1. The susceptibility χ_1 describing the critical behavior of the order-parameter correlator $\langle \varphi_1^2 \rangle$

$$\chi_1 = \left(\frac{\partial^2 \Delta P_{\text{cunz.}}}{\partial h_1^2} \right)_{h_2} = \left(\frac{\partial \varphi_1}{\partial h_1} \right)_{h_2} = \left(\frac{\partial \varphi_1}{\partial z_1} \right)_{z_2} \cdot \frac{\partial z_1}{\partial h_1} = L^{-(\beta-\delta)/\nu} \cdot \left(\frac{\partial^2 f_p^{(2)}}{\partial z_1^2} \right)_{z_2} = L^{\gamma/\nu} \cdot f_\chi^{(1)}(z_1, z_2) \quad (15)$$

has a strong divergence $\chi_1(L \rightarrow \infty) \sim \tau^{-\gamma}$, $\gamma \approx 5/4$.

2. The susceptibility χ_2 describing the critical behavior of the correlator $\langle \varphi_2^2 \rangle$

$$\chi_2 = \left(\frac{\partial^2 \Delta P_{\text{cunz.}}}{\partial h_2^2} \right)_{h_1} = \left(\frac{\partial \varphi_2}{\partial h_2} \right)_{h_1} = \left(\frac{\partial \varphi_2}{\partial z_2} \right)_{z_1} \cdot \frac{\partial z_2}{\partial h_2} = L^{(\alpha-1)/\nu} \cdot \left(\frac{\partial^2 f_p^{(2)}}{\partial z_2^2} \right)_{z_1} L^{1/\nu} = L^{\alpha/\nu} \cdot f_\chi^{(2)}(z_1, z_2) \quad (16)$$

has a weak divergence $\chi_2(L \rightarrow \infty) \sim \tau^{-\alpha}$, $\alpha \approx 0.1$ and describes thermal fluctuations of energy.

3. It is also possible to introduce the crossover susceptibility

$$\chi_3 = \frac{\partial^2 \Delta P_{\text{cunz.}}}{\partial h_1 \partial h_2} = \left(\frac{\partial \varphi_1}{\partial h_2} \right)_{h_1} = \left(\frac{\partial \varphi_2}{\partial h_1} \right)_{h_2} = L^{(1-\beta)/\nu} \cdot f_\chi^{(3)}(z_1, z_2) \quad , \quad (17)$$

which describes the critical behavior of the correlator $\langle \varphi_1 \varphi_2 \rangle$ and has an intermediate divergence with respect to susceptibilities χ_1 i χ_2 , namely $\langle \varphi_1 \varphi_2 \rangle \sim \tau^{\beta-1}$, $\beta-1 \approx -2/3$.

It is expected that the experimental studies of the dynamic light scattering [8] could confirm the existence of different critical behavior of susceptibilities in finite-size binary liquid mixtures.

3. Isomorphism of critical phenomena in confined mixtures and cell-to-cell communication in synapses

The convenient theory of cell-to-cell communication is commonly based on ideas about chemical intermediaries (for example, let us consider a typical transmitter agent – acetylcholine ACh) securing interaction between two neurons [9-12]. Sequence of major events in cholinergic synapse is as follows: ACh is synthesized and stored in spheroid vesicles in the presynaptic membrane; then ACh releases and reacts with specific acetylcholine receptors in active state (R^*); the formation of the transmitter-receptor complex ($ACh - R^*$) produces conformational changes in the postsynaptic membrane and therefore change in a membrane potential; finally ACh is either inactivated by acetylcholinesterase (AChE) or is removed by diffusion.

Kinetic equations. Such kinetic equations for concentrations x and y of receptors R^* and acetylcholine-receptor complexes $ACh-R^*$ are supposed to correspond to the cholinergic synapse:

$$\begin{cases} \frac{dx}{dt} = k_2(1-x) - k_1xy \\ \frac{dy}{dt} = f(t) - k_1xy \end{cases} \quad (18)$$

where $f(t)$ is the source function describing the intensity of ACh release from spheroid vesicles, k_i are the coefficients of reactions velocities.

It must be stressed that the process of ACh release is cooperative: about 10^7 molecules of ACh are releasing simultaneously under the influence of one nerve impulse. Such a synchronous activation of large zone of receptors by ACh can be considered in details as the process which is isomorphic to the critical phenomena in binary liquid mixtures near the critical mixing point [4].

For stationary source function ($f = const$) the stationary points are

$$x_s = 1 - \varphi, \quad y_s = \lambda\varphi/(1 - \varphi), \quad (19)$$

where $\lambda = k_2/k_1$ and $\varphi = f/k_2$. Figure 1 shows the dependence of stationary points on parameters λ and φ . It is important to stress that the concentration x_s does not depend on λ . It could be seen that stationary value of the ACh concentration y_s is increasing to infinity when the parameter φ is approaching 1. Physical sense has the situation when y_s changes in range from 0 to the critical value y_{crit} . The source

function $f \leq f_{\max} = \frac{y_{crit}}{1/k_1 + y_{crit}/k_2}$, where $f_{\max}$ gives the informational capability of the transmission channels.

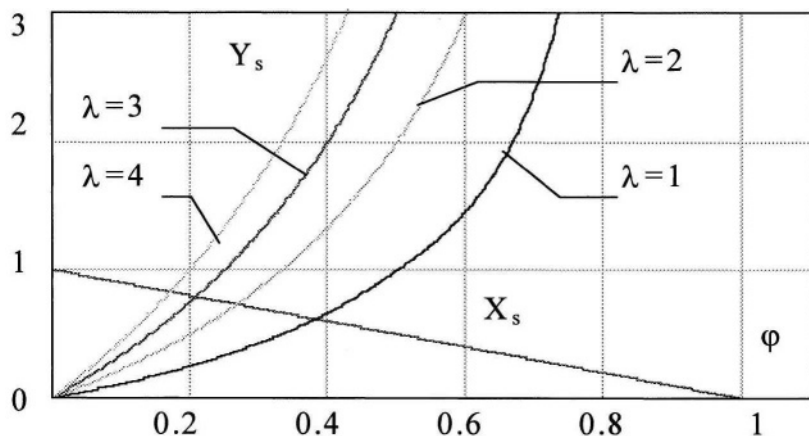


Figure 1. Dependence of the stationary points on parameters λ and φ .

The system of kinetic equations for $x(\omega)$ and $y(\omega)$ for slow oscillations of the source function has such a form

$$\begin{cases} -i\omega x(\omega) = k_2 \delta(\omega) - k_2 x(\omega) - k_1 x(\omega) y_0 - k_1 x''(\omega) y_2 \\ -i\omega y(\omega) = f(\omega) - k_1 x_0 y(\omega) - k_1 x_2 y''(\omega) \end{cases} \quad (20)$$

where $x_0 = \int x(\omega) d\omega$, $y_0 = \int y(\omega) d\omega$, $x_2 = \frac{1}{2} \int x(\omega) \omega^2 d\omega$,
 $y_2 = \frac{1}{2} \int y(\omega) \omega^2 d\omega$.

Solution of this system of differential equations is as follows:

$$\begin{aligned} x(t) &= \frac{k_2}{k_1 y_2} G(t, \frac{k_2 + k_1 y_0}{k_1 y_2}, \frac{1}{k_1 y_2}), \\ y(t) &= \frac{f(t) G(t, \frac{x_0}{x_2}, \frac{1}{k_1 x_2})}{k_1 x_2}, \end{aligned} \quad (21)$$

where the function $G(t, \alpha, \beta) = \frac{\int \exp(-\frac{t^3}{3\beta} + \frac{\alpha}{\beta} t) dt}{\beta \exp(-\frac{t^3}{3\beta} + \frac{\alpha}{\beta} t)}$.

Thus, the source function $f(t)$ modulates the temporal evolution of the ACh-R* concentration.

The activation zone for the process of synaptic transmission. For geometry of the restricted cylinder $0 \leq \rho < a$, $-h \leq z \leq h$ with zeroth boundary conditions the pair correlation function of the system “mediator-receptor” has such a form:

$$G_2(\rho, z) = \frac{1}{V} \cdot \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \frac{1}{J_1^2(\mu_m)} \frac{J_0(\mu_m \frac{\rho}{a}) \cos(\frac{\pi(n+0.5)z}{h})}{\kappa^2 + \frac{\pi^2 (2n+1)^2}{4h^2} + \frac{\mu_m^2}{a^2}}, \quad (22)$$

where $J_0(x)$ is the Bessel function, μ_m is the solution of the equation $J_0(x) = 0$, $V = \pi a^2 h$ is the volume of the synaptic cleft. Next figures 2 and 3 demonstrate the behavior of the pair correlation function $G_2(\rho, z)$ in the synaptic cleft with parameters $a = 100$ nm and $h = 10$ nm.

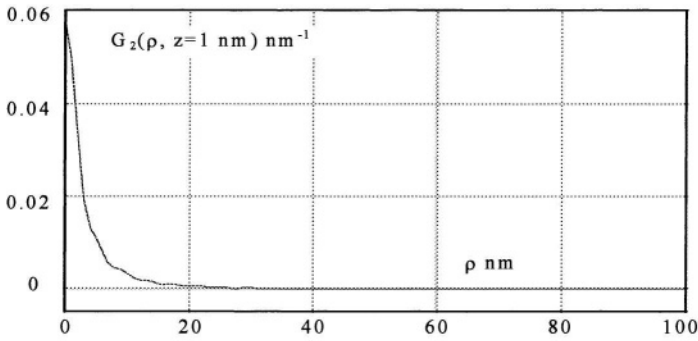


Figure 2. Dependence of the pair correlation function $G_2(\rho, z)$ on ρ .

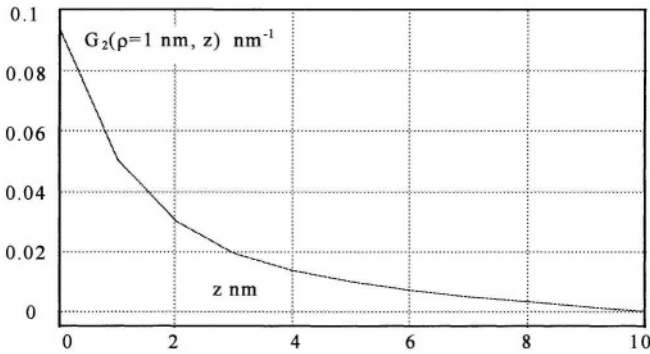


Figure 3. Dependence of the pair correlation function $G_2(\rho, z)$ on z .

The correlation length gives a linear size of the activation zone for the process of synaptic transmission

$$\xi = \sqrt{\frac{\sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \frac{(-1)^n \left[a^2 \left(1 - \frac{2J_2(\mu_m)}{\mu_m J_1(\mu_m)} \right) + h^2 \left(1 - \frac{8}{\pi^2 (2n+1)^2} \right) \right]}{(2n+1) \mu_m J_1(\mu_m) \kappa_{nm}^2}}}{\sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \frac{(-1)^n}{(2n+1) \mu_m J_1(\mu_m) \kappa_{nm}^2}}}, \quad (23)$$

where $\kappa_{nm}^2 = \kappa^2 + \frac{\pi^2 (2n+1)^2}{4h^2} + \frac{\mu_m^2}{a^2}$.

The temperature dependence of the correlation length is shown on the Figure 4 with $\kappa_0 \cong 10^8 \text{ M}^{-1}$ for the restricted cylindrical system.

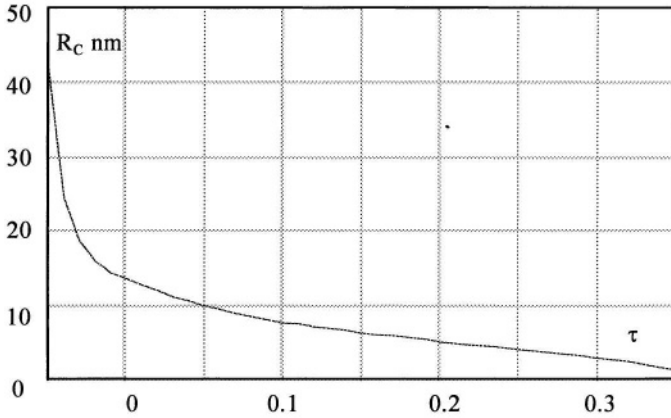


Figure 4. The dependence of the correlation length on the temperature.

The shifts of the critical temperature and critical concentration in finite-size binary liquid mixtures are as follows:

$$\Delta T_C = \frac{T_C}{1 + \left(\sqrt{\frac{\pi^2}{K_1^2} + \frac{\mu_1^2}{K_2^2}} \right)^{-\frac{1}{\nu}}}, \quad \Delta x_C = \frac{x_C}{1 + \left(\sqrt{\frac{\pi^2}{K_1^2} + \frac{\mu_1^2}{K_2^2}} \right)^{-\frac{\beta}{\nu}}}. \quad (24)$$

These shifts of the critical parameters depend on the geometrical factors $K_1 = 2h\kappa_0$ and $K_2 = a\kappa_0$. For example, for $K_1 = 25$ and $K_2 = 125$ the shift of the critical temperature $\Delta T_c \approx 10$ K while $T_c = 300$ K.

4. Conclusions

The scaling hypothesis for finite-size binary liquid mixtures is formulated and used to study the susceptibility in the liquid-liquid and liquid-vapor critical regions. The dependence of susceptibility on the temperature and field variables as well as on the scaling densities φ_1 , φ_2 and the linear size of a system are found to determine the consequences, which could be verified experimentally. Change of the critical behavior of susceptibilities connected with correlators $\langle \varphi_1 \varphi_1 \rangle$, $\langle \varphi_2 \varphi_2 \rangle$ and $\langle \varphi_1 \varphi_2 \rangle$ has to exist for the liquid-vapor critical state in the finite-size binary liquid mixture. The limiting transition is examined for the susceptibility of the finite-size binary liquid mixture to the susceptibility of such a system when all its linear sizes become infinite.

The process of synaptic transmission is isomorphic to the critical phenomena in binary liquid mixtures near the critical mixing point. A system of kinetic equations for concentrations of receptors and acetylcholine-receptor complexes are derived for the cholinergic synapse. The stationary points of the concentration of R^* and $ACh-R^*$ as well as the informational capability of the transmission channels depend on the kinetic coefficients. Therefore, changes in the temperature and influence of different external fields affect on the kinetic coefficients and as the result on the stationary points and the informational capability of the channels.

The source function (in the case of its slow oscillatory behavior) modulates the temporal evolution of the $ACh-R^*$ concentration. The correlation length determines the zone of reagents activation. It depends on the geometric factor of the cleft and on the temperature as well. Thus, the geometrical form of the synaptic cleft and temperature affects on the activation zone of acetylcholine-receptor complexes. As the result of the space limitation, shifts of the critical temperature and concentration take place. All these abovementioned results must be taken into account while studying isomorphism of critical phenomena in confined liquid mixtures and cell-to-cell communication in synapses.

5. References

1. Fisher, M.E. (1971) *Critical Phenomena. Proceedings of the International School of Physics "Enrico Fermi"*, ed. M.S.Green, Academic, New York.
2. *Finite Size Scaling and Numerical Simulation of Statistical Systems* (1990), ed. Privman, V., World Scientific, Singapore.
3. Binder, K. (1992) Phase transitions in reduced deometry, *Annu. Rev. Phys. Chem* **43**, 33-59.
4. *Dynamical Phenomena at Interfaces, Surfaces and Membranes* (1993) Eds.
5. Beysens, D., Boccara, N., and Forgacs, G. Nova Science Publishers, New York.
6. Chalyi, A.V., Chalyi, K.A., Chernenko, L.M., and Vasil'ev, A.N. (2000) Critical behavior of confined systems, *Cond. Matt. Phys* **3**, 335-358.

7. Anisimov, M.A. (1987) *Critical Phenomena in Liquids and Liquid Crystals*, Nauka, Moscow (in Russian).
8. Patashinskii, A.Z. and Pokrovskii, V.L. (1987) *Fluctuation Theory of Phase Transitions*, Nauka, Moscow (in Russian).
9. Anisimov, M.A., Agayan, V.A., Povodyrev, A.A., and Sengers, J.A. (1998) Two-exponential decay of dynamic light scattering in near-critical fluid mixtures, *Phys. Rev. E* **57**, 1946-1961.
10. Volkenstein, M. V. (1981) *Biophysics*, Nauka, Moscow (in Russian).
11. *Biophysics* (1983) Ed. By Hoppe, W. et al., Springer-Verlag, Berlin.
12. *Biophysics* (1988) Ed. by Kostuyk, P.G. et al., Vyscha Shkola, Kyiv (in Russian).
13. Chalyi, A. V. (1997) *Non-Equilibrium Processes in Physics and Biology*, Naukova Dumka, Kyiv (in Russian).

MODEL OF THE CRITICAL BEHAVIOR OF REAL SYSTEMS

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1. Introduction

The history of critical phenomena studying goes back about 200 years. During the last 40 years, the main efforts of both theorists and experimentalists were primarily aimed at comprehensive investigations of singularities in the behavior of matter in the region of fully developed large-scale fluctuations near a critical point (see e.g.[1–3]).

In the classic Ginzburg study dated 1960 [4], applicability ranges of the Landau theory for second-order phase transitions were determined. In fact, it was shown that, on the basis of the ratio between the correlation energy and the volume one, a temperature region near a critical point might be indicated where the role of fluctuations couldn't be disregarded. In this region, classical theories of the Landau type (van der Waals theory for liquids, Weiss theory for magnets, and Bragg–Williams one for binary alloys) no longer adequately describe the situation. At present, it is well known that, as a critical point is approached, the mean-field (classical) behavior of a system gives place to an Ising-type (fluctuational) behavior. The position of such a transition, if it exists, is specified by the Ginzburg criterion [4]. Thus, such a transition (it is often referred to as a crossover) from the classical type of behavior to the Ising-type one divides the region near the critical point into two parts. For the reasons substantiated in the analysis given below, we will call it *the first crossover*.

Despite these considerable achievements (the efforts were culminated in the formulation of the modern renormalization-group (RG) theory of critical phenomena by K. Wilson, who was awarded a Nobel prize in 1982), there remain as-yet-unresolved problems first indicated by Ginzburg about 30 years ago (see, e.g., [5]). These problems are associated with the behavior of systems whose inhomogeneities are caused by the presence of walls, flows, external fields, etc. From the most general standpoint, we can state that, in this case, we are dealing with critical phenomena in nonideal systems or in systems affected by the action of various physical fields. By a field, we imply here all possible additional disturbances, such as the gravitational and Coulomb fields, surface forces, shear stresses, turbulence, and the presence of boundaries. It is for any system subjected at least one of such fields that we shall use a name “nonideal” or “real”.

The main question to be answered in this connection is whether the behavior of a real system changes (and if it does, what is the character of these changes) as a system moves deeply into the fluctuation region. The goal of the present communication is to

demonstrate that there is a positive answer to this question, but this answer is quite paradoxical: the region immediately adjacent to the critical point again becomes a van der Waals-type domain. And by analogy we shall call this transition from the Ising-type of behavior to the classical one *the second crossover*.

2. Second crossover. Experimental facts

It is common practice to characterize a matter behavior near critical point with a set of critical exponents. In asymptotic vicinity of the critical point different physical properties may be represented as simple power dependencies, irrespective of classical or fluctuation alternative for a critical behavior description. Exponents of the leading term of the appropriate asymptotic – critical indices, which have been introduced into practice by van der Waals, play a key role in any theory of critical phenomena. This is due to the fact that one or another set of the critical indices and the type of the critical behavior are rigidly bound. Fortunately, critical exponent values in contrast with a full power dependence may be derived from experimental data.

As far back as the mid-1970s, we performed a precision ppT experiment with pure SF_6 (99.9995% purity) in the immediate vicinity of the critical point. In the conditions of the same experiment, it was for the first time found a simultaneous trend of three static critical exponents, namely, β for the coexistence curve, γ for the isothermal compressibility in the single-phase region, and δ for the critical-isotherm, towards their classical values (see, e.g.[6–8]). The changes found were for the first time attributed to gravity. The determination accuracy for the state parameters (including critical ones) in those studies, performed at a unique setup in the laboratory headed by I.R. Krichevskii, corresponded to a metrological level. It was $\pm 2 \cdot 10^{-4} \text{ K}$ in the proper temperature scale, $\pm 0.001\%$ in the pressure scale, and $\pm 0.02\%$ in the density scale. The critical parameters were determined independently by visual observing the appearance and disappearance of the two-phase state of matter in the constant-variable volume piezometer [6, 7]. About 800 experimental points obtained were concentrated in a narrow temperature range ($-0.3 < T - T_c < 1.3 \text{ K}$, where T_c is the critical temperature) and density range ($|\Delta\rho^*| \leq 0.15$, where $\Delta\rho^* = (\rho - \rho_c)/\rho_c$, with ρ_c being the critical density) near the critical point. As a result, it was established [6–8] that, within the ranges under investigation, there are own “far” and “near” regions. In the “far” region, the critical exponents β , γ , and δ had values close to the Ising ones, whereas in the “near” region they again acquired values characteristic of the mean-field (classical) behavior (Figs. 1–3). For a long time, these works were the only studies in the scientific literature where such a behavior was found and attributed to the effect of gravity. Now, the situation has essentially changed.

In the study [9], which appeared in 1992, the immediate vicinity of the SF_6 critical point was investigated anew with the help of a completely automated, specially designed high-precision ppT setup. In that study, our results and their interpretation [6–8] were at last independently corroborated. Later, in addition to SF_6 [6–8, 10], the fact that in the immediate vicinity of the critical point the critical exponents are changed towards their classical values under the effect of gravity was also observed for CO_2 [10]. The investigation of the critical behavior in the conditions of shear flow, which were performed in

[11, 12], led to conceptually the same result as in our experiments with a pure liquid in the presence of gravity: the critical exponents also are changed from the Ising values to the mean-field ones. This was simultaneously shown both theoretically by Onuki and Kawasaki in their fundamental research [11] based on the RG approach and experimentally by Beysens and co-workers for aniline–cyclohexane binary mixture in the study [12].

Other examples also can be presented. Thus, in [13] the intrinsic gravitational effect has been examined theoretically. It was shown that near a critical point gravity changes the local properties of a liquid, thereby modifying the very nature of a phase transition. Light scattering experiment carried out in [14] has shown that, in a guaiacol–glycerin solution with the addition of a small amount of water, the critical exponent of the correlation radius, ν , is changed from nearly-Ising values to values characteristic of the mean-field behavior as the system approaches the double critical point. The Monte Carlo simulation performed in [15] revealed that, upon taking into account dimensional effects within the two-dimensional Ising model, the critical exponent β takes the fluctuational value $\beta = 1/8$ far from the critical point and the classical value $\beta = 1/2$ near the critical point.

Thus, we can see that a general picture of real system behavior near the critical point is more complicated and may involve not only the first crossover from the mean-field behavior to the Ising one, but it can also include the second crossover in the immediate vicinity of the critical point in the inverse direction, namely, from the fluctuational type of behavior to the classical one. Therefore, the closest vicinity of the critical point again becomes the region of the mean-field type of behavior [16–18].

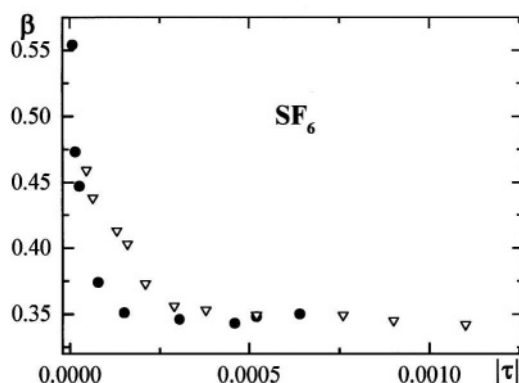


Figure 1. Behavior of the critical exponent for the coexistence curve near a critical point. Experimental points (●) are plotted according to data of [6]; the piezometer height is 8 mm, and the displayed data correspond only to the liquid branch; experimental points (▽) are plotted according to data of [9]; the piezometer height is 30 mm, and the displayed data correspond to both branches; $\tau = (T - T_c)/T_c$.

All the dependencies in Figs. 1–4 illustrating the behavior of various critical exponents in the second-crossover region were plotted [16–18] on the basis of own data and the data available from other studies.

From Figs. 1 and 2, one can see that the position of the second crossover for the critical exponents β and γ depends on the height of the piezometer used. This is an additional confirmation of the gravitational nature of these changes. By comparing these figures one can also notice that the positions of this crossover for the exponents β and γ , in terms of the relative proximity to the critical point in the temperature scale, differ by approximately two orders of magnitude. The observed isothermal compressibility is more sensitive to the effects of various perturbations (in particular, to the effect of gravity). This seems to be quite natural from the physical standpoint. It is worth noting that, apparently, the positions of the first crossover can differ significantly for different thermodynamic properties of the same system, although the Ginzburg criterion based on the anomaly in the heat capacity does not suggest this *a priori* [4]. Figure 3 demonstrates that, in real systems, a transition to classical values of the critical exponents can occur as the system approaches a critical point not only in the temperature scale but also in the density one. In the author's opinion, the second crossover in the behavior of the critical exponents β , γ , and δ (Figs. 1–3) is due to the intrinsic gravitational effect.

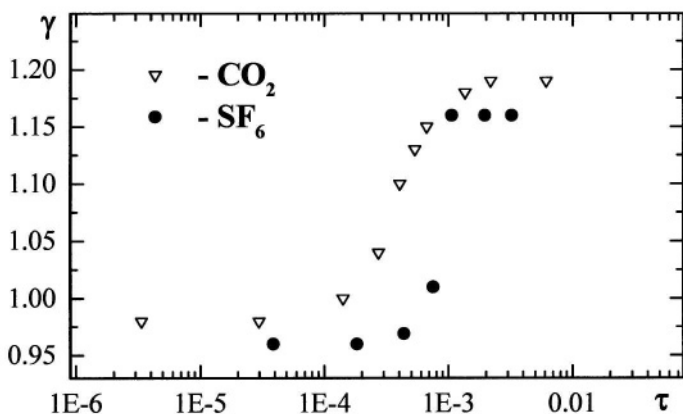


Figure 2. Variation of the critical exponent for the isothermal compressibility in the single-phase region, at the approaching to the critical point. The experimental points ($\bullet$) and (∇) are plotted according to data of [8, 19] and [10]; the piezometer height are 8 and 30 mm, respectively.

A specific reason for the variation of the exponent ν (Fig. 4) was not established [14]. However, by analogy with the effect of the gravitational field (Figs. 1–3), we may assume that the Coulomb field of water dipoles played the role of a disturbing factor in that experiment [18]. In any case, the evolution of the critical exponent of the correlation radius is such that it fits well into the proposed pattern. Thus, we have grounds to believe that

such behavior is inherent not only in static critical exponents [8], but is also a universal property of the immediate vicinity for a critical point of real systems [16–18].

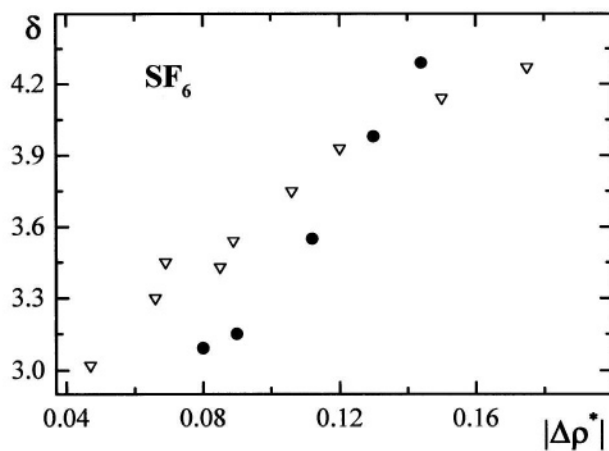


Figure 3. Variation of the critical exponent for the critical isotherm at the approaching to the critical point in the density scale. The experimental points (●) and (▽) are plotted according to data of [7] (the piezometer height is 8 mm; the displayed data correspond only to the liquid branch) and [9] (the piezometer height is 30 mm; the displayed data correspond to both branches).

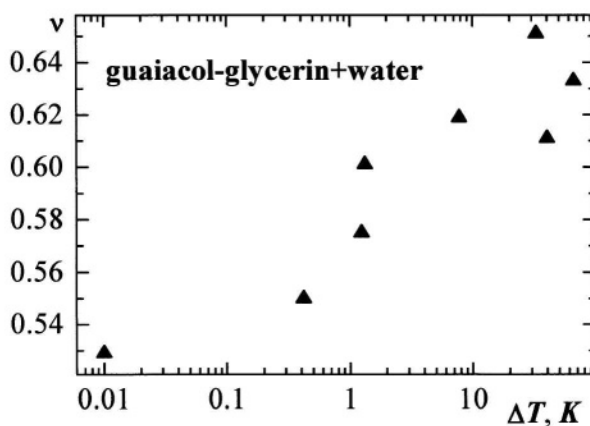


Figure 4. Critical exponent for the correlation radius as a function of the distance from double critical point (in the temperature scale) in the presence of water. Displayed data are plotted in [17] according to data of [14].

3. Phenomenological model of critical behavior of nonideal systems

We have seen that the change of the type of behavior in the immediate vicinity of a critical point from Ising-like to mean-field critical behavior (second crossover) is observed for a broad range of systems subjected to perturbations of various physical origins. This fact indicates that this phenomenon is most likely universal. Moreover, although the appearance of such a behavior is nontrivial, but, in our opinion, it is quite natural [16–18]. For an explication of this a simple phenomenological model of critical behavior of nonideal systems based only on the “first principles” of the critical phenomena theory can be proposed [18].

Let a real physical system approaches a critical point e.g. in the temperature scale. Starting with a certain temperature T_1 (Fig. 5) the fluctuations of the order parameter increase and at the temperature T_1' become so large that their radius (correlation length ξ) gets, in accordance with a basic Kadanoff scaling idea, an unique dimension which determines the critical behavior of the system [20]. At this point the system locates in the domain II (Fig. 5) and definitely completes its passage from the classical type of behavior to the fluctuational (in particular, Ising-like) type. This passage ($T_1 \Rightarrow T_1'$) was above called *the first crossover*; it is its position that is determined by the Ginzburg criterion. The change of the type of behavior of the ideal systems is presumed to occur near the critical point only once. However it is rightful to raise such a question concerning nonideal systems. Is it valid to say that the critical behavior of nonideal systems is the same?

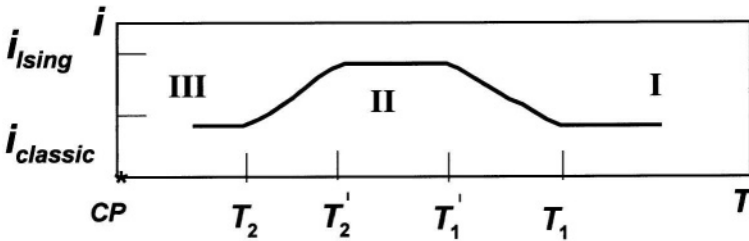


Figure 5. Shape of a curve modeling the critical exponents (i) behavior of nonideal systems near the critical point (CP) in the temperature scale (a curve in the density scale is similar). If $i_{ising} < i_{classic}$ (e.g. for critical exponent β) the curve is reflection symmetric about the horizontal axis, passing through $i = i_{classic}$, and flat part of the curve corresponds to $i = i_{ising}$ for this case [18].

It is well known that, as the system approaches a critical point, the development of large-scale order parameter fluctuations is accompanied by a continuous increase in the susceptibilities of the critical system, in particular, susceptibilities to various perturbations of the different physical nature. On this basis, we can assume that, eventually, the effect of various disturbing factors (fields), which are insignificant under the usual con-

ditions, will lead, in the presence of continuously and indefinitely growing of a system susceptibility, to a deformation (suppression) of these fluctuations¹. As a consequence, the mean-field (classical) behavior in the system [3] must be restored (domain III in Fig. 5). It is this transition ($T_2' \Rightarrow T_2$), which occurs in the inverse direction, i.e., from the Ising-type of behavior to the classical type, that we called above *the second crossover*.

This phenomenon is quite simply to understand by using the Kadanoff concept [20] concerning critical fluctuations: if a system has fully developed large-scale isotropic fluctuations (domain II in Fig. 5), the critical behavior of such a system is fluctuational and critical exponents are Ising-type. If fully developed large-scale fluctuations haven't been yet formed (domain I in Fig. 5) or they have been completely suppressed by a field (domain III in Fig. 5), the critical system behavior is a mean-field type and critical exponents are classical. In the case of insufficiently developed fluctuations ($T_1 \Rightarrow T_1'$ section in Fig. 5) or in another case of fluctuations starting to take on a certain anisotropy under any field ($T_2' \Rightarrow T_2$ section in Fig. 5), the critical system behavior and the corresponding critical exponents are intermediate.

In spite of a certain sketchiness of this model some complementary hypothesis can be made. First, if internal fields are so strong that they are able to suppress the critical fluctuations at any temperature distance from the critical point, the domain II is entirely absent: such a system demonstrates only the classical mean-field type behavior. In fact, all systems with long-range forces (superconductors, ferroelectrics and so on) always display only the classical behavior.

Thus, for nonideal systems some theorem-like affirmation "on even crossovers number" may be formulated: a real system, in contrast to an ideal one, demonstrates near the critical point either two crossovers or their number is zero [18].

Second, the positions of the fluctuational domain boundaries must distinguish not only for the various nonideal systems, but also for different anomalous physical properties of the same system. The critical exponents β and γ behavior has verified this conclusion: the mean-field domain for exponent γ arises starting with $\tau \leq 10^{-3}$ (Fig. 2), whereas the same region for exponent β arises only from $\tau \leq 10^{-5}$ (Fig. 1). Taking into account this feature is very important for the test of feasibility of the universal relations existing between the critical exponents and of the universal amplitude combinations near the critical point [18].

4. Conclusions

In this study where an attempt to examine the critical behavior of different nonideal systems is made, we presented some results obtained from our comparative analysis [18] of available experimental and theoretical investigations, which support the concept discussed above. Recently, in addition to the RG-study of critical phenomena under shear flow [11] the new RG-investigation for the critical behavior of dilute electrolyte solutions is appeared [21]. This study had for an object to examine the exponent γ tem-

¹ As a last resort, the sample boundaries will play a role of such a field.

perature dependence near the critical point of those systems, which were earlier experimentally determined [22]. The results are displayed in Figure 6. Constant b responds for the interaction between the order parameter and the ion density. One can see that for $b = 0$ (the Coulomb forces are absent) the curve has only one – the first crossover and it is quite similar to the right-hand section of the line in Fig. 5, for $b = 3$ (the internal Coulomb field is sufficiently strong) the number of the crossovers is two² as it was predicted above. Hence, this is one more RG-confirmation of the supposed simple phenomenological model of the critical behavior of nonideal systems.

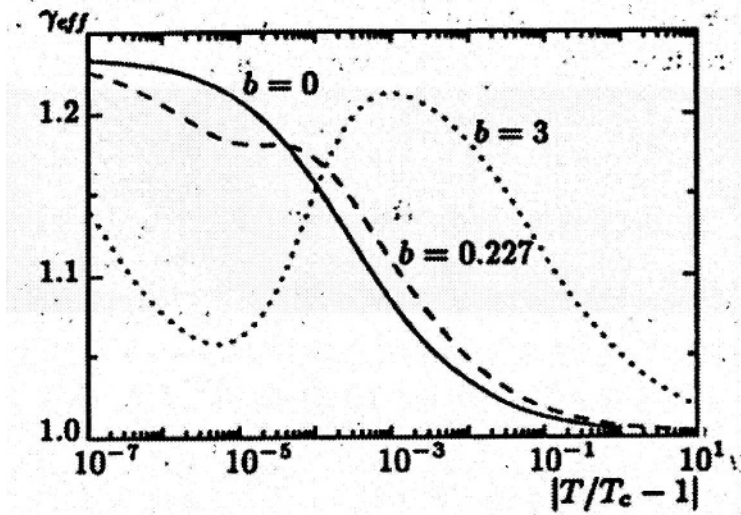


Figure 6. Temperature dependence for effective value of the susceptibility critical exponent for a model ionic system [21].

Thus, we can conclude that, in the general case, as a critical point is approached a non-ideal system can twice change its critical behavior: from the classical to the Ising type and back. Therefore, the nearest vicinity of the critical point becomes the region of the mean-field type of behavior [16–18].

In conclusion, the following comment is worth noting. It is usually assumed that the gravitational field has an adverse effect upon experiments in the immediate vicinity of a critical point, for example, by distorting the shapes of the curves and values of the critical exponents so that they cease to be true ones. However, all the above-mentioned suggests that the existence of an additional factor in the form of an effect of the gravitational field or another arbitrary field is not, in fact, adversarial. On the contrary, this makes it possible to reveal new features in the critical behavior. It is only necessary to adopt a different point of view: the values of the critical exponents are not distorted by the effect of these fields but in fact are obtained in the presence of these fields, i.e., that

² The author himself [21] left this fact without any comments

they are valid just for these conditions. Such an approach radically changes the situation, making it possible to obtain deeper insights into the nature of critical phenomena.

5. Acknowledgements

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6. References

1. Ma, S. (1976) *Modern Theory of Critical Phenomena*, W. A. Benjamin, Inc.
2. Anisimov, M.A. (1987) *Critical Phenomena in Liquids and Liquid Crystals*, Nauka, Moscow.
3. Stanley, H.E. (1971) *Introduction to Phase Transitions and Critical Phenomena*, Clarendon Press, Oxford.
4. Ginzburg, V.L. (1960) Some remarks on second order phase transitions and microscopic theory of ferro-electrics, *Fiz. Tverd. Tela (Leningrad)* **2**, 2031–2043 [*Sov. Phys. Solid State* **2**, 1824].
5. Ginzburg, V.L. (1984) On the perspectives of the development of physics and astrophysics in the late XX century, in *Physics in XX Century: Development and Progress*, Nauka, Moscow, pp. 281–330.
6. Ivanov, D.Yu., Makarevich, L.A., and Sokolova, O.N. (1974) Shape of the coexistence curve of pure matter near the critical point, *Pis'ma Zh. Eksp. Teor. Fiz.* **20**, 272–276 [*JETP Lett.* **20**, 121–122].
7. Ivanov, D.Yu. and Makarevich, L.A. (1975) Shape of the critical isotherm of pure matter, *Dokl. Akad. Nauk SSSR* **220**, 1103–1105.
8. Ivanov, D.Yu. and Fedyanin, V.K. (1974) An equation of state for the classical liquid near the critical point, Preprint No. P4-8430, OIYaI (Joint Institute for Nuclear Research.), 28 p.
9. Wagner, W., Kurzeja, N., and Pieperbeck, B. (1992) The thermal behaviour of pure fluid substances in the critical region – experiences from recent $\rho\rho T$ measurements on SF_6 with a multi-cell apparatus, *Fluid Phase Equilibria* **79**, 151–174.
10. Kurzeja, N., Tielkes, Th., and Wagner, W. (1999) The nearly classical behavior of a pure fluid on the critical isochore very near the critical point under influence of gravity, *Int. J. Thermophys.* **20**, 531–562.
11. Onuki, A. and Kawasaki, K. (1979) Non-equilibrium steady-state of critical fluid under flow. Renormalization group approach, *Ann. Phys.* **121**, 456–528.
12. Beysens, D., Gbadamassi, M., and Boyer, L. (1979). Light-scattering study of a critical mixture with shear flow, *Phys. Rev. Lett.* **43**, 1253–1256.
13. Sengers, J.V. and van Leeuwen, J.M.J. (1985) Critical phenomena in gases in the presence of gravity, *Int. J. of Thermophys.* **6**, 545–559.
14. Krivokhizha, S.V., Lugovaya, O.A., Fabelinskii, I.L., Chaikov, L.L., Citrovskii, A., and Yani, P. (1993) Temperature dependence for the correlation radius of concentration fluctuations of a guaicol-glycerin solution in the region of the double critical point, *Zh. Eksp. Teor. Fiz.* **103**, 115–124.
15. Panagiotopoulos, A.Z. (1994) Molecular simulation of phase coexistence: finite-size effects and determination of critical parameters for two- and three dimensional Lennard-Jones fluids, *Int. J. of Thermophys.* **15**, 1057–1072.
16. Ivanov, D.Yu. (1996) Macroscopic field influence on the critical exponents, *Proceedings of the 14th. European Conference on Thermophysical Properties*, Lyon–Villeurbanne, France, P. 463.
17. Ivanov, D.Yu. (2002) Behavior of critical exponents in the immediate vicinity of a critical point for non-ideal systems: The Second Crossover, *Doklady Akademii Nauk* **383**, 478–481 [*Doklady Physics* **47**, 267–270].
18. Ivanov, D. Yu. (2003) *Critical Behavior of Nonideal Systems* (in Russian), Fizmatlit, Moscow, 248 p.
19. Makarevich, L.A., Sokolova, O.N., and Rozen, A.M. (1974) The SF_6 compressibility along the critical isochore (about value of the critical exponent γ), *Zh. Eksp. Teor. Fiz.* **67**, 615–620 [*Sov. Phys. JETP* **40**, 305].
20. Kadanoff, L.P. (1966) Scaling laws for the Ising models near T_c , *Physics* **2**, 263–268.
21. Muratov, A.R. (2001) Critical behavior of dilute electrolyte solutions, *Zh. Eksp. Teor. Fiz.* **120**, 104–108.
21. Jacob, J., Kumar, A., Anisimov, M.A., Povodyrev, A.A., and Sengers, J. V. (1998) Crossover from Ising to mean-field critical behavior in an aqueous electrolyte solutions, *Phys. Rev.* **E58**, 2188–2200.

THE METHODS OF PREDICTION OF THE PROPERTIES FOR SUBSTANCES ON THE COEXISTENCE CURVE INCLUDING VICINITY OF THE CRITICAL POINT.

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Abstract. In present study we have applied a scaling principle to the prediction of the thermal properties and critical parameters of pure substances on the saturation line and for prediction of the refractive index, dielectric permittivity on the liquid-liquid coexistence curve for the binary mixtures. Universality of the behavior in the wide range of critical point for the crossover functions at the critical exponents for the density on the coexistence curve and dielectric permittivity on the liquid-liquid coexistence curve have been demonstrated and analyzed.

1. Introduction

Proposed method of prediction of the thermophysical properties for the substances on the saturation line is based on the following scientific statements. First statement connected with *determinative* influence of the fluctuations to the behavior of the thermodynamic functions. The fluctuations are increasing with the approaching to the critical point. Semenchenko [1] firstly mentioned about influence of the fluctuations to the changing of thermodynamic properties of the substances. He claimed that "...with physical point of view, the fluctuations do not determine the value of the energy, entropy, volume, etc but determine their behavior, their change". When temperature increases on the saturation line the fluctuations grow, but at the same time, a stability of equilibrium decreases. Extreme case when fluctuation is reached to the infinite quantity is a critical point. Consequently, we can make assumption – *the universal changing of the fluctuations on the saturation line may define similarity in changing of the different thermodynamic functions*. We examined of the temperature dependence for the fluctuations of the density for verification of their universality. It can be calculated from data for the isothermic compressibility [2, 3]:

$$\alpha_T = -\frac{1}{\rho} \left[\frac{\partial \rho}{\partial P} \right]_T \quad (1)$$

with using well-known formulae [1]:

$$\overline{(\Delta \rho)^2} = \rho^2 \cdot T \cdot k_B \cdot \alpha_T \quad (2)$$

where k_B is a Boltzmann constant.

The results of calculation for the isothermic compressibility and $(\overline{\Delta\rho})^2$ for different non-associated substances were presented in Figs. 1-4. It can be seen in the logarithmical coordinates that behavior of the fluctuations for the liquid and the saturated vapor looks similar (with taking into account of uncertainty for the calculated data).

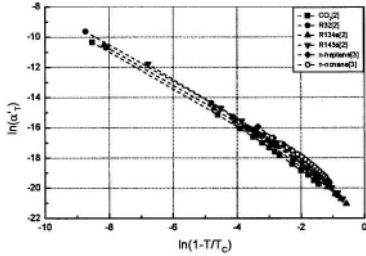


Figure 1. Temperature dependence for the isothermic compressibility on the boiling curve

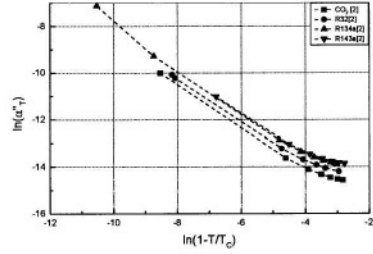


Figure 2. Temperature dependence for the isothermic compressibility on the condensation curve

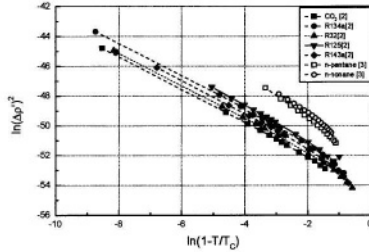


Figure 3. Temperature dependence for the fluctuation of the density on the boiling curve

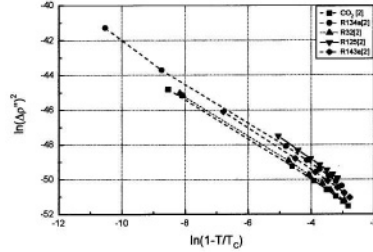


Figure 4. Temperature dependence for the fluctuation of the density on the condensation curve

At the same time the isothermic compressibility functionally connected with radial distribution function $g(r)$:

$$\alpha_T \cdot R \cdot T \cdot \rho = 1 + \frac{4\pi}{v} \int_0^{\infty} [g(r) - 1] \cdot v^2 dr \quad (3)$$

That function defines structure of the fluid. In that case, a similar behavior of the $\ln(\overline{\Delta\rho})^2 = f(t)$ shows general regularities in the changing of the structure for vapor and liquid phases for non-associated substances. *It should be pointed out here that structural behavior of short - range ordering for vapor and liquid phase of the non-associated fluids changes universally.* Correspondingly, we may obtain generalized correlations for the thermophysical properties in the wide range of state parameters. The series of universal correlations based on principle of corresponding states for

determination of the thermophysical properties were reported in [5-8]. Let us consider that correlations for calculation of the thermodynamic function from reduce parameters must be similar in form and the coefficients of equations must be connected to each other. *Thermodynamically consistent correlations for prediction of properties for the substances on the coexisting curve were reported in [9]. Scaling principles were applied for the prediction of the thermodynamic properties.* Additional development of this method will be presented below.

2. Application of a Scaling Principle to the Prediction of the Thermodynamic Properties

The essence of proposed prediction methods is in application of the simple power dependences:

$$|Y - Y_c| = A_0 |X - X_c|^{\lambda} \quad (4)$$

where Y is a thermodynamic function, A_0 is a critical amplitude, $|X - X_c|$ is a parameter of order and λ is a exponent dependent on temperature. In critical point λ has meaning of a critical exponent.

Ratio of the similarity (scaling) between critical exponents and universal complex of amplitudes allow to create a new methods for prediction of the thermodynamic properties for substances. Existing phenomenological theory of the phase transition permits to describe of the thermodynamical properties in the vicinity of critical point or in wide range of the parameters [10,11]. As example, proposed equation of extended scaling of form

$$Y_i = A_0 |T_c - T|^{\lambda} \left(1 + C_i |T_c - T|^{\Delta} + A_i + \dots \right) \quad (5)$$

contains different number of the individual coefficients A_i , A_0 , C_i . Application of the Eq.(5) requires to use a large set of the experimental data. Moreover, connection between numerous coefficients in equations similar to the Eq.(5) is complicated. Therefore, these equations do not use for the prediction.

In recent years the scaling conception was developed and applied to the polymer systems [12, 13]. The essence of this methodology is in using of different values of exponents in equations (similar to Eq.4) from corresponding parameter, as example, from temperature. Unfortunately, this prospective methodology had not widely applied to the prediction of the properties for different substances.

It should be noted that using of two-constant equations similar to the Eq.(4) can be applied for prediction of the thermodynamic properties. Their coefficients have thermodynamical meaning. Determination of the coefficients of the Eq.(4) do not require a large set of the experimental data. Moreover, a theory of the critical exponents [10,14-16] can be involved for prediction of the thermophysical properties for poorly studied substances. The values of the critical exponents define of the degree of approximation to the critical point. A comparison between exponents defined from different models and exponents obtained from experimental data let us concluded about validity of the proposed model. Scaling gives possibility to create correlation between critical exponents. Well-known correlations between critical indexes can be found

elsewhere [10, 14-16].

Important consequence from the thermodynamic theory of critical exponents for the universal correlations between amplitudes of Eq.(5) was presented in [10, 14-16]. Connection between critical exponents and amplitudes allows to reduce a set of the experimental data for determination of unknown constants in Eq.(5) [10, 14-16]. In addition, a sign of equality in expressions between critical exponents is correct only in critical point. It may serve the explanation why using of the scaling principles was not widely disseminated for the prediction of the thermophysical properties for substances.

At the same time the thermodynamically consistent method for calculation of the capillary constant a^2 , surface tension σ and for difference of the density on the coexisting curve $\Delta\rho = \rho' - \rho''$ was reported in [9,17]. On the basis of proposed methodology following correlations were proposed:

$$a^2 = a_0 t^{\phi\psi(t)}, \quad (6)$$

$$\Delta\rho = B_0 t^{\beta F(t)}, \quad (7)$$

$$\sigma = (a_0 \rho_0 / 2) g t^{\mu\psi(t) - \beta F(t)} = \sigma_0 t^{\mu f(t)}, \quad (8)$$

$$\ln \omega' = B_1 \Omega^{\beta_1 F_1(\Omega)}, \quad (9)$$

$$\ln \omega'^{-1} = B_2 \Omega^{\beta_2 F_2(\Omega)}, \quad (10)$$

where a_0, ρ_0, σ_0 are amplitudes, $\Omega = \ln(T_c / T)$ and $t = 1 - T / T_c$ are reduce temperatures, ϕ, β, μ are critical exponents, $\omega' = \rho / \rho_c$ and $\omega'' = \rho_c / \rho''$ are reduce density, $\psi(t), f(t), F(t), F_1(\Omega), F_2(\Omega)$ are universal crossover function. At the same time, the universal crossover function can be calculated as:

$$f(t) = 1 - 1.227817 \left(\frac{t^2}{\ln(t)} \right) + 1.328263 \left(\frac{t^3}{\ln(t)} \right), \quad (11)$$

$$F_1(\tau) = 1 - 1.113 \tau^{0.4} / \ln \tau, \quad (12)$$

$$F_2(\tau) = 1 + 4.861 \tau^{0.6} / \ln \tau, \quad (13)$$

The temperature dependence for the crossover functions $\beta F(t), \beta_1 F_1(\Omega), \beta_2 F_2(\Omega)$ is shown in Fig.5.

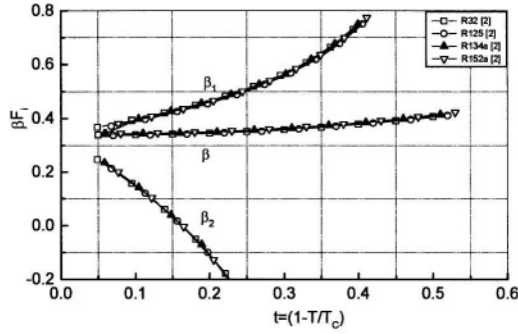


Figure 5. The temperature dependence of the effective exponent β

Proposed Eqs.(6-11) have strong extrapolation abilities and allow to define the thermodynamic functions in wide range of the existing of liquid phase including vicinity of the critical point. The coefficients of equations do not depend from interval of parameters, where they can be found from experimental data [18]. These coefficients can be connected with each other with the help of thermodynamic correlations on the assumption of universality of the critical exponents $\beta = \beta_1 = \beta_2 = 0.325$:

$$B_0 / \tilde{\rho}_c = B_1 + B_2 \quad (14)$$

Eq.(14) gives possibility to conclude about thermodynamical consistency of the thermodynamic properties on the saturation line. It should be mentioned that Eqs.(6-10) were used for verification of published experimental data [18].

The use of individual values for the ϕ, β and μ for every substances does not contradict to the theory of critical phenomena. First, the range of validity of Eqs. (6-10) is far from the critical region asymptotic behaviour, which, according to Sengers [11], lies near values of reduced temperatures less then 5×10^{-4} . Second, even the most accurate experiments on light scattering generally do not give the asymptotic values of the critical indices, but give instead "effective" values in some restricted region of the reduced temperature [19].

It seems that the universality of substance behaviour near a phase transition is not absolute. This state consistent with the thermodynamic similarity theory. Not all substances are thermodynamically similar, because there are more than two individual constants which characterize the nature of substance.

Novikov [20] has an interesting observation on this subject. During phase transitions the third individual constant appeared to some extent (in the form of a space dimension in the phase mathematical model, and it was not necessary for this to be equal to three). So, there are classes of universality instead of an absolute one, and they may be regarded as analogs of groups of thermodynamically similar substances in the liquid and gaseous states with individual values of indices. This idea has been developed in [14].

At present, there are no theoretical grounds for the universality of the crossover

functions $\psi(t), f(t), F(t), F_1(\Omega), F_2(\Omega)$ [9,17]. These crossover functions were obtained by the empirical way. However, Eq.(4) have high conformity for description of the experimental data [9,17,18]. However, existence of generalized relations for the isothermic compressibility α_T and the isobaric capacity c_p [5,21], which are the fluctuations of density and entropy demonstrate an universality of their behaviour.

3. The Method of Prediction of the Physical Properties on the Phase Transition lines

The aim of the present study can be shortly formulated as:

1. the verification of the universality influence of the fluctuation to the different properties on the line of the first order phase transition.
2. the consistency of the critical point with thermodynamic and electrophysical properties on the coexisting curve.
3. the application of scaling principle to the prediction of the properties of substances on the coexisting curve using limited empirical information.

We have demonstrated that fluctuations of the density change universally for the different substances. It leads to universal changing of the density on the coexistence curve [9,17,18]. Well-known fact that fluctuations and dielectric permittivity functionally connected. In addition the dielectric permittivity reflected behavior of the orientational fluctuations [22]. Moreover, the value like inverse of a dielectric permittivity has meaning of the stability factor [22]. With take into account all above-mentioned statements we can make following assumptions:

- Eqs. (7,9-13) can be applied for procedure of the consistency of the critical point parameters with the property of substances on the line of first order phase transition.
- Eqs (7,9-13) can be applied for description of the different thermodynamic and electrophysical properties on the line of first order phase transition and for determination of the critical parameters on the coexisting curve.

For demonstration our statements let us analyze a following set of equations for consistency of the critical point with the density ρ and the refractive index n on the coexisting curve and for the permittivity ε and with the concentration x on the liquid-liquid curve:

$$\left. \begin{aligned} \rho' &= \rho_c \exp[B_{1\rho} \tau^{\beta_{F_1}}], \\ \rho'' &= \rho_c \exp[B_{2\rho} \tau^{\beta_{F_2}}], \\ \Delta\rho &= B_{0\rho} t^{\beta_F}, \\ B_{0\rho} / \rho_c &= B_{1\rho} + B_{2\rho}. \end{aligned} \right\}, \quad (15)$$

$$\left. \begin{aligned} \varepsilon' &= \varepsilon_c \exp[B_{1\varepsilon} \tau^{\beta_{F_1}}], \\ \varepsilon'' &= \varepsilon_c \exp[B_{2\varepsilon} \tau^{\beta_{F_2}}], \\ \Delta\varepsilon &= B_{0\varepsilon} t^{\beta_F}, \\ B_{0\varepsilon} / \varepsilon_c &= B_{1\varepsilon} - B_{2\varepsilon}. \end{aligned} \right\}, \quad (16)$$

$$\left. \begin{aligned} n' &= n_c \exp[B_{1n} \tau^{\beta_{F_1}}], \\ n'' &= n_c \exp[B_{2n} \tau^{\beta_{F_2}}], \\ \Delta n &= B_{0n} t^{\beta_F}, \\ B_{0n} / n_c &= B_{1n} - B_{2n}. \end{aligned} \right\}, \quad (17)$$

$$\left. \begin{aligned} x' &= x_c \exp[B_{1x} \tau^{\beta_{F_1}}], \\ x'' &= x_c \exp[B_{2x} \tau^{\beta_{F_2}}], \\ \Delta x &= B_{0x} t^{\beta_F}, \\ B_{0x} / x_c &= B_{1x} - B_{2x}. \end{aligned} \right\}, \quad (18)$$

Analogous set of equations can be written for the isothermic compressibility, isochoric heat capacity, etc.

Thermodynamic consistency of the critical point to information for the properties was carried out as solution of the reduced set of Eqs. (15-18). As initial information was taken an experimental data presented in [23-32]. We should emphasize that during prediction the value of the determined coefficients of the properties from limited experimental information must be minimal. Therefore, in first stage of the investigation a value of critical exponent was taken as $\beta=0.325$ [14]. In the process of computation the “optimal” values of critical parameters [18] and amplitudes for Eqs.(15-18) are calculated and listed in Table 1. The quality of the description of the experimental data is shown in Figs.6-13.

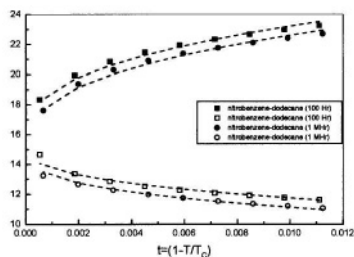


Figure 6. Temperature dependence for the dielectric permittivity of the liquid-liquid coexistence curve [23]

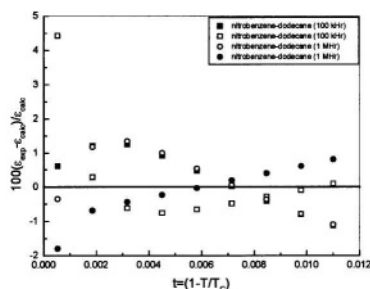


Figure 7. Deviation of the experimental data [23] from calculated by Eq.(21)

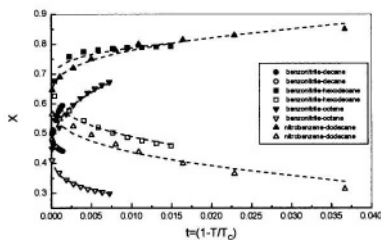


Figure 8. Temperature dependence of the concentration on the liquid-liquid coexistence curve [24]

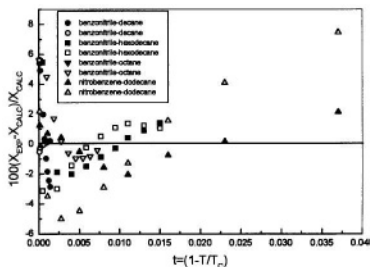


Figure 9. Deviation of the experimental data [24] from calculated by the Eq.(18)

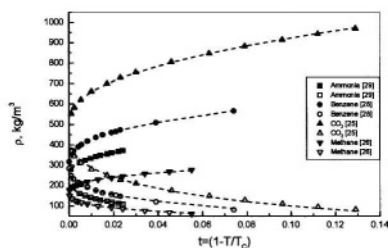


Figure 10. Temperature dependence of the density on the saturation line

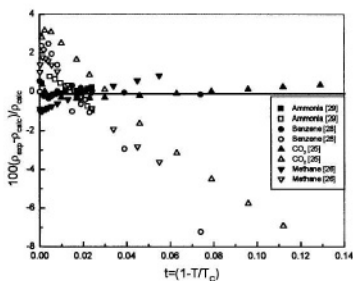


Figure 11. Deviation of the experimental data for the density [25, 26, 28, 29] from calculated by Eq.(15)

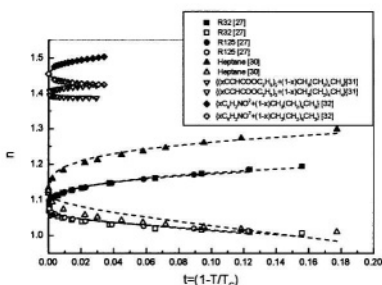


Figure 12. Temperature dependence for refractive index on the saturation line

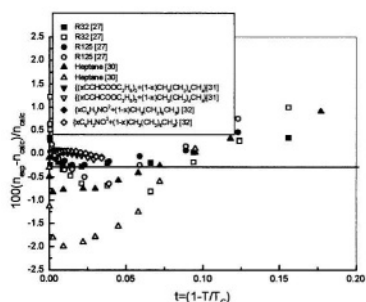


Figure 13. Deviation of the experimental data [27, 30-32] from calculated by Eq.17

Analysis of the tendency for deviation of the experimental data from calculated value by Eqs.(15-18) shows that Eqs.(7,9,10) proposed for description of the density may adequately describe different thermophysical and electrophysical properties on the coexisting curve. Consequently, influence of the fluctuations of the density to the behavior of structure of the characteristic (short range ordering for the non-associated substances) has universal behavior on the boundary curves. Furthermore, universality of the crossover functions proposed in [9,17] is consequence from similar changing of the structural characteristics of substances. Hence, we are proving first and second assumption. Proposed set of Eqs.(15-18) can be applied for verification of the reliability of the experimental information. The test of validity is deviation between experimental and calculation data. Last remark is important because very difficult to estimate of the global uncertainty for experimental data. Furthermore, proposed method can be applied for the determination of the critical parameters using limited experimental information obtained on the boundary curves.

TABLE 1. Values of the coefficient for Eqs.(15-18)

The dielectric permittivity								
Substance	Temperature range $t \in (t_1 - t_2)$	$B_{0\epsilon}$	$B_{1\epsilon}$	$B_{2\epsilon}$	T_c, K	$T_{c(1)}, K$	ϵ_c	$\epsilon_{c(1)}$
Nitrobenzene – dodecane (100 Hz) [23]	$5.3 \cdot 10^{-4} - 0.011$	50.694	1.908	1.12	302.56	302.68	16.74	15.59
Nitrobenzene – dodecane (1 MHz) [23]	$6.61 \cdot 10^{-4} - 0.011$	50.489	1.929	1.2	302.6	302.61	16.13	15.76
The liquid-liquid coexistence curve								
Substance	$t \in (t_1 - t_2)$	B_{0x}	B_{1x}	B_{2x}	T_c, K	$T_{c(1)}, K$	x_c	$x_{c(1)}$
Benzonitril-dekan [24]	$6.96 \cdot 10^{-5} - 1.39 \cdot 10^{-3}$	1.15	1.277	1.008	287.30	-	0.503	-
Benzonitril-gexodekan [24]	$4.27 \cdot 10^{-4} - 0.015$	1.337	0.729	1.301	304.35	-	0.658	-
Benzonitril-oktan [24]	$6.74 \cdot 10^{-5} - 7.22 \cdot 10^{-3}$	1.814	2.307	1.666	281.835	-	0.457	-
Nitrobenzene-dodecane [24]	$9.93 \cdot 10^{-5} - 0.037$	1.542	1.081	-1.408	302.03	-	0.62	-
The density on the saturation line								
Substance	$t \in (t_1 - t_2)$	$B_{0\rho}$	$B_{1\rho}$	$B_{2\rho}$	T_c, K	$T_{c(1)}, K$	$\rho_c, \text{kg} \cdot \text{m}^{-3}$	$\rho_{c(1)}, \text{kg} \cdot \text{m}^{-3}$
Ammonia [29]	$9.13 \cdot 10^{-4} - 0.024$	51.558	1.571	-2.206	405.37	405.37	232.07	235
Benzene [28]	$1.78 \cdot 10^{-5} - 0.074$	1107	1.667	-2.2022	561.78	561.77	300.19	300.6
CO ₂ [25]	$1.02 \cdot 10^{-3} - 0.129$	1727	1.65	-2.043	304.11	304.14	467.71	467.6
Methane [26]	$1.05 \cdot 10^{-4} - 0.055$	534.684	1.466	-1.804	190.55	190.55	163.51	162.66
R 32 [2]	$7.40 \cdot 10^{-4} - 0.203$	1691	1.753	-2.24	351.26	351.26	423.51	424
R 125 [2]	$1.03 \cdot 10^{-3} - 0.196$	2173	1.676	-2.138	339.35	339.33	569.80	571.3
The refractive index on the saturation line								
Substance	$t \in (t_1 - t_2)$	B_{0n}	B_{1n}	B_{2n}	T_c, K	$T_{c(1)}, K$	n_c	$n_{c(1)}$
R 32 [27]	$5.85 \cdot 10^{-4} - 0.156$	0.34	0.225	0.074	351.39	351.36	1.1373	1.0828
R 125 [27]	$5.73 \cdot 10^{-4} - 0.123$	0.332	0.21	-0.082	339.45	339.33	1.136	1.0848
Heptane [30]	$0 - 0.177$	0.508	0.271	-0.128	539.86	539.86	1.272	1.1262
The refractive index on the liquid-liquid coexistence curve								
Substance	$t \in (t_1 - t_2)$	B_{0n}	B_{1n}	B_{2n}	T_c, K	$T_{c(1)}, K$	n_c	$n_{c(1)}$
CHCOOC ₂ H ₅ +CH ₃ (CH ₂) ₄ CH ₃ [31]	$9.28 \cdot 10^{-4} - 0.029$	0.115	0.059	-0.024	292.9	292.85	1.4002	1.3999
C ₆ H ₅ NO ₂ +CH ₃ (CH ₂) ₆ CH ₃ [32]	$3.48 \cdot 10^{-3} - 0.034$	0.234	0.117	-0.0439	293.06	293.05	1.455	1.4563

It should be mentioned that gravitational-hydrostatic effect has negligible influence during measurement on the liquid-liquid curve. Therefore, deviations of experimental data from calculated by Eqs.(15-18) do not demonstrated of systematic behavior. On the contrary, deviations of experimental data for the density of vapor phase [2,25,26,29] show systematic behavior. Following explanations can be considered:

- Gravitational - hydrostatic effect has influence on the asymmetry of the density's profile in the experimental cell [10, 33-36]. In that case, the value of the critical exponent β_2 can be different from universal value of $\beta=0.325$.

- Polymolecular sorption and capillary condensation of the saturated vapor on the surface of the experimental cell [37-39].

We can conclude that these explanations have a physical meaning. Above-mentioned factors have influence on the accuracy of determination of the density near critical point. Therefore, the exponents β, β_1, β_2 may change in a wide range of values [10, 16].

Critical exponents determined from experimental data for the density [25,26] significantly distinguished, i.e. $\beta_1 \neq \beta \neq \beta_2$. In that case, Eq.(14) will be incorrect. It may explain a deviation of the calculated values of the density for the saturated vapor from experimental data [25,26,29]. At the same time the Eqs.(7,9,10) with individual value of the critical exponent can be used for prediction of the density on coexistence curve or for prediction of critical parameters [18]. Values of the critical parameters and coefficients for Eqs.(9,10) for individual and universal values of exponent are listed in Tables 2 and 3. Quality of calculated data obtained with using limited initial information is shown in Figs.14-15.

TABLE 2. The values of the coefficients for Eqs.(9, 10) at the individual value of exponent β

Substance	T_c, K	B_1	β_1	B_2	β_2	$\rho_c, \text{kg}\cdot\text{m}^{-3}$	$\rho_{c(1)}, \text{kg}\cdot\text{m}^{-3}$
CO ₂ [25]	304,136	1,6959	0,335	-2,1536	0,343	465,875	467,6
NH ₃ [29]	405,367	1,6569	0,325	-2,3777	0,353	235,584	235
CH ₄ [26]	190,551	1,5797	0,337	-1,90444	0,341	162,62	162,66

It should be pointed out here that for prediction of the density the universal value of exponents $\beta_1 = \beta = \beta_2 = 0.325$ can be applied. Reasonableness of last state was confirmed by the good agreement of the experimental data [25,26,29] to calculated value by the Eqs. (9,10) (see Figs. 16, 17).

TABLE 3. The values of the coefficients for Eqs.(9, 10) at the universal value of exponent $\beta = 0.325$

Substance	T_c, K	β	B_1	B_2	$\rho_c, \text{kg}\cdot\text{m}^{-3}$	$\rho_{c(1)}, \text{kg}\cdot\text{m}^{-3}$
CO ₂ [25]	304,136	0.325	1.7080	-2.1534	454.669	467,6
NH ₃ [29]	405,367	0.325	1.6569	-2.1631	235.584	235
CH ₃ [26]	190,551	0.325	1.5967	-1.8814	158.04	162,66

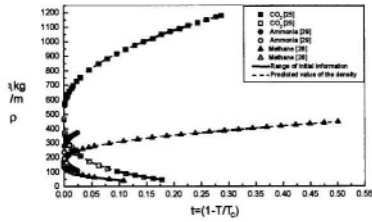


Figure 14. Temperature dependence for the density on the saturation line

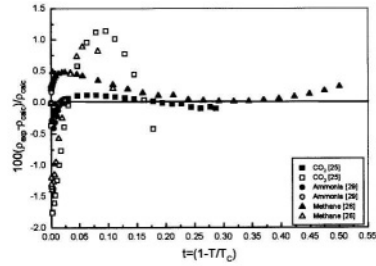


Figure 15. Deviation of the experimental data for the density on the saturation line [25, 26, 29] from calculated by Eqs.(9,10) with individual value of the exponents.

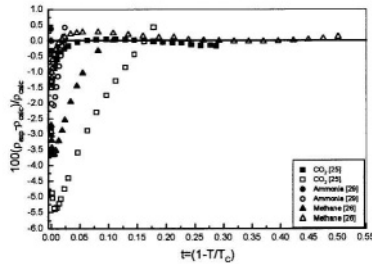
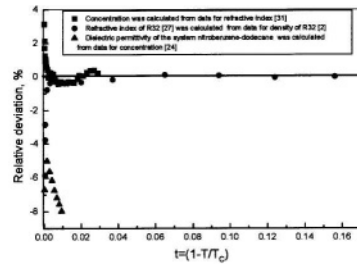


Figure 16. Deviation of the experimental data for the density of the saturation line [25, 26, 29] from calculated by Eqs.(9,10) with exponent $\beta = 0.325$



Finally, the universality in changing of the crossover functions, general analytic form of the Eqs.(15-18) allow to receive simple correlations for connection of the different physical properties on the coexistence curve. As example, very easy to obtain analytical equations which will be connected the density and refractive index, permittivity and concentration on the liquid-liquid curve:

$$\ln \frac{\rho}{n} = A_{\rho n} + B_{\rho n} (\ln \tau)^{B_{\rho n}} \quad (19)$$

$$\ln \frac{n}{x} = A_{nx} + B_{nx} (\ln \tau)^{B_{nx}} \quad (20)$$

$$\ln \frac{\varepsilon}{x} = A_{ex} + B_{ex} (\ln \tau)^{B_{ex}} \quad (21)$$

where constants A_{ik} are logarithm of the ratio for critical parameters:

$$A_{\rho n} = \ln \frac{\rho_c}{n_c}, A_{nx} = \ln \frac{n_c}{x_c}, A_{ex} = \ln \frac{\varepsilon_c}{x_c} \quad (22)$$

where B_{ik} is a difference of amplitude:

$$B_{\rho n} = (B_{i\rho} - B_{in}), B_{nx} = (B_{ln} - B_{ix}), B_{px} = (B_{ix} - B_{ln}) \quad (23)$$

It can be seen that Eqs.(19-21) indicate a straight lines in logarithmic coordinates. Therefore, we can use limited initial information for determination one property from other. Quality of the prediction of the refractive index [31,32] from data for the concentration [31,32] and from data for the density [2], or as example, for the dielectric permittivity [23] from data for the concentration [24] is shown in Fig. 17. It should be noted that uncertainty of the experimental data commensurable to the deviation of calculated values.

4. Conclusion

Method for prediction of the dielectric permittivity, refractive index on the liquid-liquid curve, refractive index and density on the saturation line is reported. Methods of the prediction for different thermodynamic systems are examined. Universal behavior of the temperature dependence for different of thermodynamical and electrophysical properties on the saturation line is demonstrated.

5. Acknowledgements

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6. References

1. Semenchenko V.K. (1966) Selected chapter of the theoretical physic, *Moscow, Prosveshenie. (in Russian)*.
2. REFPROP Version 6.0 "NIST Thermodynamic and Transport Properties of Refrigerants and Refrigerant Mixtures". *U.S. Department of Commerce, Gaithersburg, Maryland, 1998*.
3. Amirhanov H.I., Alibekov B.G., Vihrov D.I., Mirskaya V.A. (1981) Isochoric heat capacity and other caloric properties of hydrocarbons, Mahachkala: *Dagestans book publishing house (in Russian)*.
4. R.C. Reid, T.K. Sherwood, (1966) The Properties of gases and liquids. Their estimation and correlation, *McGraw-Hill, New York*.
5. Phillipov L.P. (1988). The methods of calculation and the prediction of properties for substance. *Moscow University Press, Moscow (in Russian)*.
6. Phillipov L.P., (1978) Similarity of the substance properties, *Moscow University Press, Moscow. (in Russian)*.
7. Bolotin N.K., Shelomencev A.M. (1979) Analytic expressions for calculation of the thermophysical properties of gases and liquids on the saturation line, *Calculation thermophysical properties of hydrocarbons, their mixtures, oils and oil friction ratio. (2). p. 6-13. (in Russian)*.
8. Viktorov M.M. (1977) The computing technique of physicochemical quantities and reduced calculations. *Leningrad., Khimiya. (in Russian)*.
9. Zhelezny V.P., Kamenetsky V.P., Romanov V.K. (1982). The calculation of the physicochemical properties for normal liquids in the saturation conditions. *J.Phys.Chem.* **56**, (1), 103-105 (in Russian).
10. A. Anisimov, (1987) Critical phenomena in liquids and liquid crystals, *Nauka, Moscow. (in Russian)*.
11. Sengers J.M., Sengers J.V. (1980) Perspectives in statistical physics - *Amsterdam (North-Holland), Ed. H.J. Raveche., Chp.14*.
12. De Gennes P.G. (1979) Scaling concepts in polymer physics. *New York, Cornell Univ.Press*.
13. Nesterov A.E., Lipatov Yu.S. (1984) The thermodynamics of solutions and mixtures of the polymers. *Kiev, Naukova Dumka. (in Russian)*.
14. Rabinovich V.A., Sheludyak Yu.E. (1999) Thermodynamics of Critical Phenomena: New Analysis of the Evaluation of Properties. *New York, Begell House Inc. Publishers*.

15. Bazarov I.P. (1983) Thermodynamics. 3-rd Edition, Moscow, Vishaya Shkola. (in Russian).
16. Rabinovich V.A., Sheludyak Yu.E.(1986) Modern theoretical estimations of the values of the critical exponents. *J. Phys. Eng.* **51**, (5), 758-764.
17. V.P. Zhelezny, Yu A. Kachyurka, L.D. Lyasota, Yu V. Semenyuk, (1988), Scaling principles to prediction of the non-associated liquids and their binary mixtures on the saturation line. *In Reports on the Eighth Conference on Thermophysical properties of substances (Novosibirsk)*, p. 31-32 (in Russian).
18. Zhelezny V.P., Zhelezny P. V., Medvedev O.O. (2003) Thermodynamically consistent method for determining critical point parameters. *Int. J. Thermophys.* (in press)
19. V.L.Ginsburg, U.I.Goldberg, and V.A.Golovko (1990) Light scattering near phase transitions. *Nauka, Moscow.* (in Russian)
20. Novikov I.I. (1989) The prediction of the thermophysical properties of substances. "Thermophysical properties of substances and metals (GSSSD)". (Ser. "Physic constants and properties of substances" **29**., 4-21.
21. Gerasimov A.A. (2000) Caloric properties of the normal alkanes and multi-component hydrocarbon mixtures at liquid and gaseous phases including the critical region. *Ph.D thesis.. Moscow Energetical Institute.* (in Russian)
22. Semenchenko V.K.(1964), To the static theory of dipole moments. *J. Phys. Chem.*, **38**, 2080-2084.
23. Malik P., Rzoska S.J., Drozd-Rzoska A., Jadzyn J (2003), . Critical behavior of dielectric permittivity and conductivity in temperature and pressure studies above and below the critical consolute point., *J. Chem. Phys.* (in press).
24. Experimental data from Institute of Physics, *Silesian University (Katowice, Poland)*
25. Dushek W., Kleinrahm R., Wagner W. (1990) Measurement and correlation of the (pressure, density, temperature) relation of carbon dioxide. II. Saturated –liquid and saturated –vapour densities and vapor pressure along the entire coexistence. *J. Chem. Thermodynamics.* **22**, 841-864.
26. Kleinrahm R., Wagner W. (1986) Measurement and correlation of the equilibrium liquid and vapor densities and the vapor pressure along the coexistence curve of methane. *J. Chem. Thermodynamics.* **18**, 739-760.
27. Schmidt J.W., Moldover M.R. (1994) Alternative refrigerants CH_2F_2 and C_2HF_5 ; critical temperature, refractive index, surface tension, and estimates of liquid, vapour and critical densities. *J. Chem. Eng. Data.* **39**, (1), 39-44.
28. Shimansky Yu.I., Shimanskaya E.T. (1996) Scaling, crossover, and classical behavior in the order parameter equation for coexisting phases of benzene from triple point to critical point. *Int. J. of Thermophys.* **17**.,(3). 651-662.
29. Edison T.A., Sengers J.V. (1999) Thermodynamic properties of ammonia in the critical region. *Int. J. of Ref.* **22**., 365-378.
30. Artyuhovskaya L.M., Shimanskaya E.T., Shimanskiy Yu.I. (1972) The coexistence curve of the heptane near critical point. *J. Exp. Theor.. Phys.* **63**., (6). 2159-2164. (in Russian)
31. An X., Mao C., Sun G., Shen W. (1998) The coexistence of $\{(x\text{CCHCOOC}_2\text{H}_5)_2 + (1-x)\text{CH}_3(\text{CH}_2)_4\text{CH}_3\}$ in the critical region. *J. Chem. Thermodyn.s.* **30**., 689-695.
32. An X., Jiang F., Zhao H., Chen C., Chen W. (1998) Measurement of coexistence curves and turbidity for $\{x\text{C}_6\text{H}_5\text{NO}_2 + (1-x)\text{CH}_3(\text{CH}_2)_6\text{CH}_3\}$ in the critical region. *J. Chem. Thermodyn.* **30**., 751-760.
33. Makarevich L.A., Sokolova E.S. (1966) The boundary curve liquid-gas for hexafluoride sulfur in the vicinity of the critical point. *Letter to GETF.* **4**, (10), 113-126. (in Russian)
34. Golik A.Z., Shimanskiy Yu.I., Alehin A.D. (1975) The investigation of gravitational effect in vicinity of critical point for individual substances and solutions. Equation of state of gases and liquids. *Moscow, Nauka*, 189-216. (in Russian)
35. Ivanov D.Yu., Makarevich L.A., Sokolova O.N. (1967) The shape of coexistence curve of pure substance in the vicinity of critical point. *Letter to GETF.* **20**.,(4)., 272-276. (in Russian)
36. Novikov I.I. (1990) To the theory of critical point. "Thermophysical properties of substances and materials" (GSSSD. Ser. "Physic constants and properties of substances"). **29**., 5-21. (in Russian)
37. Chernyak Yu. A., Zhelezny V.P., Yokozeki A.(1999) The influence of adsorption on PVT measurements in the gaseous phase. *Int. J. Thermophys.* **20**., (6), 1711-1719.
38. Kuleshov G. G. (2000), A Thermodynamic perturbation approach for the phase transition parameters consistence. *Paper was presented at the Fourteenth Symposium on Thermophysical Properties, Boulder, Colorado (USA).* - 2000.
39. Moldover M.G., Gammon R.W. (1984) Capillary rise, wetting layers and critical phenomena in confined geometry . *J. Chem. Phys.* **80**., (1), 528-535.

PHASE EQUILIBRIUM IN COMPLEX LIQUIDS UNDER NEGATIVE PRESSURE

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Abstract: Liquids under some specific external condition are referred as complex liquids. One of these specific conditions is the stretching of liquids, where the pressure can be negative. There are several studies of the behaviour of these extended liquids, but only a very few of them are concerned with the phase equilibrium. Because no gas phase can exist under negative pressure, these equilibria can be only liquid-liquid or liquid-solid ones.

Here we present experimental and theoretical results concerning liquid-liquid equilibrium in liquids under negative pressure. There are three groups of liquids which have been studied experimentally, namely binary solution of small molecules, binary polymeric liquids and liquid crystals

The phase diagrams of these systems close to zero pressure are usually smooth extension of the region of the phase diagram at positive pressure, however, at large negative pressures unexpected behaviour can appear: the liquids can reach the liquid-vapour instability line (spinodal), i.e. the liquid-liquid phase diagrams cannot be extended to arbitrarily low pressures, they have to terminate before crossing the spinodal. We present results of some calculations showing that in some binary liquids the liquid-liquid phase equilibrium at negative pressure is limited by an unstable critical curve.

1. Introduction

States under absolute negative pressure are often considered as impossible ones, although for condensed matters there is no thermodynamic restriction for such kind of states [1]. These states are not just theoretically possible in liquids, also they can be observed experimentally [2-4]. Although the positive-to-negative transition is a smooth one (i.e. $p=0$ is not a special state for liquids), there are several phenomena which can be seen only or better under negative pressure.

In this paper we give a short introduction to the experimental results on the phase

equilibrium of complex liquids under negative pressure. In the second and third Sections, brief theoretical and historical overview is given. In the fourth Section a few examples are given for the appearance of the negative pressure in nature and in the lab. In the fifth Section some information about the extensibility of phase diagrams to negative pressure including the “how to do” are given.

2. Theoretical background

Researcher are usually very rarely confronted with negative pressure and therefore the pressure is usually believed to be only positive. In the following we show why states at negative pressure are possible and how they can be reached.

A good example to show the existence of states at negative pressure is the analysis of equations of state (EOS). The simplest EOS is the ideal gas equation:

$$pV = nRT \quad (1)$$

Here p is pressure, V is volume, n is mole number, R is the gas constant and T is the temperature. This equation suggests that approaching zero pressure corresponds to infinite volumes, therefore, the pressure cannot be below zero. This consideration is obviously true only for gases, however, for liquids the situation is different. Nevertheless the impossibility of negative pressure for gases contributed to the misconception that pressure always has to be positive.

In gases the entropy takes the absolute maximal value as a function of the relevant extensive variables like the volume goes to infinity. In this way one can obtain a thermodynamic postulate:

$$\lim_{V \rightarrow \infty} \left(\frac{\partial S}{\partial V} \right) = 0 \quad (2)$$

which means that states at zero pressure can be reached only for infinite volume and negative pressure only corresponds to negative volumes for gases, which is impossible. But this postulate forbids states at negative pressure for gases only; in systems with upper bound for the volume, e.g. where it cannot continuously increase to infinity, this postulate is not valid. For condensed matters such upper bound exists, and hence states at negative pressure are possible (ref. [1] and references therein).

A little bit more complex EOS than Eq. (1) is the van der Waals EOS (introduced by James Thomson in 1871, a couple of years before van der Waals [5]), which can describe not only gas but liquid states too

$$\left(p + \frac{a}{V_m^2} \right) (V_m - b) = RT \quad (3)$$

Here, V_m is the molar volume, a and b are substance-dependent constants. Using this EOS one can obtain isotherms as plotted in Figure 1. The subcritical isotherms

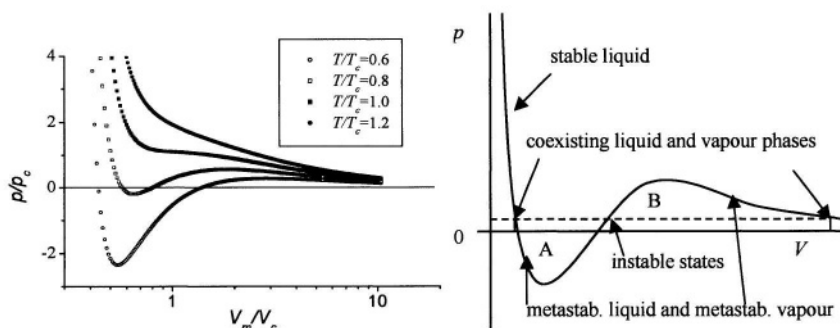


Figure 1. a) Van der Waals isotherms for different reduced temperatures. Above the critical temperature ($T/T_c > 1$) the isotherms are monotoneous; below that value they have local maximum and minimum and the fluid can split into the liquid and the vapour phase. b) The coexisting liquid and vapour phases can be determined by using the so-called Maxwell construction which is derived from the thermodynamic equilibrium condition. With this construction one obtains the tie line as a line parallel to the volume axis in such a way that the area A and area B will be equal.

corresponding to $T/T_c < 1$ have a local maximum and a local minimum. Between these two extremes the system is unstable, showing negative compressibility. The Maxwell construction (Figure 1/b), which is a special application of the general thermodynamic equilibrium conditions for pure fluids, gives the stable coexisting phases. The metastable states neighboring to the stable phases are overheated or stretched liquids such as liquids at negative pressure.

In the next Section we give a short historical overview of early experiments dealing with liquids under negative pressure. These experiments demonstrate that negative pressure states can be generated easily in normal liquids and these states can exist on a macroscopic time scale.

3. Historical background

The first indication for the existence of negative pressures in liquids is the hardly-known experiment of Huygens shown in Figure 2 [6]. In his experiment in 1663 he tried to reproduce the famous Toricelli-experiment. Both of them used a glass tube sealed at the top, filled by mercury at the bottom, and immersed into mercury. Toricelli noted that the mercury column always fell back to approximately 76 cm level, and he concluded correctly that this should be equal with the pressure of the outer air. His only mistake was the “always”. Huygens noted that several times the mercury column in his glass tube did not drop but remained hanging. Being the pressure proportional to the height, pressure at the top of hanging mercury column has to be around -1 bar in his experiments. Since this experiment turned out to be irreproducible, which is because of the metastability of mercury under negative pressure, and unexplainable due to the lack of knowledge about adhesion at this time, Huygens gave up these experiments. The experiments were successfully reproduced and explained by adhesion between the mercury and the wall by Donny more than one and a half century later [2]. The existence of negative pressures were mentioned later in connection with the Bernoulli-

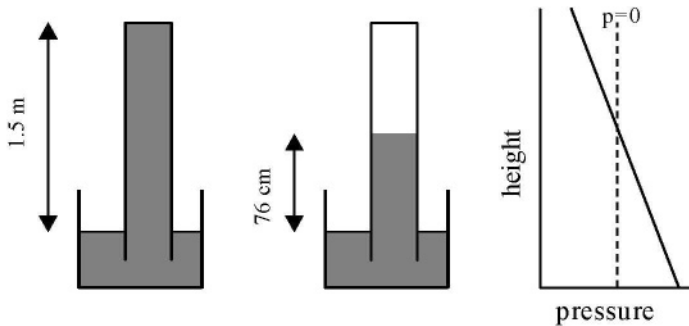


Figure 2. The experiments of Huygens and Toricelli. For the Toricelli experiment the mercury fell down to 76 cm, while for Huygens experiment, it stucked sometimes, and 1.5 m mercury column was hanging down, stretching the upper part of the liquid and causing approx. -1 bar negative pressure at the top.

law describing the pressure drop in liquids flowing through a tube with changing diameter. Changing the velocity of the fluid one might obtain pressure drop and even negative pressure at high velocity which can be described by the Bernoulli equation.

4. Negative pressure in the laboratory – negative pressure in the Nature

First we would like to introduce a simple method for generating relatively large negative pressure up to minus few MPa, which lasts minutes or even hours for macroscopic amount of liquids. The method is known as Berthelot method named after the French scientist who developed it (in the mid-14th century) to study liquids under negative pressure. Negative pressure is generated by cooling down a liquid closed into a solid container. Having no gas phase, i.e. the container is totally filled with the studied liquid, the liquid cannot shrink faster than the inner volume of the solid container (i.e. the liquid stuck to the wall, due to the adhesion), so sooner or later the liquid will be isotropically stretched. Details are given in the forthcoming sections. In this way one can easily generate negative pressure in the order of several MPa and can maintain it for minutes to days [7]. There are also several other methods [2], but this is the most simple and most well-known.

The classical experiment of this field is the study of the tensile strength of different liquids. The tensile strength is the deepest negative pressure which a particular liquid can endure without vapor-liquid phase splitting. The phase splitting can occur in three different ways: The first one is heterogeneous nucleation, when the liquid splits at a contamination or at a solid wall. The solid-liquid adhesion is weaker than the cohesion within the bulk liquid. Heterogeneous nucleation can be initiated by pre-existing microbubbles too. The second way is the homogeneous nucleation, when the bubbles of the same substance as the liquid appear in the bulk liquid. The third type of separation is the spinodal decomposition, when no bubble nucleation happens but the whole liquid reaches its stability limit and spontaneously phase separates. In most experiments, usually the heterogeneous nucleation is the limiting factor, although the homogeneous

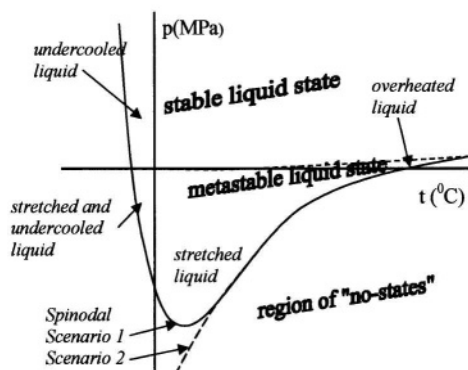


Figure 3. Schematic phase diagram of water after Angell [8] (Scenario 1) and Skripov [9] (Scenario 2), showing that overheated ($p > 0$) and stretched ($p < 0$) states are related; they are parts of the big metastable region located below the vapour pressure curve (short dashed line) which is the border between stable and metastable liquid states. The border between metastable and unstable liquid states is the spinodal line (solid and long dashed lines). The whole window represents approximately the -100 – $+400$ Celsius and -200 – $+200$ MPa region.

limit can be approached by careful cleaning of the sample. The spinodal cannot be reached experimentally because of prior phase separation. In Figure 3 a schematic phase diagram for water is shown [8,9].

One can find liquids under negative pressure not only in the lab but also in the Nature. The sap in the trees can be moderately stretched to help the trees to suck up water [10]. Octopi can make their grab more stickier by stretching the water located between their sucker and the skin of their prey. This negative pressure can reach -3 bar [11]. Positive pressure waves can have a rarefaction wave with negative pressure [12]. The part of the wave at negative pressure can cause cavitations (bubbles) in the liquid. In case of large pressure waves and big liquid volumes, it can cause a lot of bubbles: a good example for this phenomena is the explosion of mud-volcanoes close to the oil-field of Azerbaijan [13], where underground explosions generated cavitations in the oil, and the freed gas should comes out with mud.

The largest negative pressures in nature can be found in inclusions of crystals [14]; these small liquid inclusions can be under -100 MPa and they can hold this pressure for millions or billions of year demonstrating that metastable states can have extremely long lifetime.

5. Liquid-liquid phase equilibrium under negative pressure

Mixing two liquids together, one might face three different situations: the two liquids can be completely immiscible in the accessible range of conditions; they can be completely miscible or they can be partially miscible. In the latter case, changing the conditions such as pressure, temperature or concentration, one can generate a liquid-liquid phase transition when the initially homogeneous liquid splits into two liquid phases. Experimentally this can be observed as cloudiness of the liquid.

Partially miscible liquids can be divided into two major classes: weakly and strongly interacting mixtures. As a simplification, one can say that most aqueous solutions are in the strongly interacting group, while organic mixtures including polymer solutions are mainly in the first group. The principal difference between these groups is that weakly interacting mixtures can be heterogeneous at low temperature, get homogeneous upon heating and then heterogeneous again on further heating, while some strongly

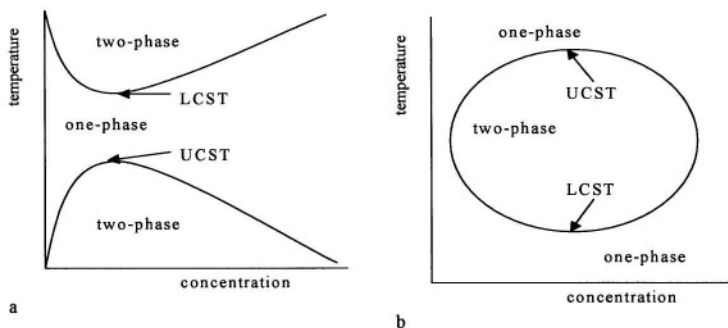


Figure 4. Schematic representation of liquid-liquid phase diagrams typically for weakly interacting (a) and typically for strongly interacting (b) binary liquid mixtures.

interacting mixtures can be homogeneous at low temperature, become heterogeneous upon heating and can be homogeneous again on further heating. Schematic concentration-temperature phase diagrams of these two groups are shown in Figure 4. There are two critical points for each systems; the maximum and minimum on these diagrams are called Upper Critical Solution Temperature (UCST) and Lower Critical Solution Temperature (LCST).

5.1 Liquid-liquid phase diagram of binary weakly interacting mixtures

A classical example for this group is the solution of polystyrene in different organic solvents, like cyclohexane, methylcyclohexane or acetone. Comparing with other materials, polymers have an additional variable parameter: the chain length N . Varying the chain length can cause drastic changes in the solubility of the polymer. For example, polystyrene with more than 200 repeating units cannot be dissolved in acetone at atmospheric pressure, but with decreasing polymerisation degree it becomes soluble (ref. [15] and references therein). A schematic representation of this phenomena in the temperature-pressure diagram is shown in Figure 5 [16]. For long chains the bottom part of the solubility branch virtually disappears from the positive pressure region. But this disappearance can be easily explained by the existence of negative pressure states since the minimum of the LL curve simply shifts to negative pressure.

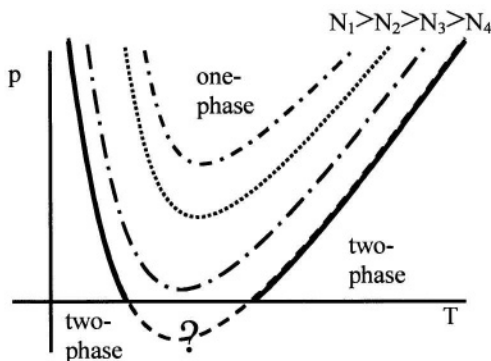


Figure 5. (left) Schematic representation of the effect of chain-length (with fixed concentration) on polystyrene solubility in acetone. For N_4 the bottom of the L-L curve virtually disappears: it shifts below zero pressure.

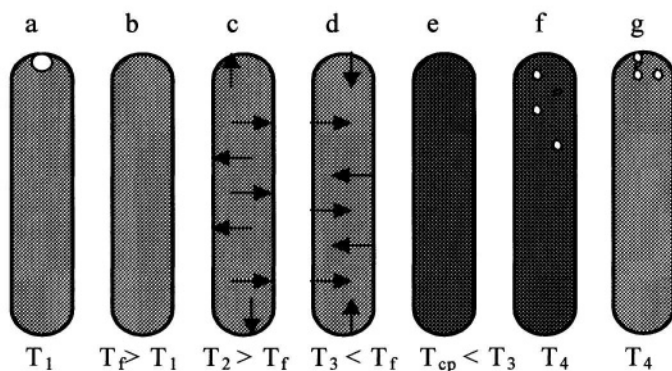


Figure 6. Schematic representation of the Berthelot method (see text).

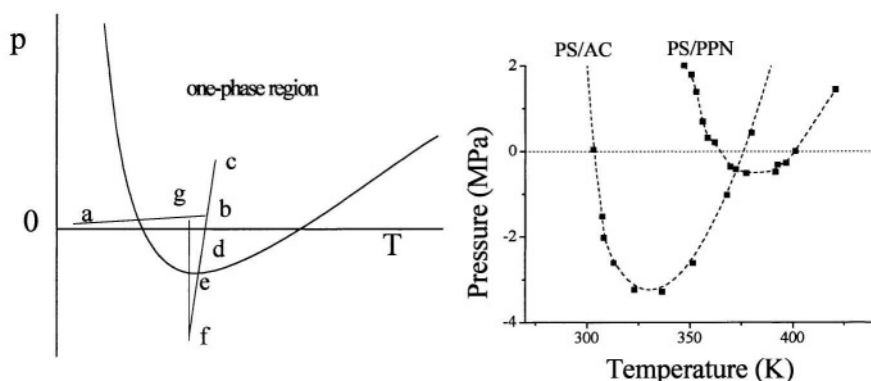


Figure 7. (left): Schematic representation of the usability of the Berthelot method to determine the liquid-liquid phase equilibrium curve.

Figure 8. (right) Extension of the liquid-liquid solubility branches in polystyrene/propionitrile [18] and polystyrene/acetone [19] systems.

It is straightforward to prove the existence of critical curve at negative pressure in an experiment. The Berthelot method mentioned before can be used for such experiment [16, 17].

In Figure 6 one can see a Berthelot tube at different temperatures and pressures. The phase diagrams according to states in these tubes are shown in Figure 7. First, one has to fill a heavy-wall glass capillary with degassed liquid, then seal it with flame under vacuum. In this way, the capillary will contain liquid with a very minor vapour phase (Fig. 6/a). Then the whole system has to be heated up, until the disappearance of the bubble (Fig. 6/b). During this heating, the pressure of the liquid will be the equilibrium vapour pressure (line a-b in Fig. 7). For further isochoric heating, the pressure will increase drastically (Fig. 6/c and point c in Fig. 7), for example, for water around room

temperature, the pressure changes approx. with 1 MPa/K rate. By cooling, one might obtain a sharp pressure drop. Coming back from point c (Fig.7) and passing point b one can expect the re-appearance of the bubble, but due to the adhesion between the glass and the liquid, the liquid is kept at the wall. After sufficiently deep cooling, the pressure of the liquid passes $p=0$, which is not a special point for a liquid, and the pressure becomes negative (Fig. 6/d and point d in Fig.7). During the cooling the system moves with good approximation along a quasi-isochor neglecting the volume change of the glass container. This isochor can cross the liquid-liquid phase transition line. At that point the initially transparent liquid becomes cloudy. Applying an equation of state for the liquid, one can estimate the negative pressure at which the phase transition occurs. Under certain circumstances the pressure can be measured directly [2,7] using a different method. By further cooling, the negative pressure decreases, until the system forms cavities (point f). At that state, the pressure of the liquid jumps back to the positive vapour pressure. Then the liquid-liquid curve will be crossed again, but in this case the conditions cannot be controlled, they can change rapidly, and phase equilibrium measurements are not possible. Using this method, the complete liquidus can be mapped point by point. Up to now, three systems have been studied in this way: polystyrene/propionitrile [18], polystyrene/methyl acetate [20] and polystyrene/acetone [19] (see Figure 8).

5.2 Liquid-liquid phase diagram of binary strongly interacting mixtures

One of the most known strongly interacting binary system – at least the one with a well-known phase diagram [21] - is the methylpyridine/water system. Actually the use of singular is not correct, one should use plural: methyl pyridines/waters, because the three different methylpyridines (2,3 and 4, marked as 2MP, 3MP and 4MP) can be mixed with water or heavy water and can exhibit various phase diagram. In the early fifties Timmermans and Lewin [22] were the first who tried to measure liquid-liquid phase equilibrium in 3MP/water system under negative pressure, but the success came

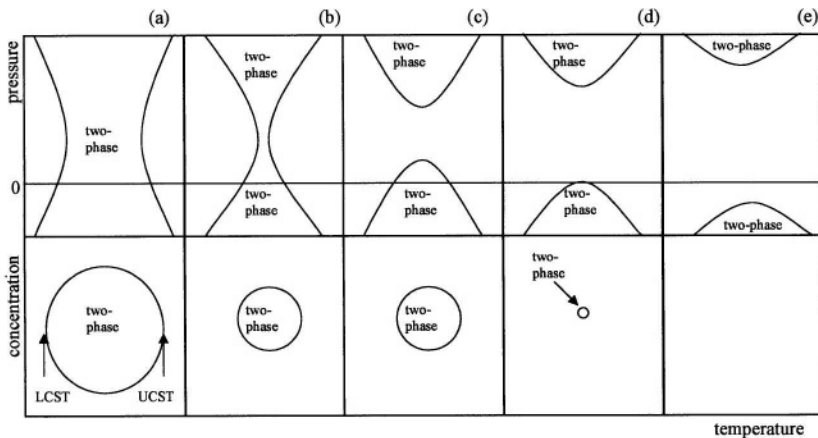


Figure 9. Schematic representation of the effect of pressure and concentration in a strongly interacting binary mixture.

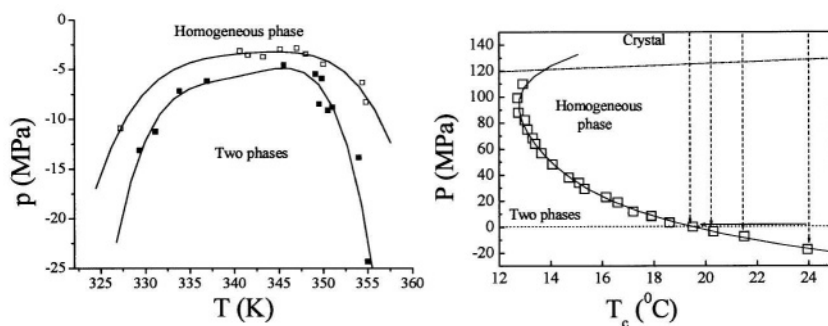


Figure 10. (left) Liquid-liquid phase equilibrium curves in two 3MP/H₂O/D₂O mixtures. Circles: 27w% 3MP (14.9 w% D₂O in the H₂O/D₂O mixture). Triangles: : 30w% 3MP (12.9 w% D₂O in the H₂O/D₂O mixture) [23]. The lines only for guiding the eyes.

Figure 11. (right) Liquid-liquid phase diagram of nitrobenzene/n-hexane system obtained by dielectric measurements and extended below $p=0$.

only a half century later, when Visak et al. were able to find the liquid-liquid locus below zero pressure [23]. In these systems the branch of the critical curve or the cloud point curve at negative pressure is not simply the extension of the one seen at positive pressure. Schematic phase diagrams are shown in Fig. 9. The phase diagram measured by Visak et al. in 3MP/water+heavy water system [23] are shown in Figure 10. Although this is a ternary system, it can be handled as a quasi-binary one.

5.3 Determination of binary liquid-liquid phase diagram by an indirect method

The rarity of phase equilibrium measurements under negative pressure is due to the experimental difficulties to work with metastable liquids. One can avoid these difficulties by using an indirect method to study phase diagrams. There are two kinds of indirect methods. The first one is the direct extrapolation of the phase diagrams measured at positive pressure as shown in Figure 5. Sometimes this method gives reasonable results, however, the low temperature branch can also exhibit a positive slope instead of the negative slope shown in Figure 5. An additional extreme can be found at the liquidus curve, when it turns back to higher temperatures [19, 24]. Such kind of behaviour cannot be obtained by interpolation.

Another way is to extrapolate a property which is measured at positive pressure and shows a pre-transitional effect. This is, for example, the Nonlinear Dielectric Effect or dielectric permittivity measured in the homogeneous phase [25]. Keeping the temperature and changing the pressure while approaching the liquid-liquid phase transition curve one can observe some change in the dielectric response caused by the pretransitional effect. This change is sufficient to estimate the location of the phase transition boundary. Testing this method at positive pressure has shown that it is sensitive enough to predict the phase transitions with sufficient accuracy even from 50 MPa distance. An experimental phase diagram determined with this method is shown in Fig. 11.

5.4 Limits of liquid-liquid phase diagrams under negative pressure

Extrapolations, as mentioned in the previous section, can cause errors. For example, a simple 4th degree polynomial fit of polystyrene/propionitrile data between 0 and +5 MPa [18] predict a minimum around -1 MPa instead of the real value -0.5 MPa (Figs. 5 and 8). Another problem is that by such extrapolation one might expect a liquid-liquid locus in some pressure-temperature region, where no phase transition can exist.

The reason for such artefacts can be an extrapolation of the critical curve below the homogeneous nucleation limit or even below the spinodal which are usually close to each other. These are limiting curves of the metastable liquid state and below them a liquid state or possible liquid-liquid critical curve cannot exist. A way to avoid such erroneous extrapolation is the estimation of the spinodal or the homogeneous nucleation limit. The spinodal can be calculated from an equation of state, while for the homogeneous nucleation limit, other methods are necessary [4, 28 and references therein]. In the above shown nitrobenzene/n-hexane mixture both the spinodal and the homogeneous nucleation limits are around -20 MPa.

Furthermore, theoretical studies of the phase behaviour [27, 28] show that a phase diagram as shown in Figure 5 can exist, in which the critical curve at negative pressure is interrupted. Such hole is caused by the presence of a second liquid-liquid branch, which is unstable and can merge with the stable. This results in a discontinuity such as shown in Figure 12. The possibility of the existence of a hole like this requires extreme caution when one would like to extend any phase diagram to negative pressure.

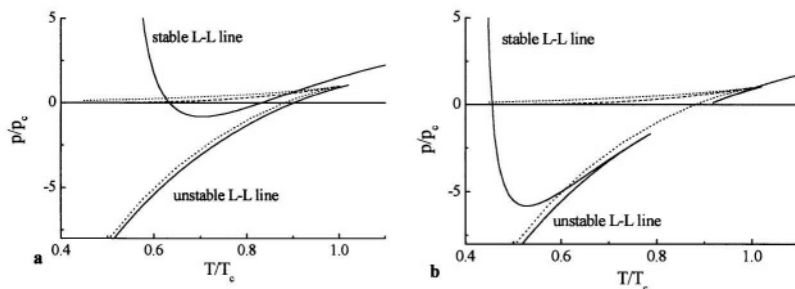


Figure 12. Stable and unstable liquid-liquid critical curves (solid lines) in a model fluid (eight-unit oligomer in a monomer [26]). a: the unstable line is much below the stable one. b: the two lines intersect each other, causing a „hole“ in both locus, giving a temperature-range where no phase transition occurs upon decreasing pressure. The dotted curves represent the liquid-vapour and vapour-liquid spinodal of the more volatile component (the monomer) and the dashed curves represents its vapour pressure curve.

5.5 Isotropic-Nematic phase transition in liquid crystals at negative pressure

Liquid crystals can exhibit isotropic (no ordering) as well as several partially ordered phases. The transition between these phases are pressure dependent and can also be extended to negative pressure [29, 30]. A classical example for this dependence is shown in Figure 13, where a liquid crystal phase diagram with an isotropic-nematic (I-N) phase transition is plotted. The solid line represents the phase transition line; coming from the isotropic side, the system becomes metastable here and turns into nematic phase, although theoretically it can stay in metastable isotropic phase for a while. The dashed line represents the line of instability (spinodal) below which no

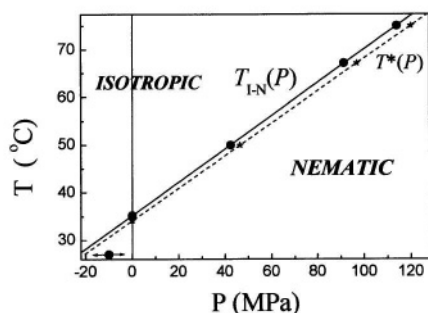


Figure 13. The pressure dependence of the isotropic-nematic phase transition on 5CB.

isotropic liquid can exist. The slope of these two lines is slightly different. Hence, they can further approach at negative pressure, however, they can also become curved at negative pressure and an extrapolation might be inaccurate. The experimental accessibility of the behaviour of these lines at negative pressure is an interesting task answering questions about the appearance-disappearance of the metastable region. Up to now – due to experimental difficulties we were not able to locate that point, but we

have some preliminary results indicating that the two lines might be curved rather than linear in the region of negative pressures.

6. Conclusions

The conclusions can be summarised as follows:

- Liquids can endure absolute negative pressures. Since these states are metastable, they can be accessed experimentally.
- Although zero pressure is not a special point for liquids, there are several phenomena which can be observed only or better at negative pressure.
- Due to the possible presence of further unstable states the extension towards negative pressure has to be accomplished with care. The knowledge of a phase diagram at negative pressure obtained from theoretical approaches is useful in such cases.

7. Acknowledgement

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8. References

1. Imre, A., Martínás, K. and Rebelo, L.P.N. (1998) Thermodynamics of Negative Pressures in Liquids, *J. Non-Equilib. Thermodyn.*, **23**, 351-375
2. Trevena, D.H. (1987) Cavitation and Tension in Liquids, Adam Hilger, Bristol
3. Debenedetti, P.G. (1996) Metastable Liquids: Concepts and Principles, Princeton University Press, Princeton, N.J.
4. Liquids Under Negative Pressure (Eds.: A.R. Imre, H. J. Maris and P.R. Williams), NATO Science Series, Kluwer, Dordrecht, 2002
5. Thomson, J. (1871) Speculations on the continuity of the fluid state of matter, and on relations between the gaseous, the liquid, and the solid states, *Report of the Meeting of the British Association for the Advancement of Science*, **41**, 30-33
6. Kell, G.S. (1983) Early observations of negative pressures in liquids, *Am. J. Phys.*, **51**, 1038-1041
7. Henderson, S.J. and Speedy, R.J. (1980) A Berthelot-Bourdon tube method for studying water under tension, *J. Phys. E.*, **13**, 778-782
8. Zheng, Q., Durben, D.J., Wolf, G.H. and Angell, C.A. (1991) Liquids at large negative pressures: water at the homogeneous nucleation limit, *Science*, **254**, 829-832
9. Skripov, V.P. (1993) The phase diagram for water at negative pressures, *High Temperature*, **31**, 448-454
10. Steudle, E. (1995) Trees under tension, *Nature*, **378**, 663-664
11. Smith, A.M. (1991) Negative pressure generated by octopus suckers: a study of the tensile strength of water in Nature, *J. Exp. Biol.*, **157**, 257-271
12. Imre, A.R., Házi, G. and Besov, A. (2003) Negative pressure tail of a reflected pressure pulse: Comparison of a lattice Boltzmann study to the experimental results, *Int. J. Mod. Phys.C.*, in press
13. Veliyev, F.H. and Guliyev, I.S. (2003) Phenomenon of a negative pressure: possible technologic and geologic effects, in Proceedings - The Sciences of Earth
14. Green, J.L., Durben, D.J., Wolf, G.H. and Angell, C.A. (1990) Water and solutions at negative pressure: Raman spectroscopy study to -80 Megapascals, *Science*, **249**, 649-652
15. Imre, A., and Van Hook, W.A. (1996) Liquid-liquid demixing from solutions of polystyrene. 1. A review. 2. Improved correlation with solvent properties. *J. Phys.Chem. Ref. Data*, **25**, 637-661 (Erratum: 1996, **25**, 1277)
16. Imre, A., Van Hook, W.A. (1998) Liquid-liquid equilibria in polymer solutions at negative pressure, *Chem. Soc. Rev.*, **27**, 117-123
17. Visak, Z.P., Rebelo, L.P.N. and Szydłowski, J. (2002) Achieving absolute negative pressures in liquids: Precipitation phenomena in solution, *J. Chem. Edu.*, **79**, 869-873
18. Imre, A., Van Hook, W.A. (1994) Polymer-Solvent Demixing Under Tension. Isotope and Pressure Effects on Liquid-Liquid Transitions. VII. Propionitrile-Polystyrene Solutions at Negative Pressure, *J. Polym. Sci. B*, **32**, 2283-2287
19. Rebelo, L.P.N., Visak, Z.P. and Szydłowski, J. (2002) Metastable critical lines in (acetone+polystyrene) solutions and the continuity of solvent-quality states, *Phys. Chem. Chem. Phys.*, **4**, 1046-1052
20. Imre A. and Van Hook W. A. (1997) Continuity of solvent quality in polymer solutions. Poor-solvent to Θ -solvent continuity in some polystyrene solutions. *J. Polym. Sci. B*, **35**, 1251-1259
21. Schneider, G. M. (1972) Phase behavior and critical phenomena in fluid mixtures under pressure, *Ber. Bunsen Ges.*, **76**, 325-331
22. Timmermans, J. and Lewin, J. (1953) A forgotten theory: the "negative saturation curve", *Discuss. Faraday Soc.*, **15**, 195-201
23. Visak, Z.P., Rebelo, L.P.N. and Szydłowski, J. (2003) The "hidden" phase diagram of (water+3-methylpyridine) at large absolute negative pressures, *J. Phys. Chem. B*, in press.
24. Imre, A.R., Melnichenko, G. and Van Hook, W.A. (1999) Liquid-liquid equilibria in polystyrene solutions: the general pressure dependence, *Phys. Chem. Chem. Phys.*, **1**, 4287-4292
25. Drozd-Rzoska, A., Rzoska, S. J., and Czaprynski, K. (2000) Phase Transitions from the isotropic to liquid crystalline mesophases studies by linear and nonlinear dielectric permittivity, *Phys. Rev. E*, **61**, 5355-5360
26. L.V. Yelash and T. Kraska (1999) Statistical associating fluid theory for chains of attractive hard-spheres: Optimized equations of state, *Phys. Chem. Chem. Phys.*, **1**, 2449-2452
27. A. van Pelt, C.J. Peters, J. de Swaan Arons and P.H.E. Meijer, (1993) Mathematical double points according to the simplified-perturbed-hard-chain theory, *J. Chem. Phys.*, **99**, 9920-9929
28. A.R. Imre, A. Drozd-Rzoska, T. Kraska, S. J. Rzoska and L. V. Yelash (2003) Liquids Under Absolute Negative Pressure, in Complex Systems in Natural and Social Sciences (Eds.: E. Hídeg, K. Martínás, M.

Moreau, D. Meyer), ELFT, Budapest, in press

29. Manjuladevi, V., Pratibha, R., and Madhusudana, N. V. (2002) Phase transitions in liquid crystals under negative pressures, *Phys. Rev. Lett.* **88**, 055701(1-4)

30. Rzoska, S.J. and Drozd-Rzoska, A. (2002) On the tricritical point of the isotropic-nematic transition in a rod-like mesogen hidden in the negative pressure region, in *Liquids Under Negative Pressure* (Eds.: Imre, A.R., Maris, H.J. and Williams, P.R.) NATO Science Series, Kluwer, Dordrecht, 117-125.

NEW APPROACHES TO THE INVESTIGATION OF THE METASTABLE AND REACTING FLUIDS

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Abstract. We are developing experimental approaches to the investigation of superheated liquids based on the procedures of automatic selection of heating function for a thin wire probe, the monitoring of a phase stability boundary of a superheated liquid by the characteristic break on the time dependence of the heat flux from the probe, and the calculation of effective thermophysical properties from the data of pulse experiment and the model of the process.

1. Introduction

The properties of fluids are usually investigated in stable states of a system. Such states are retained as long as one likes under invariant environmental conditions and, therefore, are convenient for performing measurements by both stationary and nonstationary methods. In particular, measurements of thermal transport properties as functions of pressure and temperature are carried out under small temperature perturbation with respect to thermostat temperature. The binding with thermostat provides the upper limit of the temperature range in thermophysical experiment. As a result, the most interesting region, especially, the region beyond the line of absolute stability of a fluid remains poorly known so far [1].

We are most interested in the region of relatively stable (superheated) states of a complex liquid characterized by a set of finite life times. Our aims are as follows:

- to clarify the characteristic features of high-temperature part of phase diagram of thermally unstable systems;
- to investigate thermophysical properties of liquids in short-lived states – superheated with respect to the liquid-vapour equilibrium temperature and/or to the temperature of thermal decomposition of molecules in quasi-static process;
- to develop the pulse method of monitoring of an actual state of a complex fluid.

The objects of our investigation were polymeric liquids (as typical thermally unstable systems) and gas-saturated liquids (as systems with extended metastable region).

Let us consider, as an introduction, the phase diagram of a simple liquid in pressure-temperature plane (Figure 1). The region of superheated states at positive pressures is limited from below by the binodal and from above by the spinodal of the liquid. (On the contrary, the spinodal for supercooled liquids is absent [2].) Dots trace the experimental

line of attainable superheat, or, in other words, the line of spontaneous boiling-up of the liquid. The very possibility of unambiguous detection of this line is caused by the character of spontaneous boiling-up of highly superheated liquid, which is almost threshold in temperature. An understandable limitation is imposed on the volume of superheated sample and the time of its observation t_{exp} in the course of experiment [3].

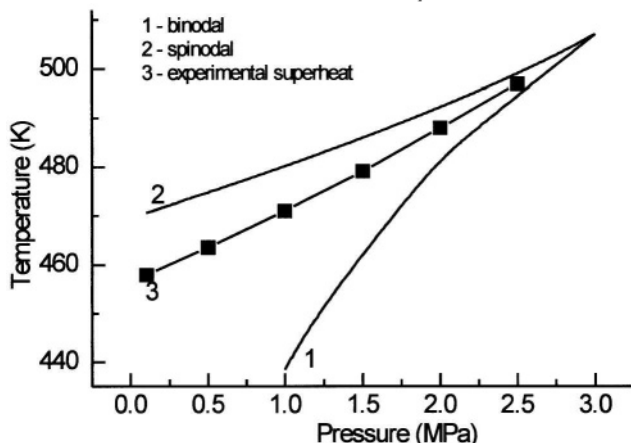


Figure 1. Liquid-vapour phase diagram for n-hexane: binodal $T_b(p)$ (1), estimation for spinodal (2) and experimental temperature of attainable superheat $T^*(p)$ for nucleation rate $\lg J \approx 20 \text{ m}^{-3}\text{s}^{-1}$ (3)

For further discussion it is useful to introduce the notion of well-defined metastable state [3]. Naturally, the experimental time should be shorter than the life time t_l of the metastable state. Let us denote as t_i the set of relaxation times for the representative volume by all the signs $\{i\}$, which are not connected directly with metastability. These times should be shorter than experimental time to ensure the attainment of quasi-equilibrium state in the course of experiment: $t_i < t_{exp} < t_l$. According to this relation a well-defined metastable state refers to a homogeneous metastable system that has relaxed by other signs. A similar superheated liquid has quite definite thermophysical properties. They can be found by experiment or determined as a smooth extrapolation of the properties referring to stable states, for instance, by isotherms. The reliability of such an approach will be sufficiently high, if we take into account the comparatively small scale of the extrapolation for a pure liquid at positive pressures, see Figure 1.

But such a procedure becomes less reliable in passing to binary systems. Due to the appearance of additional, diffusion metastability the extent of the region of two-phase equilibria increases significantly, as is easy to see on Figure 2. The shape of the binodal $T_b(p; c = \text{const})$ varies essentially with addition of the second component. As for performing measurements on superheated mixtures, this circumstance presupposes at best a reserve of facilities of experimental techniques developed for pure substances.

Let us go on and consider a liquid consisting of long-chain molecules. We shall return to the phase diagram of a simple liquid (Figure 1) and begin to increase the chain length in step by step manner. At a certain step of the chain length increment the critical temperature of the liquid and then the line of its attainable superheat will exceed the onset temperature of thermal decomposition of molecules in a quasi-static process T_d .

The number of such steps does not need to be very great. For instance, for poly(ethylene glycol) all the homologues are thermally unstable, including the first term of the series.

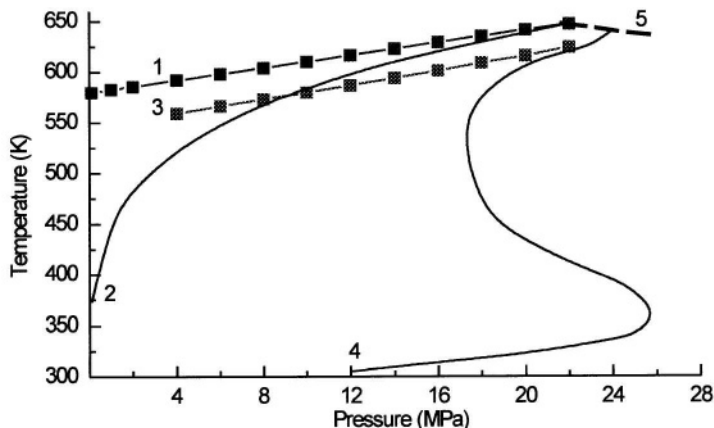


Figure 2. The characteristic scale of the region of metastable states of two-component system **water + CO₂**, (3 and 4) with respect to that of pure water (1 and 2): the lines of attainable superheat (1, 3), binodals $T_s(p; c = \text{const})$ (2, 4 – from Ref. [4]) and critical curve (5). The content of CO₂ in liquid phase is $c \approx 0.023$ mol. fr.

In going deeper into the region of thermal instability (with chain length increase) coordinates of the line of attainable superheat trace the initial stage of thermal decomposition, which is responsible for the very possibility of the polymeric liquid boiling-up. So, the liquid-vapour phase transition ceases to be pointlike with respect to temperature and proves to be dependent on the heating time (or heating rate). The line of attainable superheat $T^*(p)$ transforms into characteristic “wing” surface $T^*(p, t)$ (Figure 3). The region between this surface and the temperature level $T = T_d$ is just our working place. The data on substance properties in this region are absent.

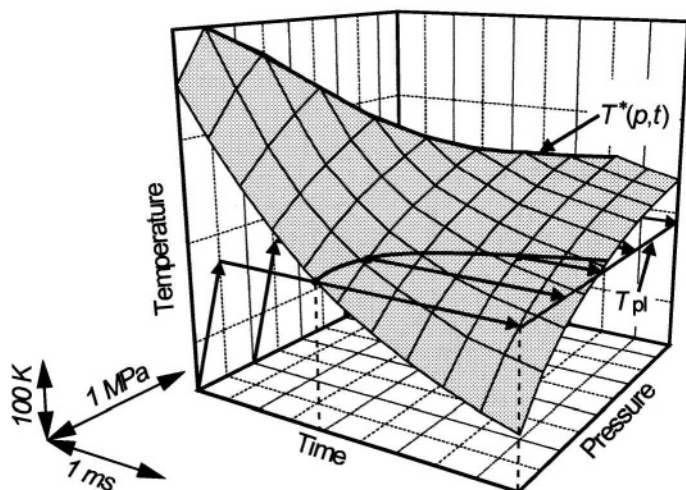


Figure 3. The schematic plot of attainable superheat temperature of molten polystyrene vs. pressure and time of linear heating. The arrows show the chosen approach, namely, the ways of the probe pulse heating, $T_{pl} > T_d$.

2. The choice of approach

The solution of the problems raised here required the development of fast-acting procedures for controllable pulse heating of a low-inertial probe. The choice of the approach is shown in Figure 3. Here one can see smoothed data on the attainable superheat temperature for a polymer melt depending on the pressure at different rates of linear heating. The method of linear heating of thin wire probe ($d = 20 \mu\text{m}$) was described elsewhere [5, 6] in connection with the attainable superheat measurements and development of a model of equation of state of polymer melt taking into account thermal decomposition of macromolecules. In our case it is necessary to find a new procedure of pulse heating being in agreement with the characteristic life time of a chemically reacting system $t_f(T)$ and with a suitable model of heat transfer from a superheated probe to a substance at a chosen probe temperature.

We have chosen the approach which is aimed at creating short-term quasi-isothermal conditions in a microvolume of chemically reacting system. We looked for the ways to rapid stop of a probe temperature rise on a given level and keeping it up for the time being. Forced temperature fixation at a given level ensures certain definiteness in comparison of the characteristics of heat transfer and the mean life-time of different systems. As a result, the basic method – method of thermostabilization of a pulse-heated wire probe, see Figure 4, has been developed [6-8]. We select a combination of a short “heating” pulse ($t < t_{pl}$) and a more longer “thermostating” pulse which balances out the heat flux into the medium in the course of experiment. The pulse parameters are fitted to the conditions of a concrete task and the medium properties.

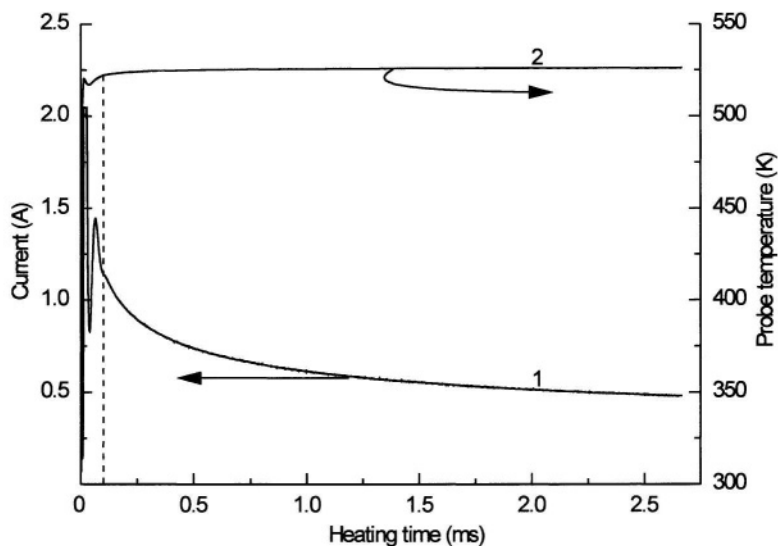


Figure 4. The details of the method of thermostabilization of the probe superheated with respect to bulk temperature. The characteristic data on current across the probe (1) and temperature of the probe (2) as functions of time in the course of the probe thermostabilization are shown. The dashed line corresponds to the time of the temperature plateau establishment $t = t_{pl}$.

The method enables one to increase rapidly the probe temperature up to the chosen value and to maintain this temperature during the time interval necessary for a measurement. This regime is convenient, because the characteristics of heat transfer are referred to a definite temperature value and the probe temperature can be gradually increased (from pulse to pulse) up to the attainable superheat temperature of a substance for a given heating time. In addition, we can compare the heat transfer picture immediately before and after the spontaneous boiling-up of a liquid. For example, Figure 5 shows the heating function near the spontaneous boiling-up temperature $T_{pl} = T(t_{exp} \approx t_l)$ at a characteristic heating time $t_{exp} = 2.7$ ms. Heat exchange between the probe and substance is perturbed in the course of boiling-up. The spontaneous boiling-up region (to the right from the phase stability boundary) is characterized by a confined in time perturbation of thermal resistance of substance. This “unexpected” perturbation is detected by the fast feedback system and is compensated by the corresponding change in the heating function. Compensating heating function has proved to be a sensitive tool for a phase transition resolution.

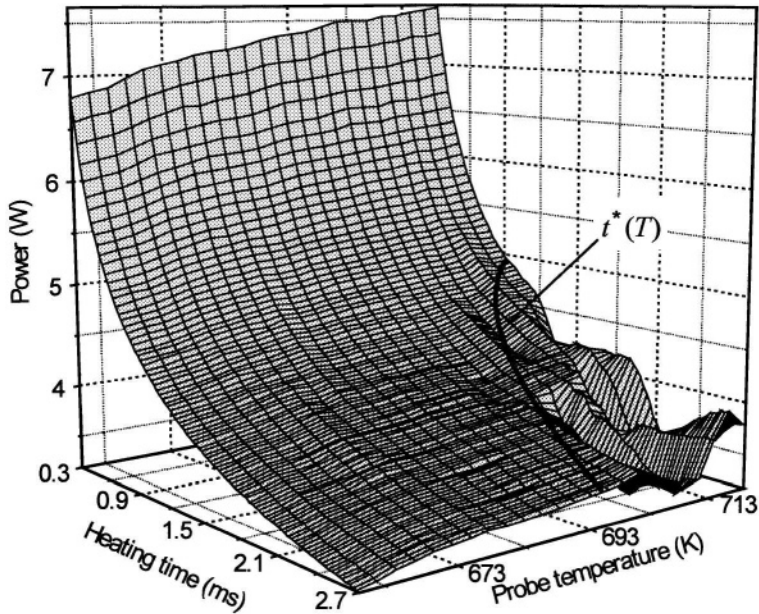


Figure 5. An example of study of a short life-time system. On-line data on the heating power that must be released in the probe for its thermostabilization in the oil XMPA [8] is shown as a function of time and temperature of thermostabilization. Data on $Q(t, T = T_p)$ to the left from the phase stability boundary ($t = t^*(T)$) are used for the calculation of thermophysical properties of locally superheated liquids, see Figure 7.

Data to the left from this boundary are used for quantitative estimation of thermal transport properties of a substance based on the suitable model of non-stationary heat flux from instantaneously thermostated linear source into an infinite medium with zero temperature [9].

3. Results and discussion

The first aim of our investigation is related to the details of phase diagram of thermally unstable systems inaccessible for traditional experimental techniques. In addition to the pulse determination of the upper boundary of two-phase equilibrium region, we will consider the approximation of the critical locus of mixture with thermally unstable component. High resolution of the spontaneous boiling-up temperature allows one to approach the critical point along the line of attainable superheat of a substance $T^*(p)$ independent of its phase or chemical stability. (For chemically reacting systems one should apply a procedure of extrapolation to zero heating time $T^*(p; t^* \rightarrow 0)$.) Figure 6 shows an example of boiling-up for gas-saturated oil at different pressures in liquid phase and at given heating rate. The line of attainable

superheat, by definition, is ended in the critical point, where the properties of two phases become undistinguishable. Indeed, the amplitude of the signal shows the monotonic decrease with pressure, and on achieving a certain value of p_{c*} , it is no longer resolved. This pressure value is taken as an approximation for the critical pressure. The corresponding value of temperature $T^*(p = p_{c*})$ is taken as an approximation for the critical temperature of the system. Some results for liquid + gas mixtures are presented elsewhere [10].

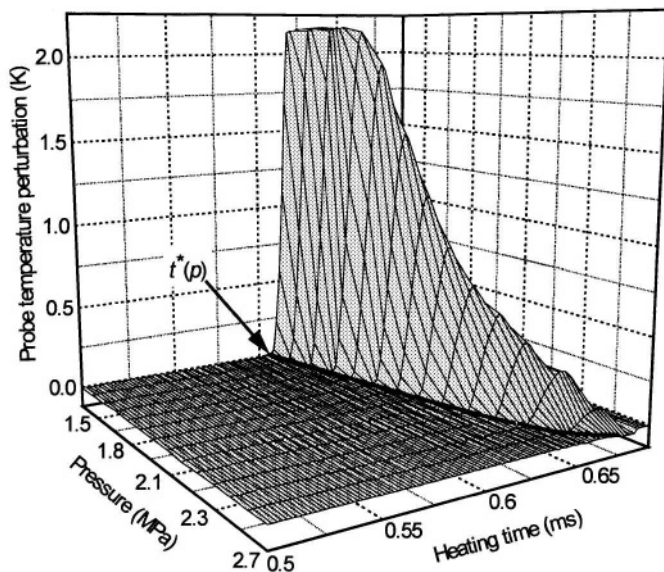


Figure 6. An example of estimation of critical parameters for a mixture with thermally unstable component from experimental data obtained by the method of linear pulse heating. The amplitude of boiling-up signal (probe temperature perturbation [5, 6]) separated from the background of smooth heating for CO_2 solution in the oil Mobil EAL Arctic22 at different pressures and given heating rate ($0.8 \text{ K}/\mu\text{s}$) is shown.

The second aim is related to the estimation of thermal transport properties of a system in a short-lived states. Figure 7 shows the results on thermal properties for PMS-350 and two oils calculated from the electric characteristics recorded in the course of probe thermostabilization using the chosen model. The details of calculations are presented elsewhere [9]. The temperature T_{pl} was increased up to the values corresponding to the minimum life time of the system which was equal in these experiments to 1 ms. In the temperature range admissible for quasi-static measurements our data agree with those obtained by the method of cylindrical thermal waves [11]. These data were obtained under conditions of the linear relationship between heat flux and temperature field and may be referred to the “classical” thermophysical properties. We have no data for the comparison in the region of relative stability of these substances.

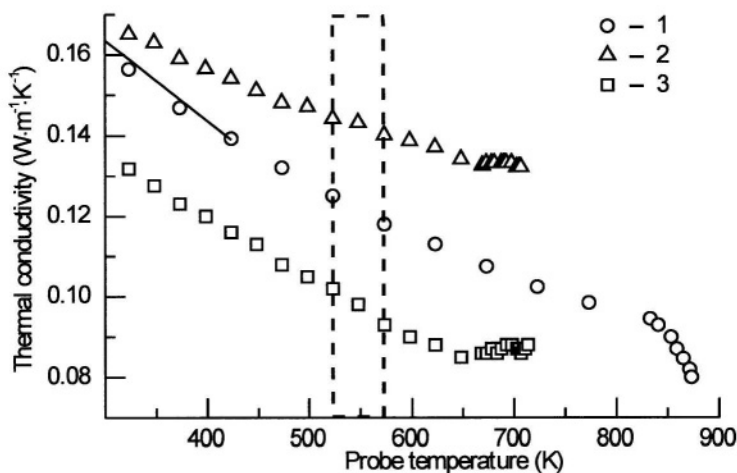


Figure 7. Thermal conductivity of polydimethyl siloxane PMS-350 (1), refrigeration oils XMPA (2) and Mobil EAL Arctic22 (3) at atmospheric pressure, calculated on the basis of experimental data from the method of probe thermostabilization. The solid line approximates data from Ref. [11] obtained for the identical PMS-350 sample. The temperature T_d interval for these substances is bounded on dashed lines.

It should be noted that with an increase in the probe superheat and with penetration deeper into the region of relative stability of a substance the task becomes essentially non-linear. Naturally, our data take on the meaning of effective values. They describe the generalized heat transfer in confined in time process in a system far from the equilibrium state. Moreover, the superheated substance may be in disagreement with the notion of well-defined metastable state introduced earlier. In this connection we call attention to the high-temperature “tails” on the Figure 7, which deviate from the smooth extension of the dependencies. The changes in the curves trend are due, in our opinion, to the contribution of the processes of thermal decomposition and microphase separation of components to the process of heat transfer in a chemically reacting mixture.

Thus, an analysis of the time dependence of heating power in the course of probe thermostabilization makes it possible to compare with a high precision the intensity of heat transfer for different samples in different temperature ranges. Let us pay attention to the fact that the resolution of the method increases with increasing value of superheat. Actually, the highest resolution of the electrical quantities traced in the experiment, which are directly connected with the heat transfer properties, we have in states with the shortest life-times (all other factors being equal).

This methodical feature proved to be useful in practice. It triggers off development of the procedure of local monitoring of an actual state of a system. The parameters of pulses were selected in accordance with the type of the process to be traced. In particular, for revealing the presence of impurities in a substance we have developed the technique of thermal shock (Figure 8). In this case the chosen value of the stabilization temperature T_{pl} was comparatively low, in the region of guaranteed thermally stable state of the substance, $T_{pl} < T_d$. At a certain instant of time the peaking pulse was superimposed on the basic pulse. It increased the probe temperature by several hundred

degrees in a few microseconds. The run of the curve of the subsequent probe cooling proved to be sensitive to the system composition and, first of all, to the presence of volatile impurities or their traces.

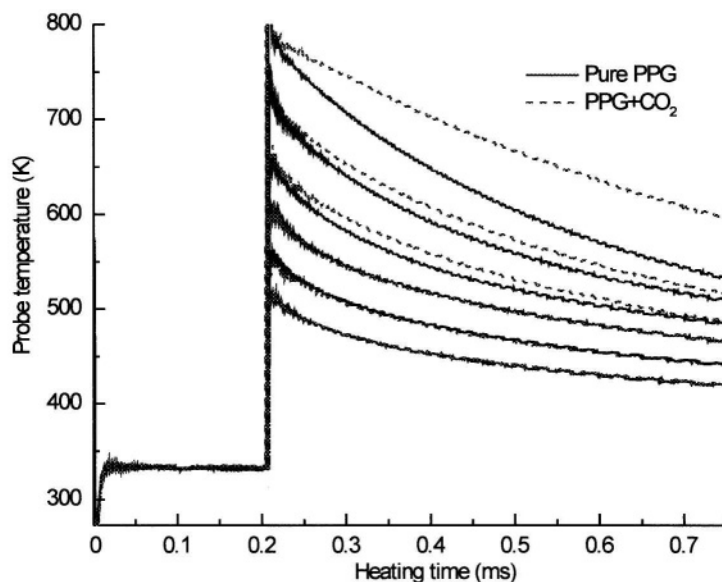


Figure 8. An example of experiment on the probe peak heating for revealing of traces of volatile impurities. The set of response signals corresponding to the set of pulses with a step-by-step increase of energy released in the probe is shown for polypropylene glycol PPG-1025 (solid lines) and for PPG-1025 + CO₂ mixture (dashed lines). The content of CO₂ in liquid phase is approximately equal to $c \approx 0.01$ wt. fr.

Figure 8 presents the response signals for pure polymeric liquid and the polymer + carbon dioxide mixture. In experiment a set of pulses was recorded with a step-by-step increase of the energy released in the probe. From a certain step of the heating energy increment one can observe an appearance of discrepancy between the response signals for the compared systems. Sooner or later, but this discrepancy will necessarily happen. In the course of monitoring of an actual state of a system one could periodically reproduce a pulse with the most effective value of energy release for the expected impurity.

4. Conclusions

New experimental approach to studying the thermophysical properties of locally superheated liquids and the relationship between pulse heating conditions and relative stability boundary for a reacting system is developing by us. The approach provides a

real understanding for the behaviour of complex samples, such as polymer solutions and liquid-gas mixtures, being in the high temperature region of risky measurements inaccessible for presently available experimental techniques and simulations of satisfactory accuracy. It can be applied to rapid composition-oriented measurements for combinatorially synthesized compounds [1] and to monitoring of an actual state of a complex fluid.

5. Acknowledgment

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6. References

1. Harvey, A.H. and Laesecke, A. (2002) Fluid Properties and New Technologies: Connecting Design with Reality, *Chem. Eng. Progr.* Febr. 2002, 34-41.
2. Skripov, V.P. and Koverda, V.P. (1984) *Spontaneous Crystallization of Supercooled Liquids*, Nauka, Moscow (in Russian)
3. Skripov, V.P. (1992) Metastable States, *J. Non-Equilib. Thermodyn.* **17**, 193-236.
4. Takenouchi, S. and Kennedy, G.C. (1964) The binary system H_2O-CO_2 at high temperatures and pressures, *Amer. J. Sci.* **262**, 1055-1074.
5. Pavlov, P.A. and Skripov, P.V. (1999) Bubble Nucleation in Polymeric Liquids under Shock Processes, *Int. J. Thermophys.* **20**, 1779-1790.
6. Puchinskis, S.E. and Skripov, P.V. (2001) The Attainable Superheat: From Simple to Polymeric Liquids, *Int. J. Thermophys.* **22**, 1755-1768.
7. Skripov, P.V., Starostin, A.A., and Puchinskis, S.E. (2000) Heat Transfer and Thermal Fracture of Polymers in Pulsed Processes, *Doklady Physics* **45**, 663-666.
8. Chumak, I.G., Onistchenko, V.P., Zhelezny V.P., et al. (1998) New Class of Lubricant Oils Soluble in Ammonia, in *Natural Working Fluids '98*, International Institute of Refrigeration, Paris, pp. 417-419.
9. Skripov, P.V., Starostin, A.A., and Volosnikov, D.V. (2003) Heat Transfer in Pulse-Superheated Liquids, *Doklady Physics* **48**, 228-231.
10. Skripov, P.V., Starostin, A.A., Volosnikov, D.V., and Zhelezny, V.P. (2003) Comparison of thermophysical properties for oil/refrigerant mixtures by use of pulse heating method, *Int. J. Refrig.* **26** (in press)
11. Baginskii, A.V., Stankus, S.V., and Khairulin, R.A. (2002) Experimental investigation of density, heat capacity, heat conduction and thermal diffusivity for polydimethyl siloxane, in *Proceedings of X Russian Conference on Thermophysical Properties of Materials*, Butlerov Communications, Kazan; Supplement to Special Issue No. 10, pp. 149-150 (in Russian)

THE DISCONTINUITY OF THE ISOTROPIC – MESOPHASE TRANSITION IN N-CYANOBIPHENYLS HOMOLOGOUS SERIES FROM 4CB TO 14CB. NONLINEAR DIELECTRIC EFFECT (NDE) STUDIES.

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Abstract. Results of studies of the static nonlinear dielectric effect (*NDE*) in the homologous series of 4-cyano-4-*n*-alkylbiphenyls (*n*CB, from $n = 3$ to $n = 14$), exhibiting both isotropic - nematic (I-N) and isotropic - smectic A (I-SmA) phase transitions, are presented. Tests were conducted in the isotropic phase where the reciprocal of *NDE* shows a linear dependence vs. temperature or pressure, also in the immediate vicinity of the clearing point. It was found that the discontinuity (ΔT) of the isotropic – mesophase transition increases with the length of the alkyl-chain in the *n*CB molecule, from 0.7 K (4CB) to ca. 11K (14CB). Regarding the influence of pressure, it continuously increases the value of $\Delta T(P)$ for the case of the I-N transitions, as shown for 5CB up to $P = 275 \text{ MPa}$. For the the I-SmA transition discontinuity first drops down to $\Delta T(P)_{\min} \approx (1/2) \Delta T(0.1 \text{ MPa})$ and next strongly increases with pressure rising up to $P = 375 \text{ MPa}$.

Liquid crystalline phases are an intermediate state of matter between the liquid and the solid crystal. Hence, the weakly discontinuous character of the isotropic liquid – mesophase transitions is not surprising. For the simplest case of the isotropic – nematic (I-N) transition a quantitative estimations of its discontinuity were possible since the early seventies due to Kerr effect (*KE*), Cotton-Mouton effect (*CME*), light scattering (*I*), relaxation time τ , turbidity ζ and compressibility studies χ [1 – 26]:

$$I, KE, CME, \zeta, \chi, \tau \propto \frac{1}{T - T^*}, \quad T > T^C = T^* + \Delta T \quad (1)$$

where T^* denotes the extrapolated, temperature of hypothetical continuous phase transition, T^C is the clearing temperature: in this case $T^C = T_{I-N}$.

Experimental values of the discontinuity of the I-N transition are in the range of $\Delta T = 0.7 - 2 \text{ K}$ [1-26]. The application of Landau - de Gennes (LdG) and Maier - Saupe (MS) mean-field models made a quantitative parameterization of these anomalies possible [1 – 27]. However, these models overestimate the value of the discontinuity, namely giving from $\Delta T \approx 42 \text{ K}$ (1974) to $\Delta T \approx 7 \text{ K}$ (2000) [21, 28 and refs therein]. They also predict no pretransitional anomalies for the specific heat, density and dielectric permittivity in the isotropic phase, what is related to the fact that within the simple-mean field approximation the exponent $\alpha = 0$ for the specific heat related anomaly in the high temperature phase [21 - 23, 26, 27]. However, there is a clear experimental evidence of such anomalies, associated with the non-zero value of the exponent α [28, 29 – 32]. Only recently, an extension of the Landau model leading to the *fluidlike* equation of state and the *tricritical* behavior [28, 33], gave $\alpha = 1/2$ and

$\Delta T = 1-3K$ and $\beta = 1/4$ for the order parameter exponent, in a fair agreement with experiments [29 - 36]. These values are in a fair agreement with experimental values of ΔT and the recent experimental estimations for the exponents α [29-32] and β [34,35]. Beyond the simple mean field picture, still dominating in basic monographs [21 - 25], there is also the clear evidence for the non-Arrhenius and non-Debye behavior dynamics in the isotropic phase [36-40]. It was shown in the nineties that the pretransitional anomaly described by relation (1) can be also found for the static nonlinear dielectric effect (*NDE*) [30,31], describing changes of dielectric permittivity due to the application of a strong electric field:

$$\epsilon^E = \epsilon + \epsilon_3 E^2 + \dots \quad \text{and} \quad \epsilon_{NDE} = \epsilon_3 = \frac{\epsilon^E - \epsilon}{E^2} = \frac{\Delta \epsilon^E}{E^2} \quad (2)$$

where ϵ^E is dielectric permittivity under strong electric field E and ϵ is dielectric permittivity solely related to the weak, measuring field. ϵ_{NDE} is the experimental measure of *NDE*.

The application of an additional DC pulse of a strong electric field results in “nonlinear” changes of ϵ^E , detected by a weak, radio-frequency (f) measuring field. Significant factors differs *NDE* studies from *KE* or *CME* tests. Firstly, the value of the *NDE* measurement frequency can be changed. Secondly, the measurement time-scale related to $\omega^{-1} = (2\pi f)^{-1}$ may coincide with the relevant system time-scale associated with the decay time of pretransitional fluctuations (τ) [36, 38]. For the static, low frequency, *NDE* the condition $\omega^{-1} \gg \tau$ is always fulfilled in the isotropic phase (Fig. 1). Due to such experimental conditions the static *NDE* can be described within the simple mean-field LdG model in the isotropic phase of nematogens [30, 38]:

$$NDE(T) = \frac{A_{NDE}}{T - T^*} = \frac{2\epsilon_0}{3a_T} \frac{(\Delta \epsilon^0)^2}{(T - T^*)^\gamma} \propto \frac{\chi_T}{T - T^*}, \quad T > T^C = T^* - \Delta T, \quad \gamma = 1 \quad (3)$$

$$NDE(P) = \frac{A_{NDE}^P}{P^* - P} = \frac{2\epsilon_0}{3a_P} \frac{(\Delta \epsilon^0)^2}{(P^* - P)^\gamma} \propto \frac{\chi_P}{P^* - P}, \quad P < P^C = P^* + \Delta P, \quad \gamma = 1 \quad (4)$$

where a_T , a_P are constant amplitudes of the second rank term in the LdG expansion of the free energy, $\Delta \epsilon^0$ is the molecular anisotropy of dielectric permittivity of the perfectly ordered nematic sample. (T^*, P^*) are temperature and pressure coordinates of the hypothetical continuous phase transition point, (T^C, P^C) are clearing temperature and pressure. Magnitudes χ_T and χ_P denote the compressibility and the thermal expansion coefficient. [5, 26].

Experiments showed that there are no distortions from relation (3), starting from the immediate vicinity of T^C up to $T_X = T^C + (40-50K)$ [30, 36, 38]. It is noteworthy that linear dependences of $NDE^{-1}(T)$ and $NDE^{-1}(P)$ occur both on approaching nematic and smectic phases [41]. Such unique behavior, absent for all other methods

mentioned above [3, 10, 11, 12, 18, 21], makes it possible to estimate precisely the value of ΔT for any kind of the isotropic – mesophase transition.

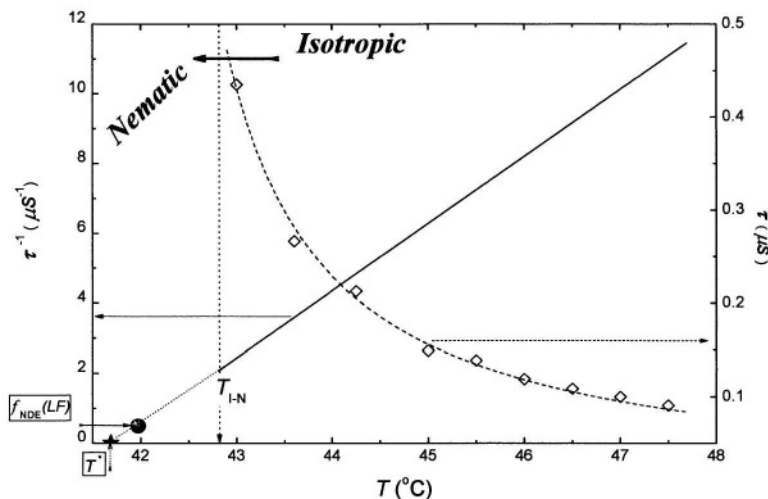


Figure 1 The temperature dependence of the relaxation time of prenematic fluctuations in the isotropic phase of 8CB. The right scale and the related open squares are for experimental data. The left scale and the solid squares are for reciprocals of experimental data. The dotted line portrays the extrapolation of the experimental dependence $\tau \propto (T - T^*)^{-1}$ below the clearing temperature (T_{I-N}). The temperature $\tau^{-1}(T) = 0$ determines the value of T^* , the temperature of the hypothetical continuous phase transition. The solid circle below T_{I-N} shows the position of the time-scale related to the applied in this paper *NDE* measurement frequency (static, low-frequency *NDE*). The Figure was prepared basing on the time-resolved KE studies by Kolynsky et al. [8].

Fig. 1 shows the relationship between time-scales related to *NDE* measurements and associated with prenematic swarms-fluctuations in the isotropic phase of 8CB, a liquid crystalline compound with the I-N transition. The solid circle, well below the clearing temperature, shows the location of the time-scale associated with the low-frequency, static *NDE*. It is clearly visible that for the static *NDE* the condition $\omega_{meas.}^{-1} \gg \tau$ is well fulfilled in the isotropic phase. For higher frequencies, the time scale of *NDE* measurements and the time-scale of prenematic fluctuations may coincide ($\omega_{meas.}^{-1} \sim \tau$), even well above the clearing temperature. In such regime a pretransitional amplitudes A_{NDE} or A_{NDE}^P depends on the distance from T^* or P^* [31, 36, 38]. Such behavior is clearly beyond the simply mean-field description but can be described starting from the dependence derived for the critical anomaly in the homogeneous phase of critical, binary mixtures [36, 38]. Results presented in this contribution were obtained due the application of the static nonlinear dielectric effect. The applied modulation – domain

principle of the *NDE* apparatus are described in ref. [42]. All measurements were conducted in a bulk sample, using measurement capacitors with $d = 0.5\text{mm}$ gap.

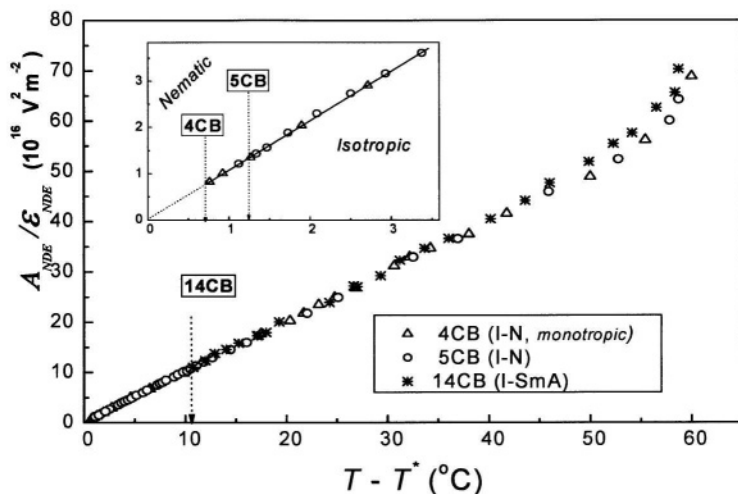


Figure 2 Reciprocals of experimental values of the static *NDE* ($f_{NDE} = 26\text{kHz}$) for three, characteristic *n*-alkylcyanobiphenyls: 4CB, 5CB and 14CB. Studies were conducted in isotropic phases. Arrows shows clearing temperatures for 4CB, 5CB and 14CB. Arrows also indicate the value of ΔT for given *n*CB. Data are superposed due the scaling of axis, following relation (3).

Studies were conducted in the isotropic phase of *n*-alkylcyanobiphenyls (*n*CB), synthesized and perfectly purified at the Military Technical University, Warsaw, Poland. Immediately prior to measurements tested samples were carefully degassed. Fig. 2 shows reciprocals of measured *NDE* values for 4CB, 5CB and 14 CB. 4CB is a monotropic liquid crystalline compound, often claim to crystallize even few decades above 16.5°C , declared as the hypothetical I-N clearing temperature [22, 26]. However, in presented studies it was found that after 3 hour of degassing the sample of 4CB crystallizes only ca. 7 K above T^* . After next degassing the I-N transition was reached. It is noteworthy that crystallization had no influence on the pretransitional behavior of *NDE* in the isotropic phase of 4CB: experimental data always followed the same pattern. For 5CB which one of the most “classical” liquid crystalline compounds, the I-N transition is detected at ca. 35°C and next the sample crystallizes at ca. 15°C . Studies in the *n*CB series are usually conducted from 5CB to 12CB [26]. Fig. 2 presents also the first ever evidence for the pretransitional behavior in isotropic 14CB, a compound with the I-SmA transition. In each tested mesogen the same simple pretransitional behavior, associated with the same exponent $\gamma = 1$ was found. Such dependence was noted from the clearing temperature up to $T_X = T^* + 40\text{K}$ without any distortions and without

additional “background” terms, often included in the analysis of *KE* or *CME* measurements [3, 10, 12, 23].

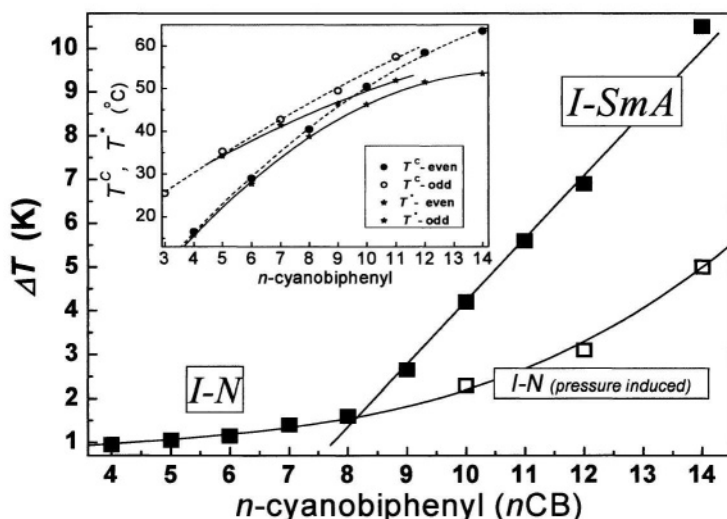


Figure 3 The discontinuity of the isotropic – mesophase transitions $\Delta T(n)$ in the homologous series of n -cyanobiphenyls (n CB) from $n = 4$ to $n = 14$. Open squares are for the pressure induced nematic phase in compounds exhibiting the *I-SmA* transition under atmospheric pressure (solid squares). The inset shows the evolution of clearing temperature $T^C(n)$ (circles) and the extrapolated temperature of the hypothetical continuous phase transition $T^*(n)$ (stars) in the series. These results are from 3CB to 14CB.

The similarity of pretransitional anomalies for compounds with *I-SmA* (14CB), *I-N* (5CB) and “crystallization-hidden” *I-N* transition (4CB) transitions is clearly visible due to the application of the scaling transformation for data shown in Fig. 2. Figure 3 shows the evolution of $\Delta T(n)$ in n CB homologous series, resulting from measurements of the static *NDE*. The Figure contains results from earlier authors studies ([41]: from 6CB to 11CB) and novel results for 3CB, 4CB, 5CB, 12CB and 14CB. When the length of the alkyl chain increases the same occurs for value of $\Delta T(n)$. This is particularly pronounced for smectogenic n CB’s. One may associate such behavior with increasing difference between symmetries of the isotropic liquid and the mesophase [41]. Numerical values for presented in Fig. 3 experimental data are collected in Table I. For 3CB only the value of T^* from *NDE* measurements is given. This sample always crystallized well before reaching the *I-N* transition. The sign (*) in Table I points the existence of the smectic phase between the nematic and the isotropic phases for the given n CB. For 9CB and

11CB the temperature the width of the nematic phase is equal only to 1.5 and 0.5 K, respectively [26].

<i>n</i> CB	$T^C(^{\circ}C)$	$T^*(^{\circ}C)$	$\Delta T = (K)$	type of the transition
3CB	-	24.5	-	I – Cryst. (*)
4CB	16.5	15.8	0.7	I – N (<i>monotropic</i>)
5CB	35.3	34.25	1.05	I-N
6CB	29	27.8	1.2	I-N
7CB	42.8	41.4	1.4	I-N
8CB	40.5	38.9	1.6	I-N (*)
9CB	49.5	46.7	2.8	I-N (*)
10CB	50.5	46.3	4.2	I-SmA
11CB	57.5	51.9	5.6	I-N (*)
12CB	58.5	51.6	6.9	I-SmA
14CB	63	52.5	10.5	I-SmA

Table I Clearing temperatures, extrapolated temperatures of the hypothetical continuous phase transition and the discontinuity of the isotropic – mesophase transition in *n*-alkylcyanobiphenyls homologous series.

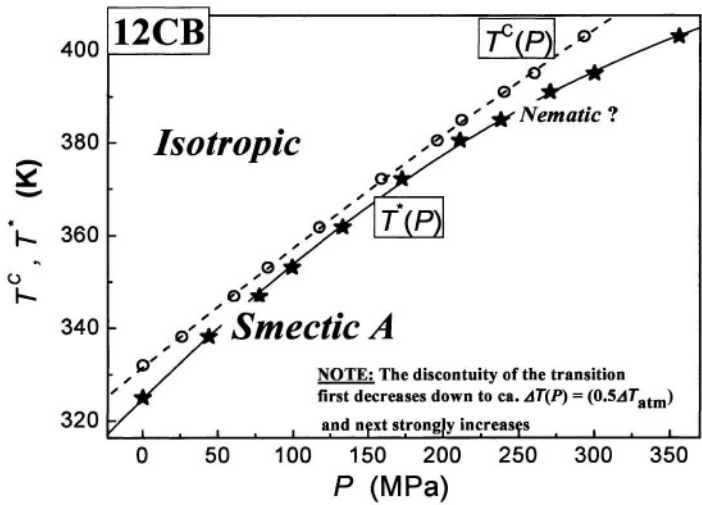


Figure 4 Pressure dependence of the clearing temperature (circles) and the temperature of a hypothetical continuous phase transition (stars) in 12CB.

There are two values of $\Delta T(n)$ for 10CB, 12CB and 14CB in Fig. 3. The lower one is for the smallest values of ΔT associated with the hypothetical pressure-induced nematic phase as shown in Fig. 4 for 12CB. Fig. 4 presents the evolution

of $T^C(P)$ and $T^*(P)$ for 12CB up to 370 MPa, the highest range of pressure applied in such studies up to now.

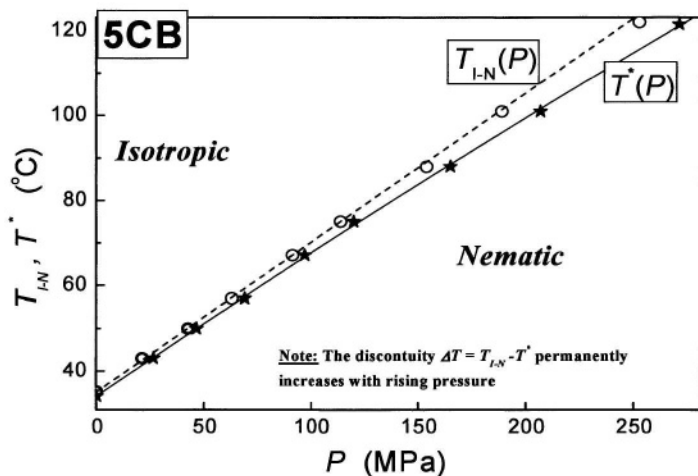


Figure 5 Pressure dependence of the clearing temperature $T^C(P) = T_{I-N}(P)$ (circles) and the temperature of a hypothetical continuous phase transition $T^*(P)$ (stars) in 5CB.

It is visible that the discontinuity of the I-SmA transition decreases with rising pressure, down to $\Delta T_{\min}(P) = (1/2)\Delta T(0.1\text{MPa})$, and next $\Delta T(P)$ strongly increases on pressurizing. The appearance of the pressure induced nematic phase, postulated by the author for higher pressures already in ref. [41], was confirmed in P - T phase diagram studies for 10CB and 12CB in ref. [43]. It is noteworthy that for the I-N transition the value of $\Delta T(P)$ always only increases with rising pressure [29-31, 41] as shown in Fig. 5 for 5CB. It is noteworthy that experimental results for $\Delta T(P)$ are scarce, probably due to technical problems associated with pressure studies. In the late seventies Lin et al. [9] determined $T^*(P)$ and $T^C(P)$ evolution for I-N transition in EBBA and MBBA basing on turbidity measurements up to ca. 150 MPa. To the best of the authors knowledge all other studies are associated with the NDE measurements. Fig. 6 shows the evolution of

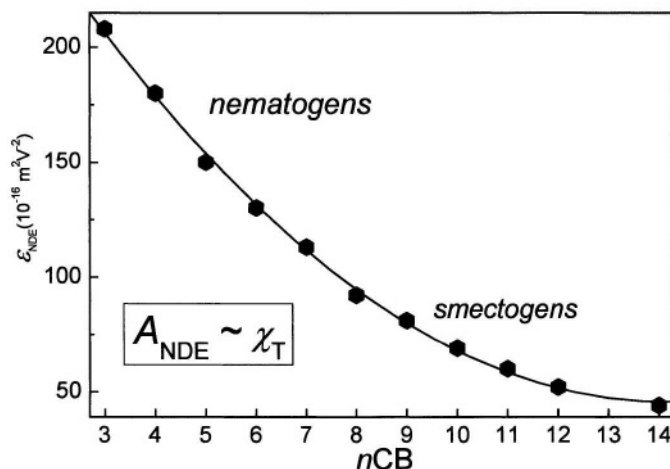


Figure 6 The amplitude of the NDE pretransitional effect in n CB homologous series.

NDE pretransitional amplitude (relation (2), which is proportional to the amplitude of the susceptibility (compressibility). It strongly increases when the length of the alkyl chain decreases. Noteworthy is the lack of the odd – even effect [26] for $\Delta T(n)$ and $A_{NDE}(n)$, which is clearly visible for $T^C(n)$ and $T^*(n)$.

Concluding, results presented above show unique possibilities of the static NDE for studying basic properties of isotropic – mesophase transitions. Particularly noteworthy is the emerging relationship of $\Delta T(P)$ and $\Delta T(n)$ dependences with the symmetry of the following mesophase. In the opinion of the authors results presented above may be essential for a general, non-phenomenological model for isotropic – mesophase transitions, not available up to now.

Acknowledgements

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References

1. Stinson T. W. and Litster J. D. (1973) Correlation length of fluctuations of short-range order in isotropic phase of liquid crystals, *Phys. Rev. Lett.* **30**, 688 – 692.
2. Madhusudana N. V., Chandrasekhar S. (1973) Magnetic and electric birefringence in the isotropic nematic liquid crystals, *Pramana* **1**, 12 – 20.
3. Poggi Y., Atten P., and Filippini J. C. (1978) Validity of the Landau approximation in the nematic phase, *Mol. Cryst. Liq. Cryst.* **37**, 1 – 7.
4. Wong G. K. L. and Shen Y. R. (1974) Study of the pretransitional behavior of laser-field induce molecular alignment in isotropic nematic substances, *Phys. Rev.* **A10**, 1277 – 1284.

5. Bendler J. (1977) Compressibility and thermal expansion anomalies in the isotropic liquid crystal phase, *Mol. Cryst. Liq. Cryst.* **38**, 19 – 20.
6. Coles H. J. (1978) Optical Kerr effect studies of octylcyanobiphenyl, *Chem. Phys. Lett.* **A69**, 276 – 278.
7. Yamamoto R., Isihara S., Hayakawa S. and Morimoto K. (1978) The Kerr constants and relaxation times in the isotropic phase of nematic homologous series, *Phys. Lett.* **A69**, 276 – 278.
8. Kolinsky P. V. and Jennings B. R. (1980) Optical Kerr effect in the isotropic phase of various alkyl-cyanobiphenyl homologous, *Mol. Phys.* **40**, 979 – 987.
9. Lin W. J., Keyes P. H. and Daniels W. B. (1980) The nematic – isotropic transition at high pressures turbidity measurements, *J. Physique II* **41**, 633 – 638.
10. Pouligny B., Sein E., and Lalanne J. R. (1980) Additional contribution, with no critical thermal behavior, to the optical Kerr effect of nematogens in their isotropic phases, *Phys. Rev.* **A24**, 1528–1548.
11. Dunmur D. A., and Tomes A. E. (1981) The pretransitional Kerr effect in 4-*n*-pentyl-4'-cyanobiphenyl, *Mol. Cryst. Liq. Cryst.* **76**, 231 – 240.
12. Zink H., and de Jeu W. H. (1985) A light scattering study of pretransitional behavior around the isotropic – nematic phase transition in alkylcyanobiphenyls, *Mol. Cryst. Liq. Cryst.* **124**, 287 – 304.
13. Rizi V. and Gosh S.K. (1988) Dynamic critical behavior above a strong first order phase transition, *Phys. Lett.* **A129**, 270 – 274.
14. Pyżuk W., Maka E., Skorczyńska R. (1990) Nonlinear Dielectric Effect in isotropic polar mesogens, *Mol. Cryst. Liq. Cryst.* **191**, 327–331.
15. Yi J.-H., Cho Ch.-H., Lee J.-H, and Chang J.-S. (1990) Measurements of induced dipole and permanent strengths in MBBA and EBBA using the DC Kerr effect, *J. Kor. Phys. Soc.* **23**, 7–10.
16. Ryumtsev E. I. and Polushin S. G. (1992) Kerr effect in isotropic liquid phase of monotropic nematogen, *Mol. Cryst. Liq. Cryst.* **212**, 271 – 278.
17. Fuchs J. and Burchard W. (1994) Pretransitional behavior of nematic liquid crystals in the isotropic phase, *J. Physique II* vol. **4**, 1451 – 1456.
18. Usha R., and Prasad Rao T. A. (1995) Electro-Optic Kerr effect relaxation studies in nematic liquid crystal 4-(trans-4'-*n*-pentylcyclohexyl)benzonitrile (PCH5), *J. Phys. Soc. Jpn.* **64**, 4029 – 4035.
19. Schneider L. and Wendorff J. H. (1997) Kerr effect studies on mixtures of liquid crystals, *Liquid Crystals* **22**, 29–36.
20. Blachnik N., Knepe H., Schneider F. (2000) Cotton Mouton constants and pretransitional phenomena in the isotropic liquid crystals, *Liquid Crystals* **27**, 1219 – 1227.
21. de Gennes P. G. (1974) The Physics of Liquid Crystals, *Oxford University Press*, Oxford.
22. Vertogen G. and de Jeu W. H. (1988) Thermotropic Liquid Crystals – Fundamentals, *Springer Series in Chemical Physics*, **45**, Berlin.
23. Anisimov M. A. (1991) Critical Phenomena in Liquids and Liquid Crystals, *Gordon and Breach*, Philadelphia.
24. Chandrasekhar S. (1994) Liquid Crystals, *Cambridge Univ. Press*, Cambridge.
25. Val'kov Yu. A., Romanov. V. P. Shalaginov, A. N. (1994) Fluctuations and light scattering in liquid crystals, *Physics-Uspeski* **37**, 139 – 183.
26. Demus D., Goodby J., Gray G. W., Spiess H. W., Vill V. (1998) Handbook of Liquid Crystals, vol.1 Fundamentals, *Wiley-VCH*, Weinheim.
27. Senbetu L. and Woo C.-W. (1982) Isotropic – nematic transition: Landau – de Gennes vs. Molecular theory, *Mol. Cryst. Liq. Cryst.* **84**, 101 – 124.
28. Mukherjee P. K. (1998) a review article: The $T_{NI} - T^*$ puzzle of the nematic–isotropic phase transition, *J. Phys. Cond. Mat.* **10**, 9191 – 9209.
29. Drozd-Rzoska A., Rzoska S. J. and Ziolo J. (1996) Critical behaviour of dielectric permittivity in the isotropic phase of nematogens, *Phys. Rev.*, **E54**, 6452 – 6456.
30. Drozd-Rzoska A. (1999) Quasicritical behavior of dielectric permittivity in the isotropic phase of *n*-hexyl- cyanobiphenyl in a large range of temperatures and pressures, *Phys. Rev.* **E59**, 5556–5561.

31. Drozd-Rzoska A., Rzoska S. J., Ziolo J. (2000) The fluidlike and critical behavior of the isotropic – nematic transition appearing in linear and nonlinear dielectric studies, *Acta. Phys. Polon.* **98**, 431-437.
32. Żywociński A. (2003) Spinodal temperatures at the nematic to isotropic phase transition from precise volumetric measurements, *J. Chem. Phys.* **B107**, 9491 – 9497.
33. Mukherjee P. K. (1998) Evidence of tricritical behavior at the nematic isotropic transition, *Int. J. Mod. Phys.* **B12**, 1585 – 1599.
34. Marinelli M. and Mercuri F. (2000) Effects of fluctuations in the orientational order parameter in the cyanobiphenyl (nCB) homologous series, *Phys. Rev.* **E61**, 1616-1621.
35. Rzoska S. J. and Drozd Rzoska A. (2002) On the tricritical point of the isotropic – nematic transition in a rod-like mesogen hidden in the negative pressure region, *NATO Sci. Series II*, vol. **84**, p. 116, eds.: A. R. Imre , H. J. Maris and P. R. Williams (Kluwer, Dordrecht).
36. Drozd-Rzoska A. (1998) Influence of measurement frequency on the pretransitional behaviour of non-linear dielectric effect in the isotropic phase of liquid crystalline materials, *Liquid Crystals*, **24**, 835 – 842.
37. Rzoska S. J., Paluch M., Drozd-Rzoska A., Janik P., Ziolo J. and Czupryński K. (2001) Glassy and fluidlike behavior of the isotropic phase of mesogens in broad-band dielectric, *Europ. Phys. Journal* **E7**, 387 -392.
38. Drozd-Rzoska A. and Rzoska S. J. (2002) Complex relaxation in the isotropic phase of n-pentylcyanobiphenyl in linear and nonlinear dielectric studies, *Phys. Rev.* **E65**, 041701.
39. Cang H., Li J., Fayer M. D. (2002) Short time dynamics in the isotropic phase of liquid crystals: the aspect ratio and the power law decay, *Chem. Phys. Lett.* **366**, 82 – 87.
40. Cang H., Li J., Novikov V. N., Fayer M. D. (2003) Dynamical signature of two „ideal glass transitions” in nematic liquid crystals, *J. Chem. Phys.* **119**, 10421 – 10427.
41. Drozd-Rzoska A., Rzoska S. J. and Czupryński K. (2000) Phase transitions from the isotropic liquid to liquid crystalline mesophases studied by “linear” and “nonlinear” static dielectric permittivity, *Phys. Rev.* **E61**, 5355-5360.
42. Górny M. and Rzoska S. J. (2004) Experimental solutions for nonlinear dielectric studies in complex liquids, *this volume*.
43. Urban S., Massalska-Arodz M., Wurflinger A., Dabrowski R. (2003) Pressure-temperature phase diagrams of smectogenic 4'-alkyl-4-cyanobiphenyls (9CB, 10CB, 11CB and 12CB), *Liquid Crystals* **30**, 313–318.

INFLUENCE OF PRESSURE ON THE DIELECTRIC PROPERTIES OF LIQUID CRYSTALS

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Abstract. Results of dielectric studies under elevated pressure of selected liquid crystalline materials are reviewed. The tensor components of the static permittivity of two nematics, 60CB and 8PCH, measured at $p = 1$ atm as a function of temperature, and at $T = \text{constant}$ as a function of external pressure, are compared. They show striking similarities, if the ranges of the nematic phase at the isobaric and isothermal conditions are normalized. The Maier and Meier equations are applied for discussing the observed behaviors. The dielectric relaxation processes in many substances exhibiting the nematic, smectic A, smectic C and smectic (crystalline) E phases were studied in the past in our group. The low frequency relaxation times characterizing the molecular rotations around the short axes were determined at the isothermal, isobaric and isochoric conditions. This allowed us to calculate three activation parameters: activation volume, activation enthalpy and activation energy, which are interrelated. In particular, it was found that the isobaric activation enthalpy is twice as large as the isochoric activation energy, independently of the phase studied. This indicates the role of steric constraints against the molecular rotations around the short axes.

1. Introduction

Pressure studies of a molecular system yield new insight into the relationships between the molecular and macroscopic behavior of the system. It is due to different changes of the physical properties caused by the pressure in respect to that observed usually in the temperature studies alone. In this article we will discuss the dielectric properties (static permittivity and dipolar relaxation process) of selected liquid crystals (LC) studied at atmospheric pressure as a function of temperature, and at constant temperatures as a function of pressure. This allows analyzing the measured quantities at isobaric, isothermal and isochoric conditions. In particular, the components of the dielectric permittivity tensor determined for two nematogens will be discussed. The majority of the results presented in the article concern the low frequency (l. f.) relaxation process characterizing the molecular rotations around the short axes in different LC phases.

Let us begin with a discussion why and in which way the pressure influences the dielectric properties of liquid crystals. In the simplest case of the nematic (N) phase Maier and Saupe [1] have proposed the orientation dependent potential energy of one molecule in the field of its neighbors in the form

$$U(\theta) = -qP_2(\cos\theta). \quad (1)$$

$P_2(\cos\theta)$ is the second rank Legendre polynomial which defines the orientational order parameter

$$S = \langle P_2(\cos\theta) \rangle = \langle (3\cos^2\theta - 1)/2 \rangle, \quad (2)$$

where θ is the angle between the molecular symmetry axis and the director $\mathbf{n}$. The strength parameter q (the nematic potential) is given by

$$q = \upsilon S. \quad (3)$$

The interaction coefficient υ determines the energy scale of the potential and is volume dependent: $\upsilon = \upsilon_0/V^\gamma$. Maier and Saupe assumed that the potential consists of the attractive part only, that is $\gamma = 2$. The exponent γ can be derived from the pressure-volume-temperature (pVT) measurements [2,3]. It was found that $\gamma > 2$ which means that the repulsive interaction part cannot be neglected. In order to perform the averaging $\langle \dots \rangle$ in (2) the interaction potential must be taken into account. This leads, of course, to the pressure (and volume) dependence of S . Figures 1 and 2 show examples of the pressure dependence of the order parameter for two nematics: PAA [4] and 7CB [5b]. (The chemical formulae of the substances considered and the used acronyms are listed in Table 1).

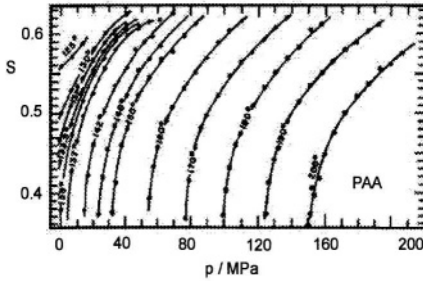


Figure 1. Nematic order parameter S as a function of pressure determined from NMR measurements for PAA (Reproduced from [4] with permission from Elsevier)

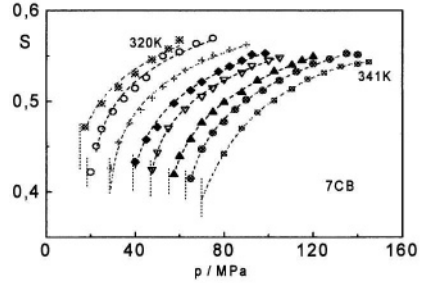


Figure 2. Nematic order parameter S determined from the dielectric relaxation data for 7CB. (Reproduced from [5b] with permission of the PCCP Owner Societies)

2. Static dielectric permittivity in the nematic phase

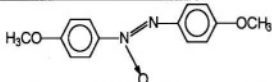
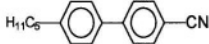
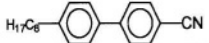
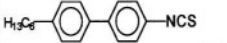
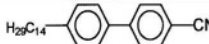
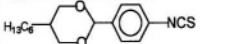
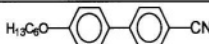
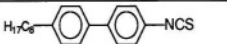
The static dielectric permittivity components of the nematic phase can be analysed with the aid of the Maier and Meier equations [6]

$$(\varepsilon_{||} - 1) = \varepsilon_0^{-1} N \cdot F \cdot h \cdot \left\{ \bar{\alpha} + \frac{2}{3} \Delta\alpha S + F \frac{\mu_{eff}^2}{3kT} [1 - (1 - 3\cos^2\beta)S] \right\} \quad (4)$$

$$(\varepsilon_{\perp} - 1) = \varepsilon_0^{-1} N \cdot F \cdot h \cdot \left\{ \bar{\alpha} - \frac{1}{3} \Delta\alpha S + F \frac{\mu_{eff}^2}{3kT} \left[1 + \frac{1}{2} (1 - 3\cos^2\beta)S \right] \right\}, \quad (5)$$

$$\Delta\epsilon = (\epsilon_{||} - \epsilon_{\perp}) = \epsilon_0^{-1} N \cdot F \cdot h \cdot [\Delta\alpha - F \frac{\mu_{eff}^2}{2kT} (1 - 3 \cos^2 \beta)] S, \quad (6)$$

Table 1. Chemical formulae of the substances considered in the paper and their acronyms

Chemical formula	Acronym	Chemical formula	Acronym
	PAA		5PCH
	5CB		5CCH
	8CB		6BT
	14CB		6DBT
	6OCB		8BT

where μ_{eff} is the effective dipole moment of the molecule which may differ from the molecular moment μ due to the dipole-dipole associations. β is the angle between the dipole moment and the long axis of the molecule. $N = \rho N_A / M$ (ρ - density, N_A - Avogadro's number, M - molar mass), $\Delta\alpha = \alpha_{||} - \alpha_{\perp}$ and $\bar{\alpha} = (\alpha_{||} + 2\alpha_{\perp})/3$ are the polarizability components and the mean polarizability, respectively. The local field parameters h and F are expressed by the mean polarizability $\bar{\alpha}$ and the mean permittivity $\epsilon = (\epsilon_{||} + 2\epsilon_{\perp})/3$: $h = 3\epsilon_s/(2\epsilon_s + 1)$, $F = 1/(1 - f\bar{\alpha})$ with $f = (N/3\epsilon_0)[(2\epsilon_s - 2)/(2\epsilon_s + 1)]$. We deal here with substances having strong dipole group ($-\text{CN}$ or $-\text{NCS}$), and in that case the dielectric anisotropy, eq. (6), may be reduced to

$$\Delta\epsilon \sim S(T)/T \quad \text{at } p = \text{constant} = 1 \text{ atm}, \quad (7)$$

$$\Delta\epsilon \sim S(p) \quad \text{at } T = \text{constant}. \quad (8)$$

Thus, one may expect that the measurements of the static permittivity components can yield the temperature and pressure dependencies of the order parameter in the N phase. Figures 3 and 4 show the results of studies of two nematogens, 6OCB [7] and 8PCH [8], at $p = 1$ atm and at $T = \text{constant}$. The data measured at both conditions were normalized to the ranges of the phase observed as is shown in the insets. As can be seen, the permittivity components coincide excellently within the N phase. Using relations (7) and (8) the temperature and pressure dependencies of the order parameter S can be determined. Taking into account the arguments quoted in [5] the order parameter S can be expressed as

$$\begin{aligned} S(T) = 0,317(T_{NI} - T)^{0.196} \quad \text{and} \quad S(p) = 0,313(p - p_{NI})^{0.192} \quad \text{for 6OCB} \\ S(T) = 0,369(T_{NI} - T)^{0.172} \quad \text{and} \quad S(p) = 0,319(p - p_{NI})^{0.160} \quad \text{for 8PCH.} \end{aligned}$$

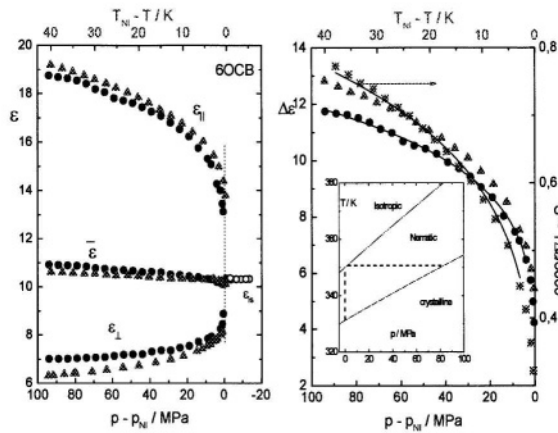


Figure 3. Permittivity components (left) and the dielectric anisotropy (right) of 6OCB obtained from the measurements at $p = 1$ atm (triangles) and $T = \text{constant} = 350.1$ K (circles) [7]. The inset shows part of the phase diagram with dashed lines indicating the isobar and isotherm at which the measurements were done.

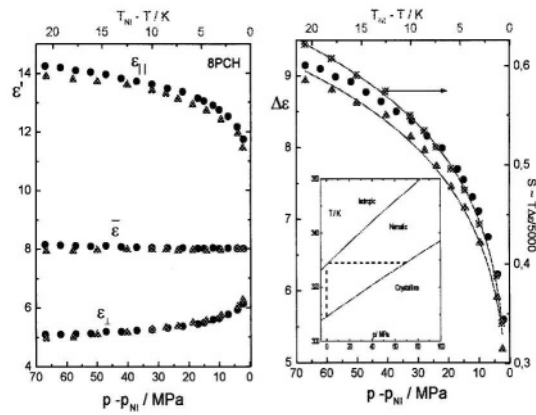


Figure 4. Permittivity components (left) and the dielectric anisotropy (right) of 8PCH obtained from the measurements at $p = 1$ atm and $T = \text{constant} = 332.8$ K. The inset shows part of the phase diagram with dashed lines indicating the isobar and isotherm at which the measurements were done. (Reproduced from [8] by permission of the Taylor & Francis).

3. Dielectric relaxation in LC phases

The l. f. relaxation process falls on the megahertz frequency range and thus is easily measured by standard impedance analyzers. In the N phase the parallel orientation of the

sample with respect to the measuring field is applied. However, in the smectic phases such orientation is hardly achieved and usually the relaxation spectra are collected for unoriented samples. Notwithstanding, all spectra corresponding to the l. f. process in different phases could be described by the Cole-Cole equation,

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{(1 + i\omega\tau)^\alpha} \quad (9)$$

with the distribution parameter α close to zero. The main quantity derived from the spectra is the relaxation time $\tau_\parallel$. According to the theories of the l. f. relaxation process [9,10] the relaxation time

$$\tau_\parallel \sim qS \sim S/V^\gamma$$

and thus must be strongly pressure (and volume) dependent. Figure 5 shows the comparison of the absorption spectra measured at isobaric and isothermal conditions for 6BT in the SmE phase [11]. A full equivalence of the spectra changes in the frequency scale caused by the temperature and pressure is clearly seen from Figure 5. The Figure shows similar plots as a function of frequency both for the temperature or pressure variation. In fact, $\tau_\parallel = 1/(2\pi f_{\max})$ exhibits an exponential dependence on p which is well seen in the $\ln\tau_\parallel$ vs. p plots – compare Figure 6 [12].

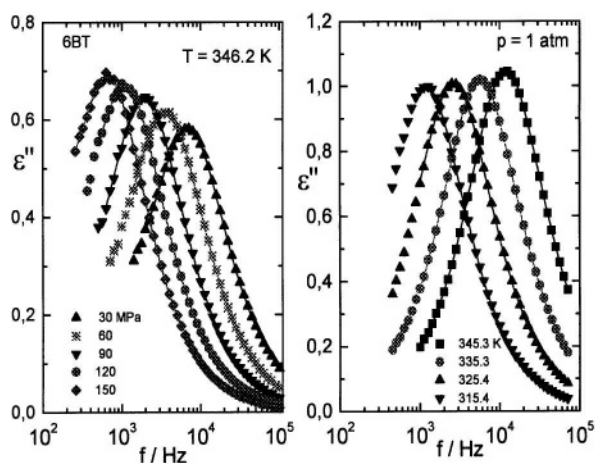


Figure 5. Dielectric loss spectra collected in the SmE phase of 6BT at constant temperature and different pressures (left), and at constant pressure and different temperatures (right). The lines are fits of the Debye equation.

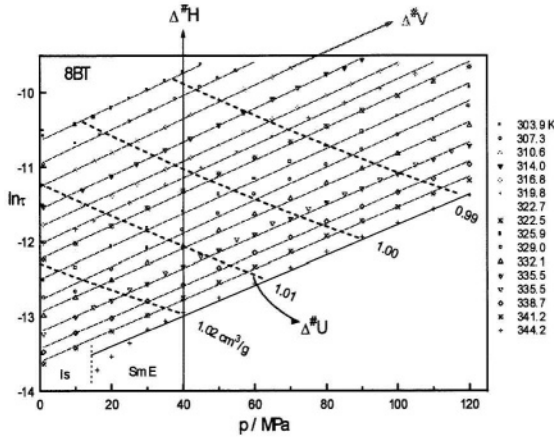


Figure 6. $\ln \tau$ vs. p plots for several isotherms in the SmE phase of 8BT. The way of calculations of the activation parameters are shown (compare equations (10) - (12)). (Reproduced from [12] by permission of the Taylor & Francis).

Having additionally the pVT data for a given substance one can derive the three relaxation quantities:

$$\text{activation volume} \quad \Delta^\#V = RT(\partial \ln \tau / \partial p)_T \quad (10)$$

$$\text{activation enthalpy} \quad \Delta^\#H = R(\partial \ln \tau / \partial T^{-1})_p \quad (11)$$

$$\text{activation energy} \quad \Delta^\#U = R(\partial \ln \tau / \partial T^{-1})_V \quad (12)$$

All activation quantities are interrelated: $\Delta^\#H = \Delta^\#U + T(\partial p / \partial T)_V \Delta^\#V$.

The activation volume can be considered as the extra volume the molecule must have in order to perform the rotational jump over the potential barrier. The energy barrier arises from the anisotropy of molecular interactions and is constrained by the thermal and steric factors. The steric effects do not affect the activation energy as this is calculated from the data obtained at constant volume (density). Thus, one may expect that $\Delta^\#H > \Delta^\#U$.

Let us consider the activation quantities characterizing the molecular rotations around the short axes in different LC phases [2,3,11-19]. Figures 7–10 present the activation volume (a) and activation enthalpy and energy (b) for several two-ring compounds studied recently by us.

4. Summary

The characteristic features of the results can be summarized as follows.

- The dielectric anisotropy normalized to the range of the nematic phase at $p = \text{constant}$ and $T = \text{constant}$ shows very similar behavior (Figures 3 and 4).
- The low frequency relaxation time $\tau_{||}$ changes exponentially with the pressure (Figure 6).

– The activation parameters increase with increasing flexibility of the molecular cores (Figure 7a).

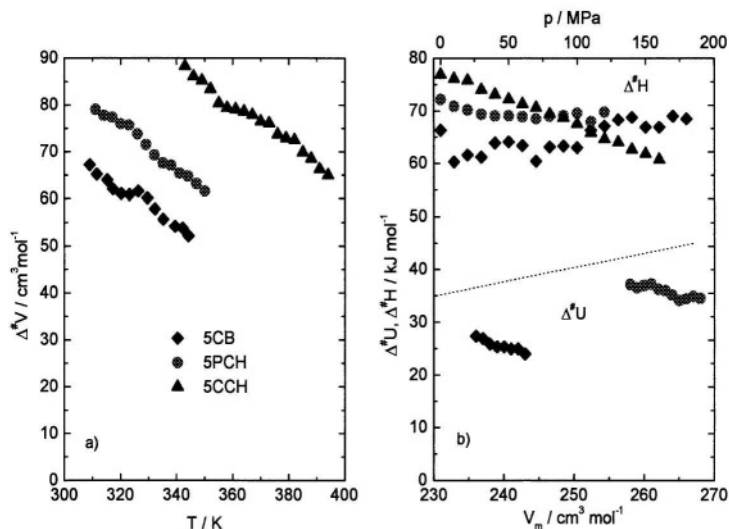


Figure 7. Activation parameters obtained for the nematic phase of three compounds with different molecular cores (compare Table 1).

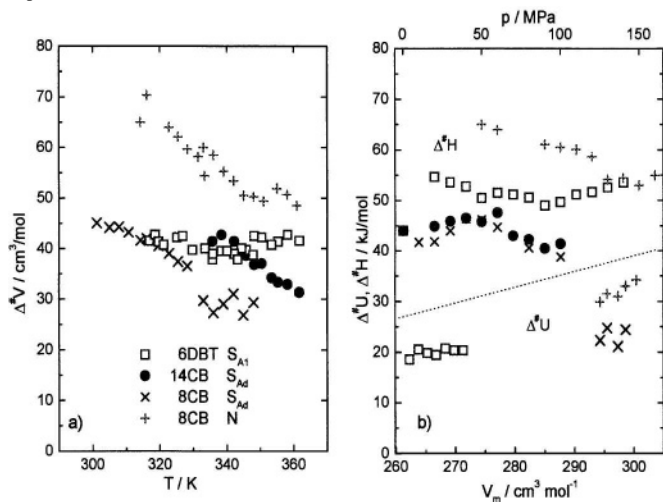


Figure 8. Activation parameters obtained for three compounds in the smectic A phase of and for 8CB in the N phase. (Reproduced from [19] by permission of the Taylor & Francis).

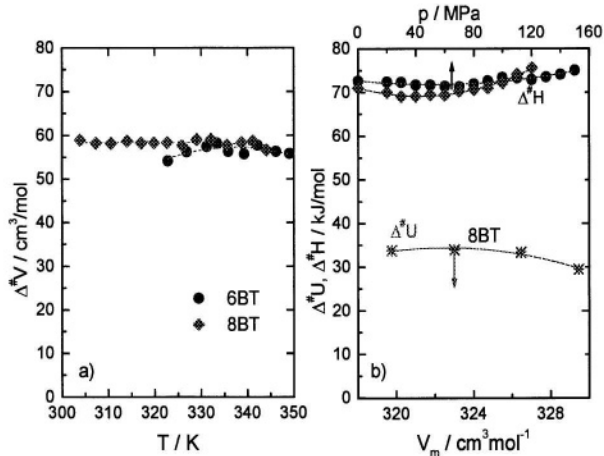


Figure 9. Activation parameters for the SmE phase of two substances, 6BT and 8BT [3,11].

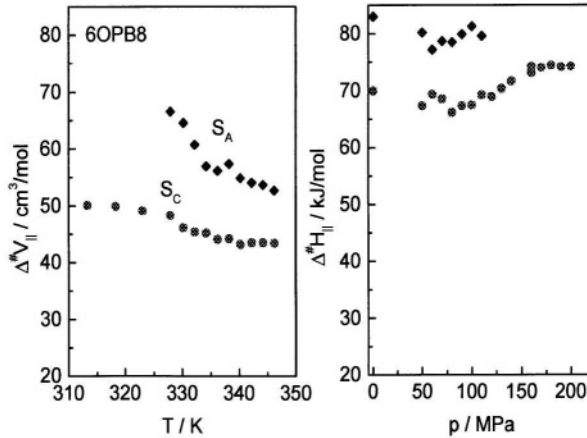


Figure 10. Activation parameters for the SmA and SmC phases of 6OPB8 [20] (the pVT data are not available for this substance).

- The activation volume consists of *c.* 20 – 25% of the molar volume (Figures 7 – 9).
- The isochoric activation energy is about two times smaller than the isobaric activation enthalpy in three tested LC phases (N, S_A and S_E) indicating an equivalency of the thermal and steric constraints for molecular rotations around the short axes (Figures 7b – 9b).

– The barriers hindering the flip-flop molecular rotations in the liquid-like and crystal-like phases of similar substances are close in spite of the fact that the molecular rates differ considerably – see Figure 11.

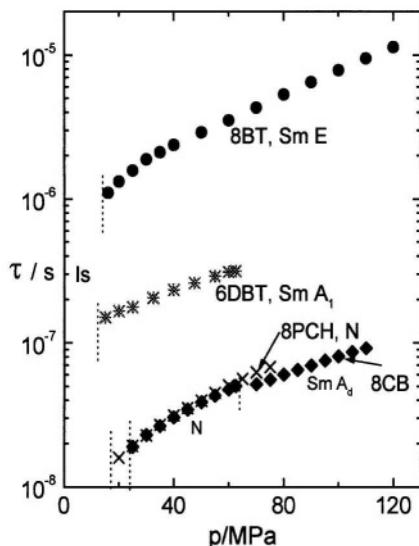


Figure 11. Comparison of the pressure dependence of the 1. f. relaxation times (in logarithmic scale) determined for similar substances in different LC phases. The vertical dotted lines mark the transition pressures. (Reproduced from [12] by permission of the Taylor & Francis).

- Activation parameters in the S_A phase do not depend on the alkyl chain length (compare values for 8CB and 14CB in Figure 8).
- Activation parameters in the S_A phase are smaller than in the N phase (Figure 8).
- Energy barriers for flip-flop molecular rotations are close in the liquid-like and crystal-like phases of similar substances. That might indicate that the barrier is mainly created by the side-side interactions.
- The activation volume and enthalpy determined for the tilted S_C phase are smaller than those obtained for the orthogonal S_A phase (Figure 10).

5. Acknowledgement

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6. References

1. Maier, W. and Saupe, A. (1959) Eine einfache molekulare-statistische Theorie der nematischen kristallenflüssigen Phase. Teil I *Z. Naturforsch.* **14a**, 982-988 (1960) Teil II, *ibid.*, **15a**, 287-292.
2. Urban, S. and Würflinger, A. (1997) Dielectric properties of liquid crystals under high pressure, *Adv. Chem. Phys.* **98**, 143-216.
3. Würflinger, A. and Urban, S. (2002) PVT measurements on 8BT at elevated pressures", *Liq. Cryst.*, **29**, 799-804 (2002).
4. McColl, J. R. (1972) Effect of pressure on order in the nematic liquid crystal p-azoxyanizole, *Phys. Lett.* **38A**, 55-57.
5. Urban, S., Gestblom, B., and A. Würflinger, (1999) On the derivation of the nematic order parameter from the dielectric relaxation times", *Phys. Chem. Chem. Phys.*, **1**, 2787- 2791; b) Urban, S., Gestblom, B., Kuczyński, W., Pawlus, S., and A. Würflinger (2003) Nematic order parameter as determined from dielectric relaxation data and other methods, *Phys. Chem. Chem. Phys.* **5**, 924-928.
6. Maier, W. and Meier, G. (1961) Eine einfache Theorie der dielektrischen Eigenschaften homogen orientierter kristallenflüssiger Phasen des nematischen Typs, *Z. Naturforsch.* **16a**, 262-267.
7. Urban, S. (1999) Dielectric studies of 6OCB at elevated pressure, *Z. Naturforsch.* **54a**, 365-369.
8. Urban, S. and Würflinger, A. (2000) Dielectric anisotropy of 8PCH as functions of temperature and pressure, *Liquid Crystals* **27**, 1119-1122.
9. Martin, A. J., Meier, G., and Saupe, A. (1971) Extended Debye theory for dielectric relaxations in nematic liquid crystals, *Symp. Faraday Soc.* **5**, 119-133.
10. Coffey, W. T. and Kalmykov, Yu. P. (2000) Rotational diffusion and dielectric relaxation in nematic liquid crystals, *Adv. Chem. Phys.* **113**, 487-451.
11. Urban, S. and Würflinger, A. (2000) Phase diagram and dielectric relaxation studies of 6BT in the smectic E phase under high pressure", *Z. Naturforsch.* **57a**, 233-236.
12. Urban, S., Würflinger, A. and Kocot, A. (2001) Phase diagram and dielectric relaxation studies of 8BT in the crystalline E phase under high pressure, *Liquid Crystals* **28**, 1331 -1336.
13. Brückert, T. and Würflinger, A. (1996) Dielectric studies of trans,trans-4'-n-pentyl-bicuclohexyl-4-carbonitrile (5CCH) under high pressure, *Z. Naturforsch.* **51a**, 306-312.
14. Urban, S., Würflinger, A., Büsing, D., Brückert, T., Sandmann, M., and Gestblom, B. (1998) Volumetric and dielectric studies of 5CB under high pressure, *Polish J. Chem.* **72**, 241-250.
15. Markwick, P., Urban, S., and Würflinger, A. (1999) Dielectric studies in the isotropic, nematic and smectic A phases of 8CB under high pressure, *Z. Naturforsch.* **54a**, 275-278.
16. Urban, S. and Würflinger, A. (1999) High pressure dielectric studies of a substance with the smectic A₁ phase, *Z. Naturforsch.* **54a**, 455-458.
17. Würflinger, A. and Urban, S. (2001) Thermodynamic measurements on three nDBTs (6DBT, 8DBT, 10DBT) at elevated pressures, *Phys. Chem. Chem. Phys.* **3**, 3727-3731.
18. Urban, S., Gestblom, B., and Dąbrowski, R. (2002) Retardation of molecular rotations around the short axes at the transition from the isotropic to different liquid crystalline phases, *Polish J. Chem.* **76**, 263-271.
19. Urban, S., Gestblom, B., Würflinger, A., and Dąbrowski, R. (2003) Phase diagram and dielectric relaxation studies of 14CB in the isotropic and smectic A phase at atmospheric and high pressures, *Liquid Crystals* **30**, 305-311.
20. Czub, J., Pawlus, S., Sekula, M., Urban, S., Würflinger, A., and Dąbrowski, R. (2003) DTA and dielectric studies of a substance with the nematic, Smectic A and Smectic C polymorphism at ambient and elevated pressures, *Z. Naturforsch.* **58a**, 333-340.

FREQUENCY-DOMAIN NONLINEAR DIELECTRIC RELAXATION SPECTROSCOPY

Its application to ferroelectric liquid crystals

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1. Introduction

Dielectric relaxation spectroscopy is one of the useful methods to study dynamics of material. Owing to recent instrumental development and advances in measurement technique, it is possible to obtain the dispersion of dielectric permittivity in a wide frequency range from μHz to near THz [1]. There are no other methods to cover such wide frequency range or time-scale than dielectric relaxation spectroscopy. But this method is only restricted to linear regime until recently. If the studied system responds to a sinusoidal electric field with angular frequency of ω_0 in nonlinear fashion, the induced electric displacement becomes sum of the fundamental and higher harmonic components of ω_0 . These higher harmonic components are neglected in conventional dielectric measurement. But they are expected to offer rich information on the dynamics of the studied system. As response to external field becomes easily nonlinear in soft condensed matters such as liquid crystals and polymers, we can obtain more detailed information on their dynamics than that obtained by linear spectrum only.

From the theoretical point of view, nonlinear response of a general relaxation system has been discussed phenomenologically by extending linear response theory [2, 3]. But nonlinear dielectric spectrum has been scarcely studied experimentally until recently. In this contribution, we discuss experimental method of nonlinear dielectric relaxation spectroscopy (NDRS) in frequency domain and demonstrate its usefulness by applying it to ferroelectric liquid crystals.

2. Theory of Nonlinear dielectric response in ferroelectric liquid crystals

Ferroelectric liquid crystals (FLCs) have attracted much attention of researchers from fundamental and technological points of view since the discovery of ferroelectricity

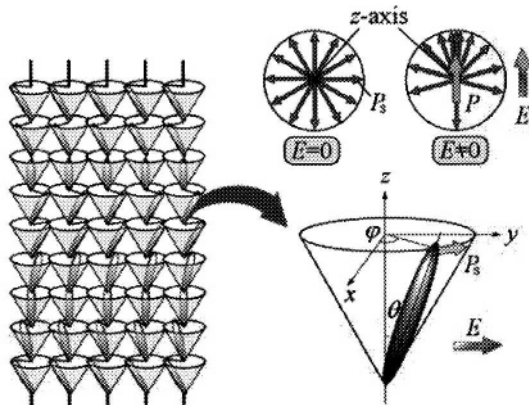


Figure 1. Schematic view of molecular alignment of FLCs in the Sm-C* phase and definition of coordinate.

in the smectic C phase consist of chiral molecules (Sm-C*) [4, 5]. In the Sm-C* phase, molecules form layered structure and tilt from the layer normal. Due to the chirality of molecules, the direction of tilt rotates along the layer normal and they form helical structure shown in Fig. 1. The spontaneous polarization P_s lies in layer plane and is perpendicular to the long axis of molecules (director).

In the low frequency region, there are two collective fluctuation of directors in the Sm-C* phase and we can observe these modes by dielectric spectroscopy [4, 5]. One is the soft (amplitude) mode, which is the fluctuation in the magnitude of the tilt angle. The other is Goldstone (phase) mode, which is the fluctuation in the azimuthal angle of the director around the helical axis. As dielectric increment and relaxation time of Goldstone mode is usually large, this mode is predominant in the dielectric response of the Sm-C* phase except at the vicinity of the SmA-Sm-C* phase transition temperature. We discuss linear and nonlinear dielectric response of Goldstone mode in the following part of this section.

In the absence of an electric field, the distribution of P_s is homogenous around helical axis and the macroscopic polarization is cancelled as a whole system. Under an electric field E , P_s tends to align parallel to E due to ferroelectric coupling between P_s and E . The macroscopic polarization P is given by special average $\langle P_s \cos \varphi \rangle$, where φ is the azimuthal angle of director shown in Fig. 1. The dynamics of $\varphi(z, t)$ around helical axis (taken as z -axis) under the electric field E applied parallel to y -axis can be discussed by a simple torque balance equation [5]:

$$K \frac{\partial^2 \varphi(z, t)}{\partial z^2} - \gamma \frac{\partial \varphi(z, t)}{\partial t} = P_s E \sin \varphi(z, t), \quad (1)$$

where K is the torsional elastic constant, γ is the rotational viscosity. In this model, the tilt angle is assumed to be independent of E .

If the applied electric field is small, the solution φ can be written as a perturbed form to the solution representing uniform helical structure. Its field- induced part can be

written as power series of E as

$$\varphi(z, t) = q_0 z + \sum_{k=1}^{\infty} \phi_k(z, t), \quad (2)$$

where q_0 is the wavenumber of helical structure and the term ϕ_k is proportional to E^k ($k=1, 2, \dots$). By using Eq. (2), Eq. (1) can be decomposed to a set of infinite equations given as

$$K \frac{\partial^2 \phi_1}{\partial z^2} - \gamma \frac{\partial \phi_1}{\partial t} = P_s E \sin(q_0 z), \quad (3)$$

$$K \frac{\partial^2 \phi_2}{\partial z^2} - \gamma \frac{\partial \phi_2}{\partial t} = P_s E \phi_1 \cos(q_0 z), \quad (4)$$

$$K \frac{\partial^2 \phi_3}{\partial z^2} - \gamma \frac{\partial \phi_3}{\partial t} = P_s E \left(-\frac{1}{2} \phi_1^2 \sin(q_0 z) + \phi_2 \cos(q_0 z) \right), \quad \dots \quad (5)$$

By solving these equations, we have

$$\phi_1(z, t) = C_{11} \sin(q_0 z), \quad (6)$$

$$\phi_2(z, t) = C_{22} \sin(2q_0 z), \quad (7)$$

$$\phi_3(z, t) = C_{31} \sin(q_0 z) + C_{33} \sin(3q_0 z), \quad (8)$$

where

$$C_{11} = -\frac{P_s}{\gamma} \int_{-\infty}^t dt_1 E(t_1) e^{-(t-t_1)/\tau}, \quad (9)$$

$$C_{22} = -\frac{P_s^2}{2\gamma^2} \int_{-\infty}^t dt_2 \int_{-\infty}^{t_2} dt_1 E(t_1) E(t_2) e^{-(4t-t_1-3t_2)/\tau}, \quad (10)$$

$$C_{31} = \frac{P_s^3}{8\gamma^3} \left[3 \int_{-\infty}^t dt_3 \int_{-\infty}^{t_3} dt_2 \int_{-\infty}^{t_2} dt_1 E(t_1) E(t_2) E(t_3) e^{-(t-t_1-t_2+t_3)/\tau} \right. \\ \left. - 2 \int_{-\infty}^t dt_3 \int_{-\infty}^{t_3} dt_2 \int_{-\infty}^{t_2} dt_1 E(t_1) E(t_2) E(t_3) e^{-(t-t_1-3t_2+3t_3)/\tau} \right], \quad (11)$$

$$C_{33} = -\frac{P_s^3}{8\gamma^3} \left[\int_{-\infty}^t dt_3 \int_{-\infty}^{t_3} dt_2 \int_{-\infty}^{t_2} dt_1 E(t_1) E(t_2) E(t_3) e^{-(9t-t_1-t_2-7t_3)/\tau} \right. \\ \left. - 2 \int_{-\infty}^t dt_3 \int_{-\infty}^{t_3} dt_2 \int_{-\infty}^{t_2} dt_1 E(t_1) E(t_2) E(t_3) e^{-(9t-t_1-3t_2-5t_3)/\tau} \right], \quad (12)$$

and τ is the relaxation time of linear response defined as $\tau = \gamma / K q_0^2$.

The induced polarization P is given by averaging $P_s \cos \varphi$ over one helical pitch,

$$P = P_s \langle \cos \varphi \rangle = P_s \left\{ -\frac{C_{11}}{2} + \left(-\frac{C_{11}C_{22}}{4} - \frac{C_{31}}{2} + \frac{C_{11}^3}{16} \right) + \dots \right\}. \quad (13)$$

In Eq. (13), the term proportional to E , named P_1 , is given as

$$P_1 = \frac{P_s^2}{2\gamma} \int_{-\infty}^t dt_1 E(t_1) e^{-(t-t_1)/\tau} \quad (14)$$

The term proportional to E^2 , named P_2 , vanishes due to the symmetry of the system to electric field ($P_2=0$). The term proportional to E^3 , named P_3 , is sum of four terms. Each term is given by a multi-convolution of electric field and exponentially decay functions,

$$P_3 = -\frac{P_s^4}{16\gamma^3} \left[\left\{ 3 \int_{-\infty}^t dt_3 \int_{-\infty}^{t_3} dt_2 \int_{-\infty}^{t_2} dt_1 e^{-(t-t_1-t_2-t_3)/\tau} + \int_{-\infty}^t dt_3 \int_{-\infty}^{t_3} dt_2 \int_{-\infty}^{t_2} dt_1 e^{-(3t-t_1-t_2-t_3)/\tau} \right. \right. \\ \left. \left. - 2 \int_{-\infty}^t dt_3 \int_{-\infty}^{t_3} dt_2 \int_{-\infty}^{t_2} dt_1 e^{-(5t-t_1-3t_2-t_3)/\tau} - 2 \int_{-\infty}^t dt_3 \int_{-\infty}^{t_3} dt_2 \int_{-\infty}^{t_2} dt_1 e^{-(t-t_1-3t_2+3t_3)/\tau} \right\} E(t_1)E(t_2)E(t_3) \right]. \quad (15)$$

Under a sinusoidal electric field with an amplitude E_0 and an angular frequency ω , $E(t)=E_0\cos(\omega t)$, the obtained electric displacement $D(t)$ becomes sum of the fundamental and higher-harmonic components of ω , which are written as power series of E_0 as

$$D(t) = 2 \sum_{n=1}^{\infty} \text{Re} \left[D_n^* e^{in\omega t} \right] = 2 \sum_{n=1}^{\infty} \sum_{m=0}^{\infty} \text{Re} \left[\varepsilon_{n,n+2m}^* e^{in\omega t} \right] (E_0/2)^{n+2m} \quad (16)$$

When E_0 is small, the contribution from the term proportional to E_0^n is dominant in respective harmonic component D_n^* . Therefore, we can experimentally obtain nonlinear dielectric permittivity $\varepsilon_n^* \equiv \varepsilon_{nn}^*$ from the applied field E_0 dependence of D_n^* as [6]

$$\varepsilon_n^* = \lim_{E_0 \rightarrow 0} D_n^* / E_0^n \cdot 2^{n-1} \equiv \varepsilon_n' - i\varepsilon_n'' \quad (17)$$

From Eqs. (14)-(17), the linear ε_1^* and the third-order nonlinear dielectric spectrum ε_3^* are respectively obtained [7-9] as

$$\varepsilon_1^* = \frac{P_s^2}{2Kq_0^2} \frac{1}{1+i\omega\tau}, \quad (18)$$

$$\varepsilon_3^* = -\frac{3P_s^4}{16(Kq_0^2)^3} \frac{1+5i\omega\tau/3-\omega^2\tau^2/3}{(1+i\omega\tau)^3(1+i\omega\tau/2)(1+3i\omega\tau)}. \quad (19)$$

The linear spectrum is given as a Debye-type relaxation spectrum (Fig. 2a). Even-order nonlinear spectrum will vanish due to the symmetry of polarization in our system. The third-order nonlinear spectrum shows a complicated profile shown in Fig. 2b. The higher-order nonlinear spectra show more complicated profile, but they are determined by a single characteristic time τ of linear spectrum. This indicates that

nonlinear response of Goldstone mode is higher-order effect to linear response. The sign of increment of ϵ_3^* is negative and this relates that the origin of this nonlinear response is the saturation of orientation of P_s under electric field. Such effect has been already studied experimentally for a model system of freely rotatable dipole-moments and its increment of ϵ_3^* also shows negative value [10].

According to the phenomenological theory of nonlinear response, nonlinear permittivity is given by a multi-Fourier transform of multi-time after-effect function. If the multi-time after-effect function is given by product of exponentially decay function of time, the n th-order nonlinear dielectric spectrum ϵ_n^* becomes product of Debye-type relaxation by n -times. The best-fitted curve of this extended Debye-type spectrum to Eq. (19) where relaxation time τ_3 is regarded as a fitting parameter ($\tau_3=1.53\tau$) is drawn as a broken line in Fig. 2b. If the distribution of τ_3 is considered by introducing Cole-Cole parameter β_3 [10,11] as

$$\epsilon_3^* = \frac{\Delta\epsilon_3}{[1 + (i\omega\tau_3)^{\beta_3}]^3}, \quad (20)$$

the agreement between Eqs. (19) and (20) is much better as is plotted in a dotted line in Fig. 2b with $\tau_3=1.51\tau$ and $\beta_3=0.97$.

3. Experimental

A sinusoidal electric field generated from a synthesizer (HP33120A) in the frequency range from 5Hz to 650kHz was applied to a sample after passing through a low-pass filter (NF3628) to reduce its harmonic distortion. The electric displacement $D(t)$ detected by a charge amplifier was digitized, averaged and

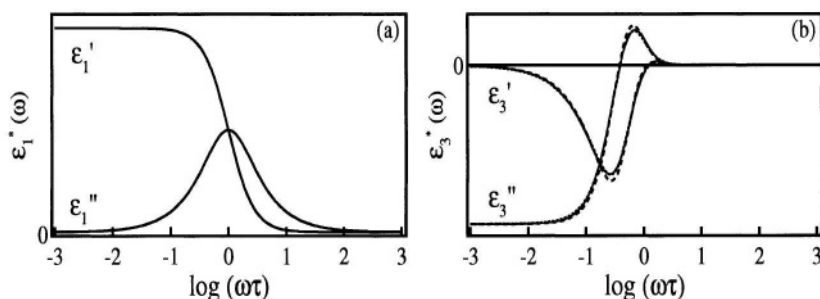


Figure 2 Frequency dispersion of (a) the linear ϵ_1^* and (b) the third-order nonlinear spectrum ϵ_3^* for Goldstone mode of FLCs. The broken and dotted lines are the best-fitted curves of Eq. (20) to Eq. (19) with $(\tau_3, \beta_3)=(1.53\tau, 1)$ and $(1.51\tau, 0.97)$.

transformed into complex data D_n^* on a vector signal analyzer (HP89410A). An advantage of the nonlinear dielectric measurement in frequency- domain is that small nonlinear response can be separated from large linear response by the frequencies where

they appear. In our system, we can detect harmonic distortion as small as 0.01% to fundamental response. This makes it possible to reduce the magnitude of applied electric field considerably.

The FLC used in this study is a commercially available mixture named CS1017 provided by Chisso Co. (Japan). A cell we used is so-called sandwich-type one made of two glass plates with indium thin oxide (ITO) electrodes. The surfaces of the cell are spin-coated with polyimide and rubbed unidirectionally to attain homogenous alignment of molecules. The thickness of a cell is determined by the measurement of capacitance of the empty cell and is about 20 μ m. The cell was set up in a holder whose temperature was monitored by a Pt-sensor and controlled within ± 0.02 K by a temperature controller (model 340).

4. Experimental results [9]

We have measured the dependence of complex amplitude of the fundamental, second-order and third-order harmonic components of $D(t)$, D_1^* , D_2^* and D_3^* on the applied electric field E_0 . When E_0 is small, it is expected that D_1^* and D_3^* have linear relations to E_0 and E_0^3 respectively. As shown in Fig. 3, D_1^* and D_3^* are respectively proportional to E_0 and E_0^3 . D_2^* is negligibly small compared to D_3^* within the range of E_0 we used. These findings make agreement with theoretical results discussed in section 2.

We can obtain the linear ϵ_1^* and the third-order nonlinear dielectric spectrum ϵ_3^* from the slopes of best-fitted lines in Fig. 3. The obtained frequency dispersion of ϵ_1^* and ϵ_3^* are shown in Fig. 4. The linear spectrum ϵ_1^* shows two relaxations of Debye-type at about 300Hz and 650kHz. The relaxation in the higher frequency region (HF relaxation) is insensitive to change of temperature and we regard this relaxation as an apparent one due to the series circuit made up of the resistance of ITO electrodes and the capacitance of liquid crystals at high frequencies. The

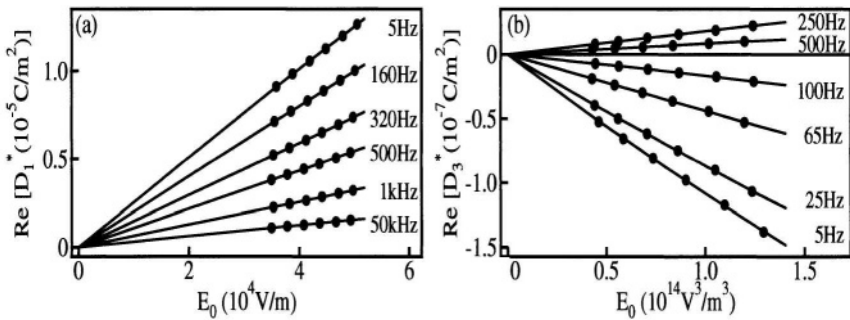


Figure 3. Dependence of (a) the fundamental D_1 and (b) the third-order harmonic component D_3 on the applied electric field E_0 at various frequencies.

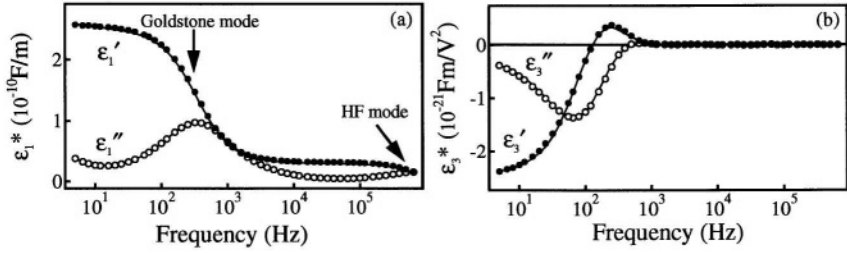


Figure 4. Frequency dispersion of (a) the linear ϵ_1^* and (b) the third-order nonlinear spectrum ϵ_3^* .

relaxation in the lower frequency region is due to the ferroelectric Goldstone mode and its spectrum is well ascribable by the modified form of Eq. (18) as

$$\epsilon_1^* = \epsilon_\infty + \frac{\Delta\epsilon_1}{1 + (i\omega\tau_1)^{\beta_1}} + \frac{C_1}{(i\omega)^{\eta_1}}, \quad (21)$$

where ϵ_∞ is the permittivity at sufficiently high frequencies, $\Delta\epsilon_1$ is the linear dielectric increment, τ_1 is the linear relaxation time and β_1 is the Cole-Cole parameter representing the broadness of relaxation times. For the better fitting of the data at low frequencies, we add the last term on the right-hand side of Eq. (21), which represents the effect of conductivity and electrode polarization. The best-fitted curve to data in which the influence of HF relaxation is introduced to Eq. (21) with $\epsilon_\infty = 2.9 \times 10^{-11}$ F/m, $\Delta\epsilon_1 = 2.2 \times 10^{-10}$ F/m, $\tau_1 = 0.47$ ms and $\beta_1 = 0.91$ is drawn as a solid line in Fig. 4a.

The third-order nonlinear spectrum ϵ_3^* shows a single relaxation and has negative increment shown as Fig. 4b. Its profile can be well ascribable by the modified form of Eq. (19) as

$$\epsilon_3^* = \frac{\Delta\epsilon_3 \{3 + 5(i\omega\tau_3)^{\beta_3} + (i\omega\tau_3)^{2\beta_3}\}}{\{1 + (i\omega\tau_3)^{\beta_3}\}^3 \{1 + (i\omega\tau_3)^{\beta_3}/2\} \{1 + 3(i\omega\tau_3)^{\beta_3}\}} + \frac{C_3}{(i\omega)^{\eta_3}}, \quad (22)$$

where $\Delta\epsilon_3$, τ_3 and β_3 are respectively the third-order nonlinear dielectric increment, relaxation time and Cole-Cole parameter. The second term on the right-hand side of Eq. (22) is necessary to fit the experimental data at low frequencies better. The best-fitted curve of Eq. (22) with $\Delta\epsilon_3 = -4.9 \times 10^{-21}$ F/m, $\tau_3 = 0.49$ ms and $\beta_3 = 0.89$ is drawn as a solid line in Fig. 4b.

5. Discussions

The magnitude of ϵ_3^* is as large as 10^{-21} Fm/V² and is extremely large compared with those of other soft condensed matters listed in TABLE 1. The sing of increment

TABLE 1. A comparison of the third-order nonlinear permittivity ϵ_3 for various kinds of soft condensed

Category	Materials	ϵ_3 (Fm/V ²)	Ref.
Ferroelectric polymers (ferroelectric phase)	Polyvinylidene fluoride (poled)	$+7.6 \times 10^{-27}$	6
	Copolymer of vinylidene fluoride and trifluoroethylene (65:35 poled)	$< 2.5 \times 10^{-25}$	12
Polar polymers (primary dispersion)	Polyvinylacetate	-2.2×10^{-28}	10
	Copolymer of vinylidene cyanide and vinylacetate	-2.0×10^{-25}	11
Liquid crystals (near N-I transition) (ferroelectric liquid crystals)	5CB	$+2.0 \times 10^{-25}$	13
	DOBAMBC	-3.8×10^{-22}	14
	DOBA-1-MPC	-3.7×10^{-20}	14

matter.

depends on the origin of nonlinear response. In the case of ferroelectric polymer in ferroelectric phase [6,12], the origin of nonlinear response is strong ferroelectric interaction between dipoles and ϵ_3^* is positive. In the case of polar polymers [10,11], the origin of nonlinear response is the saturation of arrangement of dipoles and its sign is negative. Its magnitude depends on the magnitude of dipole-moment for a motional unit. In the case of nematic liquid crystals in the isotropic phase near nematic phase [13], large nonlinear permittivity is observe due to the fluctuation of order parameter. As mentioned before, nonlinear response of Goldstone mode is also originated from similar mechanism to polar polymers and its large value is due to cooperative motion of P_S over helical structure with pitch of a few μm .

Temperature dependence of the best-fitted values of $\Delta\epsilon_i$, τ_i and β_i ($i=1,3$) are shown in Fig. 5. The increment $\Delta\epsilon_1$ shows a small peak just below the SmA-SmC* phase transition temperature (T_C) and almost constant value in the SmC* phase. The

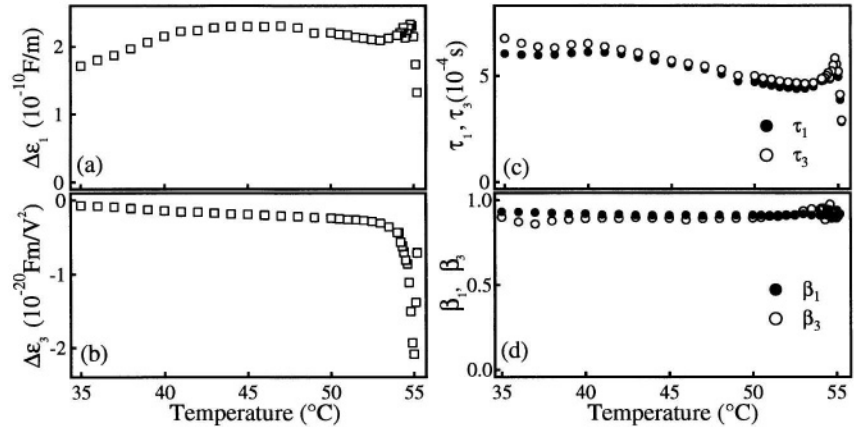


Figure 5. Temperature dependence of the best-fitted parameters (a) $\Delta\epsilon_1$, (b) $\Delta\epsilon_3$, (c) τ_1 and τ_3 , (d) β_1 and β_3 .

magnitude of $\Delta\epsilon_3$ shows a sharp peak near T_C and decreases on cooling in the SmC* phase. As $\Delta\epsilon_3$ is proportional to $-(P_s/\theta)^4/(\theta^2 q_0^6)$ from Eq. (19) and the values of P_s/θ and q_0 are finite ones at T_C [4, 5], $\Delta\epsilon_3$ is expected to diverge with a negative sign at T_C . But the nonlinear response due to soft mode is also expected to diverge with positive sign at T_C in the SmC* phase. Since the relaxation frequency of soft mode approaches to that of Goldstone mode in this temperature region, we cannot separate the contribution of Goldstone mode from the observed nonlinear response. This is the possible reason why $\Delta\epsilon_3$ decreases at the vicinity of T_C . The relaxation times τ_1 and τ_3 take almost same values and the Cole-Cole parameter β_1 and β_3 also make good agreement with each other. Therefore, we can confirm the theoretical prediction that the profile of nonlinear spectrum is determined by the relaxation time of linear spectrum.

We would like to discuss the application of nonlinear dielectric spectroscopy to the simultaneous measurement of material constants of FLCs. By combining Eqs. (18), (19) and $\tau = \gamma/Kq_0^2$, we can calculate P_s , γ and Kq_0^2 from the best-fitted values of $\Delta\epsilon_1$, τ_1 and $\Delta\epsilon_3$ as,

$$P_s = \left(-\frac{3\Delta\epsilon_1^3}{2\Delta\epsilon_3} \right)^{1/2}, \quad (23)$$

$$\gamma = -\frac{3\Delta\epsilon_1^2 \tau F}{4\Delta\epsilon_3 E}, \quad (24)$$

$$Kq_0^2 = -\frac{3\Delta\epsilon_1^2 F}{4\Delta\epsilon_3 E}. \quad (25)$$

In Eqs. (24) and (25), we regard the local field F as the electric field working on FLCs in a bulk instead of E . From the linear approximation for F , we can use the value of $F/E=1.5$ in Eqs. (23) and (24). The calculated temperature dependence of P_s and γ are drawn in Fig. 6. The spontaneous polarization is also measured by conventional polarization reverse method shown as empty circles in Fig. 6a. Both values make rather good agreement with each other except at the vicinity of T_C .

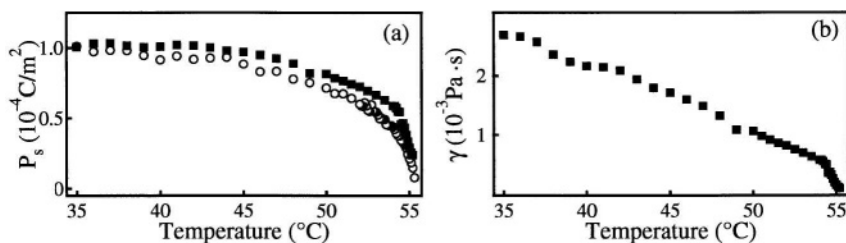


Figure 6. Temperature dependence of the best-fitted parameters (a) P_s and (b) γ . The empty circles in (a) are measured by polarization reverse method and filled square are calculated by Eq. (23).

This is mainly due to the underestimation of $\Delta\epsilon_3$ by the influence of soft mode mentioned before. The rotational viscosity γ defined by $\gamma = \gamma_0 \theta^2$, where γ_0 is the viscosity in the SmA phase, increases with decreasing temperature. As γ_0 and θ increase on cooling [4,5], γ is expected to increase from zero in the SmC* phase. If we simultaneously measure the pitch of helical structure by laser diffraction or direct measurement under microscope, we can estimate the value of K about 0.6pN by using typical measured values of $Kq_0^2 = 15\text{N/m}^2$ and $q_0 = 5\mu\text{m}^{-1}$. This is smaller than that of nematic liquid crystals because K is scaled as $K \approx K_3 \theta^2$ where K_3 is bend elastic constant and θ is as large as 10° [4].

6. Conclusions

We have presented the experimental method for nonlinear dielectric relaxation spectroscopy in frequency domain and applied it to Goldstone mode of ferroelectric liquid crystals. The linear and nonlinear dielectric spectra calculated theoretically are found to make good agreement with those obtained experimentally. Some important material constants for designing liquid crystal display can be simultaneously obtained from nonlinear spectroscopy. This shows one of characteristic usefulness of nonlinear spectroscopy in investigating soft matters.

7. References

1. Kremer, F. and Schönhal, A. (2003) *Broadband dielectric spectroscopy*, Springer, Berlin.
2. Wiener, N. (1958) *Nonlinear problems in random theory*, J. Wiley, New York.
3. Nakada, O. (1960) Theory of non-linear responses, *J. Phys. Soc. Jpn.* **15**, 2280-2286.
4. Lagerwall, S. T. (1999) *Ferroelectric and antiferroelectric liquid*, Wiley-VCH, Weinheim.
5. Musevic, I., Blinc, R. and Zeks, B. (2000) *The Physics of ferroelectric and antiferroelectric liquid crystals*, World Scientific, Singapore.
6. Furukawa, T., Nakajima, K., Koizumi, T. and Date, M. (1987) Measurements of nonlinear dielectricity in ferroelectric polymers, *Jpn. J. Appl. Phys.* **26**, 1039-1045.
7. Kimura, Y. and Hayakawa, R. (1990) Nonlinear dielectric relaxation spectroscopy of ferroelectric liquid crystals, Abst. **16th** Jpn. Liq. Cryst. Conf. 160.
8. Orihara, H. and Ishibashi, Y. (1993) A phenomenological theory of nonlinear dielectric response in a ferroelectric liquid crystal, *J. Phys. Soc. Jpn.* **62**, 489-496.
9. Kimura, Y., Hara, S. and Hayakawa, R. (2000) Nonlinear dielectric relaxation spectroscopy of ferroelectric liquid crystals, *Phys. Rev. E* **62**, R5907-5910.
10. Furukawa, T. and Matsumoto, K. (1992) Nonlinear dielectric relaxation spectra of polyvinylacetate, *Jpn. J. Appl. Phys.* **31**, 840-845.
11. Furukawa, T., Tada, M., Nakajima, K. and Seo, I. (1988) Nonlinear dielectric relaxations in a vinylidenecyanide vinylacetate copolymer, *Jpn. J. Appl. Phys.* **27**, 200-204.
12. Ikeda, S., Kominami, H., Koyama, K. and Wada, Y. (1987) Nonlinear dielectric constant and ferroelectric to paraelectric phase transition in copolymers of vinylidene fluoride and trifluoroethylene, *J. Appl. Phys.* **62**, 3339-3342.
13. Drozd-Rzoska, A., Rzoska, S.J. and Ziolo, J. (2000) The fluid-like and critical behavior of the isotropic-nematic transition appearing in linear and non-linear dielectric studies, *Acta. Phys. Pol. A* **98** 637-643.
14. Kimura, Y. and Hayakawa, R. (1993) Experimental study of nonlinear dielectric relaxation spectra of ferroelectric liquid crystals in the smectic C* phase, *Jpn. J. Appl. Phys.* **32**, 4571-4577.

PHASE BEHAVIOR OF PERTURBED LIQUID CRYSTALS

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Abstract

We study theoretically the combined effect of confinement and randomness on LC phase transitions in orientational (isotropic-nematic) and translational (nematic-smectic A) degrees of ordering. We focus to cases where these transitions are of (very) weakly 1st order. An adequate experimental realisation is, e.g., 8CB liquid crystal confined to a Controlled-Pore Glass matrix. Based on universal responses of “hard” and “soft” continuum fields to distortions we derive how different mechanisms influence qualitative and quantitative characteristics of phase transitions under consideration.

1. Introduction

The influence of randomness and confinement on phase behavior of a system is of interest for various branches of physics. A convenient system to study these phenomena are binary mixtures [A, B], where a component A presents a liquid crystal (LC) whose phase and structural behavior is influenced by a chemically inert component B. The role of the component B is in most cases restricted to enforcing either a kind of confinement or randomness, or both to A. LCs [1] are chosen because they possess a variety of different phases and structures exhibiting a rich spectrum of qualitatively different physical phenomena of universal interest. In addition, they are relatively easily experimentally monitored by virtue of their fluidity, softness, and transparency for light. Typical choices for B are various porous matrices or particle insertions [2]. As porous matrices silica aerogels [3,4], Vycor glass [5], or Controlled-Pore Glass (CPG) [6,7] are mostly used. These systems are characterized by more or less random interconnected voids hosting a LC phase. The linear size of these voids ranges between nm and μm , depending on the system preparation. As particle insertions spherular aerosil particles are mostly used [8,9]. The impact of B on phase and structural properties of A are often dramatic (e.g., change of critical behavior, temperature shifts and even change of a phase transition character), triggered by a combination of finite size effects, surface interactions and randomness [2]. Note that even a weak degree of disorder can strongly affect structural properties of LC phases that possess energetically inexpensive Goldstone modes. According to the Imry-Ma argument [10], presenting one of the pillars of statistical mechanics, even an arbitrary weak degree of disorder breaks such a system into a domain-type pattern. A typical domain size ξ_d is expected to depend only on the strength of the disorder. It should be mentioned, however, that the validity of this argument has been recently questioned [11].

In this contribution we consider a phase behavior of a liquid crystal confined to different CPG matrices. A LC of interest (e.g., 8CB - octylcyanobiphenyl) exhibits in bulk a weakly first order isotropic-nematic (I-N) and very weakly first order nematic-smectic A (N-SmA) phase transition in orientational and translational degree of ordering, respectively. A CPG matrix consists of relatively strongly interconnected, curved and cylindrically shaped voids. The void radii are relatively sharply distributed around the average radius R , characterizing the sample. In this study R ranges between nm and μm . Using a relatively simply mean field approximation (MFA) type model we show how the confinement affects these two transitions differing in a type of long-range ordering. We show that although the couplings of the nematic and smectic phase with the surface are drastically different, they nevertheless enforce similar behavior of the I-N and N-SmA transition. We further show that the competition between elasticity and randomness results in an additional characteristic length within the system that is not expected by a simple linear analysis of the model. We also offer some proofs justifying the MFA approach adopted in the study.

The plan of the paper is as follows. In Sec. 2 we present the model we use. In Sec. 3 we study the influence of confinement on the I-N and N-SmA phase transition. We show how an additional length scale enters the system due to the competition between the randomness and elasticity. In the last section we summarize our results.

2. Model

2.1. ORDER PARAMETER FIELDS

We consider ordering of rod-like molecules of thermotropic LCs. The nematic phase is characterized by the long-range orientational ordering. The elasticity of the system tends to align LC molecules (whose flow is liquid-like) homogeneously along a single symmetry breaking direction.

The orientational ordering at a mesoscopic scale is well described by a traceless tensor order parameter [1] $\underline{Q} = \sum_{i=1}^3 s_i \vec{e}_i \otimes \vec{e}_i$, where s_i and $\vec{e}_i$ represent the i -th eigenvalue and eigenvector of $\underline{Q}$. In most cases the nematic ordering is uniaxial and given by $\underline{Q} = S(\vec{n} \otimes \vec{n} - \underline{I}/3)$. Here S represents the orientational uniaxial order parameter and the nematic director field $\vec{n}$ points along the direction of uniaxial ordering. If LC molecules are rigidly locked along $\vec{n}$ then $S=1$. On contrary $S=0$ reveals the ordinary liquid (i.e., isotropic) ordering.

In the smectic A phase, in addition, a density wave appears along $\vec{n}$, yielding a layer-like profile. The resulting translational ordering is well described by a complex order parameter $\psi = \eta e^{i\Phi}$. The translational order parameter η reveals the degree of layering and the phase factor Φ defines the position of smectic layers. In equilibrium $\phi(\vec{r}) = q_0 \vec{n} \cdot \vec{r}$, i.e., the layers are stacked along $\vec{n}$ with layer spacing $d_0 = 2\pi/q_0$.

Note that the SmA phase exhibits only a quasi-long-range ordering (the so called Landau-Peierls instability [1]) because of relatively strong fluctuations in Φ . It is also important to stress that across the I-N and N-SmA phase transition the continuous rotational and translational symmetry is broken, respectively.

2.2. FREE ENERGY

We next describe the free energy F of the system. A Landau-type expansion in terms of order parameter fields is used. In the nematic phase we allow only uniaxial states (i.e., biaxiality is neglected). In addition, we introduce only the most essential contributions to F yielding at least qualitatively correct description of phenomena of interest. With this in mind we get [1,7]

$$F = \iiint (f_h^{(n)} + f_e^{(n)} + f_h^{(s)} + f_e^{(s)} + f_c) dV + \iint (f_s^{(n)} + f_s^{(s)}) dS. \quad (1)$$

Here $f_j^{(i)}$ stand for free energy density terms. Superscripts describe the nematic $^{(n)}$ and smectic $^{(s)}$ contributions. The first “volume” integral runs within the volume occupied by LC. The second “surface” integral runs over the A-B interface (i.e. over the surface of the LC body).

The structure of “volume” density terms is the following

$$\begin{aligned}
f_h^{(n)} &\approx a^{(n)}(T - T_\star^{(n)})S^2 - b^{(n)}S^3 + c^{(n)}S^4, \\
f_h^{(s)} &\approx a^{(s)}(T - T_\star^{(s)})\eta^2 - b^{(s)}\eta^3 + c^{(s)}\eta^4, \\
f_e &\approx -dS\eta^2, \\
f_e^{(n)} &\approx L_0|\nabla S|^2 + L_1S^2\left((\nabla \cdot \vec{n})^2 + (\nabla \times \vec{n})^2\right), \\
f_e^{(s)} &\approx C_{||}\left[(\vec{n} \cdot \nabla - iq_0)\psi\right]^2 + C_\perp\left[(\vec{n} \times \nabla)\psi\right]^2.
\end{aligned} \tag{2}$$

The nematic and smectic homogeneous terms $f_h^{(n)}$ and $f_h^{(s)}$ as well as the coupling term f_e between the nematic orientational and smectic translational order parameter control the I-N and N-SmA phase behaviour in the elastically undistorted LC. The positive quantities $a^{(n)}$, $b^{(n)}$, $c^{(n)}$, $T_\star^{(n)}$, $a^{(s)}$, $b^{(s)}$, $c^{(s)}$, $T_\star^{(s)}$ and d are the LC phenomenological material constants. The cubic terms in $f_h^{(n)}$ and $f_h^{(s)}$ enforce in bulk the first order I-N and N-SmA phase transitions at temperatures $T=T_{IN}$ and $T=T_{NAs}$ respectively. The coefficients $b^{(n)}$ and in particular $b^{(s)}$ (e.g. in 8CB LC) are assumed to be relatively small yielding weak and very weak discontinuities in order parameter fields at the I-N and N-SmA phase transition, respectively, even in the absence of the coupling term f_e . Note that the 1st order character of the N-SmA transition for negligible role of f_e is still questionable and is believed to arise due to coupling between ψ and fluctuations in $\vec{n}$ [12]. The coupling term f_e can drastically influence the critical behavior of the N-SmA transition. In the limit of weak coupling constant d the N-SmA transition approaches the XY universality class. With increased value of d the tricritical behavior is approached and above a critical coupling strength the N-SmA transition becomes apparently discontinuous.

The nematic ($f_e^{(n)}$) and smectic ($f_e^{(s)}$) elastic terms describe the resistance of a LC phase to long wave length distortions from the equilibrium configuration. In Eq.(2) only the most representative bare (independent of temperature) nematic (L_0 , L_1) and smectic ($C_{||}$, $C_\perp$) elastic constants are taken. For sake of clarity we henceforth discard the elastic anisotropy of the LC system and set $L \equiv L_0 = L_1$, $C \equiv C_{||} = C_\perp$.

The nematic orientational ($f_s^{(n)}$) and smectic positional ($f_s^{(s)}$) surface anchoring contributions, reflecting the anisotropic character of the LC-CPG coupling, are described in the next subsection.

2.3. SURFACE INTERACTIONS

Our study is focused on LCs immersed in the CPG matrices. In our experimental studies [7] we typically use CPG matrices with average pore radius between 10 and 200 nm. Note that these radii are comparable to LC order parameter correlation lengths. The CPG voids are strongly interconnected. The surface of voids is smooth down to the nanometer scale and is expected to enforce to LC molecules alignment in any direction perpendicular to a void's surface normal (the so called isotropic tangential anchoring condition). However, the cylindrically shaped voids are expected to break this symmetry, effectively aligning the LC molecules along a local void symmetry axis [6,7]. In case that the curvature of voids is small with respect to the relevant order parameter correlation length the effective role of the surface with respect to LC wetting is similar to the one of a locally reduced temperature. On the other hand, predominately

random inter pore connections and a more or less random cylindrical long axis void curvature introduce some disorder into the system.

We model the dominant nematic and smectic surface terms as

$$\begin{aligned} f_s^{(n)} &\approx -W^{(n)} S w(\vec{n}), \\ f_s^{(s)} &\approx -W^{(s)} (\psi + \psi^*). \end{aligned} \quad (3)$$

Here the quantities $W^{(n)}$ and $W^{(s)}$ measure the nematic and smectic anchoring strengths. The positive dimensionless function $w(\vec{n})$ is assumed to obtain its maximum value $w=1$ in the strong anchoring limit ($W^{(n)} \rightarrow \infty$). Note that both terms are linear in order parameters and they enhance the degree of LC ordering.

Our previous analyses [7] indicate that the nematic orientational anchoring strength is rather large: $W^{(n)} > 10^{-5} J/m^2$. On the other hand, the smectic coupling strength $W^{(s)}$ is believed to be substantially weaker because the smectic layers are stacked along a local void symmetry axis. Therefore only “outer” molecules of a smectic layer are in direct contact with the surface of a void.

3. Confinement and Phase Behavior

3.1. EFFECTIVE FREE ENERGY

In the following we derive an effective expression for the free energy of the system yielding the main phase behavior predictions in terms of few relevant dimensionless parameters. The basic assumption in this derivation is that locally perturbed order parameters (“hard” continuum fields) recover their equilibrium value on a length given by the relevant order parameter correlation length. Therefore, near strongly perturbed regions where order parameters significantly differ from their equilibrium value, the following approximate relations hold:

$$|\nabla S|^2 \approx (S/\xi^{(n)})^2, \quad |\nabla \eta|^2 \approx (\eta/\xi^{(s)})^2. \quad (4)$$

Here S and η stand for equilibrium order parameter values and $\xi^{(n)}(T)$, $\xi^{(s)}(T)$ represent the nematic and smectic order parameter correlation length, respectively. These lengths attain their maximum value at phase transitions, where

$$\xi^{(n)}(T_{IN}) \equiv \xi_{\max}^{(n)} \approx \sqrt{L/(a^{(n)}(T_{IN} - T_*^{(n)}))}, \quad \xi^{(s)}(T_{NA}) \equiv \xi_{\max}^{(s)} \approx \sqrt{C/(a^{(s)}(T_{NA} - T_*^{(s)}))}. \quad (5)$$

On the other hand, the nematic director field and the phase factor (“soft” continuum fields), that suffered loss of continuous symmetry at the respective phase transition, typically evolve over a scale characterizing the geometry or degree of randomness in the system. In this respect we first assume that the Imry-Ma argument is valid [10]. Therefore, we treat the CPG matrix as a source of weak disorder which breaks the system into domains of typical size ξ_d . Accordingly, the distortions in “soft” fields evolve over this scale so that it roughly holds

$$|\nabla \vec{n}|^2 \approx 1/\xi_d^2, \quad |\nabla \phi|^2 \approx 1/\xi_d^2. \quad (6)$$

It is assumed here that typically distortions evolve along the long axes of CPG voids.

We further assume that the degree of ordering close to the void surfaces is apparently different from the ordering within the voids. Therefore, the gradient contributions given in Eq.(4) are also expected there.

Taking this into account we get the following effective dimensionless free energy expression:

$$\Omega = \frac{F}{F_0} \approx q_n^2 t^{(n)} - 2q_n^3 + q_n^4 - \sigma^{(n)} q_n + A \left(q_s^2 t^{(s)} - 2q_s^3 + q_s^4 - \sigma^{(s)} q_s \right) - D q_n q_s^2, \quad (7)$$

where $q_n \approx \frac{S(T)}{S(T_{IN}^{(o)})}$ and $q_s \approx \frac{\eta(T)}{\eta(T_{NA}^{(o)})}$ are scaled order parameters, measured with respect to order parameter values at the transitions realized for $d=0$. $T_{IN}^{(o)}$ and $T_{NA}^{(o)}$ describe the bulk phase transition temperatures for $d=0$. The quantity $A = \frac{a^{(s)}(T_{NA}^{(0)} - T_*^{(s)})}{a^{(n)}(T_{IN}^{(0)} - T_*^{(n)})}$ represents

the relative weight of the nematic and smectic free energy penalty, $D = \frac{dS_0}{a^{(s)}}$ is the dimensionless coupling constant between smectic and nematic order parameters, and $F_0 = a^{(n)}(T_{IN}^{(o)} - T_*^{(n)})\pi R^2 \xi_d$. The scaled effective temperatures $t^{(i)}$, surface fields $\sigma^{(i)}$, where $i=n$ and $i=s$ stand for the nematic and smectic phase, respectively, are given by

$$t^{(n)} \approx \frac{T - T_*^{(n)}}{T_{IN}^{(o)} - T_*^{(n)}} + \left(\frac{\xi_{\max}^{(n)}}{\xi_d} \right)^2 + \frac{2 \left(\xi_{\max}^{(n)} \right)^2}{\xi^{(n)} R}, \quad (7a)$$

$$t^{(s)} \approx \frac{T - T_*^{(s)}}{T_{NA}^{(o)} - T_*^{(s)}} + \left(\frac{\xi_{\max}^{(s)}}{\xi_d} \right)^2 + \frac{2 \left(\xi_{\max}^{(s)} \right)^2}{\xi^{(s)} R},$$

$$\sigma^{(n)} \approx \frac{\left(\xi_{\max}^{(n)} \right)^2}{R d^{(n)}}, \quad \sigma^{(s)} \approx \frac{\left(\xi_{\max}^{(s)} \right)^2}{R d^{(s)}}. \quad (7b)$$

Here $d^{(n)} = L/W^{(n)}$ and $d^{(s)} = C/W^{(s)}$ stand for nematic ($d^{(n)}$) and smectic ($d^{(s)}$) surface extrapolation length.

3.1.1. Imry-Ma scenario

If the Imry-Ma argument is adopted then the value of ξ_d is universal in the nematic phase and depends only on the strength of random field imposed by the CPG matrix. In this case ξ_d is not temperature dependent and the equilibrium average order parameters

are obtained simply by solving the coupled sets of equations $\frac{\partial \Omega}{\partial q_n} = \frac{\partial \Omega}{\partial q_s} = 0$, yielding:

$$\begin{aligned} 2q_n t^{(n)} - 6q_n^2 + 4q_n^3 - \sigma^{(n)} - D q_s^2 &= 0, \\ 2q_s t^{(s)} - 6q_s^2 + 4q_s^3 - \sigma^{(s)} - \frac{2D}{A} q_s q_n &= 0. \end{aligned} \quad (8)$$

Note that in the case of negligible coupling between the smectic and nematic order parameters we get the same functional dependence for both order parameters. In this case the phase transitions can be expressed analytically. The i -th phase transition remains discontinuous if the condition $\sigma^{(i)} < 0.5$ is realized. In this case the phase transition takes place at the critical effective temperature $t_c^{(i)} \equiv t_c^{(i)} = 1 + \sigma^{(i)}$ [13]. Taking

into account Eqs.(7) the following expressions for the confinement induced transition temperatures shifts are obtained:

$$\Delta T^{(n)} = T_{IN}(R) - T_{IN}^{(o)} \approx \left(T_{IN}^{(o)} - T_{\star}^{(n)} \right) \left(\left(\frac{\xi_{\max}^{(n)}}{Rd^{(n)}} \right) - \left(\frac{\xi_{\max}^{(n)}}{\xi_d} \right)^2 - \frac{2\xi_{\max}^{(n)}}{R} \right), \quad (9)$$

$$\Delta T^{(s)} = T_{NA}(R) - T_{NA}^{(o)} \approx \left(T_{NA}^{(o)} - T_{\star}^{(s)} \right) \left(\left(\frac{\xi_{\max}^{(s)}}{Rd^{(s)}} \right) - \left(\frac{\xi_{\max}^{(s)}}{\xi_d} \right)^2 - \frac{2\xi_{\max}^{(s)}}{R} \right),$$

where $T_{IN}(R)$ and $T_{NA}(R)$ stand for the I-N and N-SmA phase transition temperature, respectively, in a sample characterized by the radius R .

Therefore, the surface interactions increase the transition temperatures and their contribution scales as $\Delta T^{(i)} \propto 1/R$. The elastic distortions, on the other hand, depress transition temperatures. Neglecting the differences in the order parameters at the void surfaces and within them one gets $\Delta T^{(i)} \propto -1/\xi_d^2$. Assuming $\xi_d \propto R$ it follows that $\Delta T^{(i)} \propto -1/R^2$. Taking into account apparently enhanced order parameters at the void surfaces one gets an additional term suppressing the transition temperature that is proportional to $-1/R$.

3.1.2. Non Universal Domain Length Dependence

Next we consider the case where the domain length is not universal and represents the variational variable of the model. In this case we restrict ourselves only to the I-N phase transition. We model the function w in Eq.(3) in terms of the following ansatz:

$$w = \frac{1}{\left(1 + \frac{(\xi_d - \xi_s)^2}{\xi_s^2} \right)^{n_a/4}}. \quad (10)$$

Here we assume that surface favors the domain size equal or smaller than ξ_s . A value of ξ_s is determined by the average geometry of the CPG sample. For $\xi_s \geq \xi_d$ one gets $f_s^{(n)} \approx -SW^{(n)}$, the latter value representing the minimum value of $f_s^{(n)}$. For larger domains the surface contribution gradually averages out with increased domain size. Using the central limit theorem [13] this reduction of the anchoring contributions scales with $1/\sqrt{N^{n_a}}$, where $N \approx \xi_d / \xi_s$ is the number of “random” sites within a cluster. The parameter n_a reveals the dimensionality of the space in which the averaging takes place. If the averaging along void long axes is dominant, then $n_a=1$. Random void interactions tend to increase the value of n_a . If they are dominant then $n_a=3$.

With assumptions described in Sec.3.1. and the ansatz Eq.(10) we get

$$\Omega \approx q_n^2 \left(t_n + \left(\frac{\xi_{\max}^{(n)}}{\xi_d} \right)^2 + \frac{2 \left(\frac{\xi_{\max}^{(n)}}{\xi_d} \right)^2}{\xi^{(n)} R} \right) - 2q_n^3 + q_n^4 - \frac{\sigma^{(n)} q_n}{\left(1 + \frac{(\xi_d - \xi_s)^2}{\xi_s^2} \right)^{n_a/4}}, \quad (11)$$

where $t_n = (T - T_*^{(n)}) / (T_{IN} - T_*^{(n)})$. The elastic distortions in the nematic director field favor $\xi_d \rightarrow \infty$ and the surface $\xi_d \leq \xi_s$. The equilibrium domain distance thus reflects the compromise between the two tendencies. The equilibrium nematic structure is now described with the equations $\frac{\partial \Omega}{\partial q_n} = \frac{\partial \Omega}{\partial \xi_d} = 0$. In Figure 1 we present some characteristic solutions. In the nematic phase it roughly holds

$$\xi_d \approx \xi_{\max}^{(n)} \left(\frac{4q_n}{\sigma_n} \right)^{\frac{2}{4-n_a}}, \quad (12)$$

where $\sigma_n = \sigma^{(n)} \left(\frac{\xi_s}{\xi_{\max}^{(n)}} \right)^{n_a/2}$. Again we see that above some critical surface field the I-N transition becomes gradual. For all fields the average cluster size gradually increases with decreasing temperature. For $n_a=3$ and neglecting temperature dependence of q_n one gets the Imry-Ma result: $\xi_d \propto 1/(\sigma^{(n)})^2$ [10].

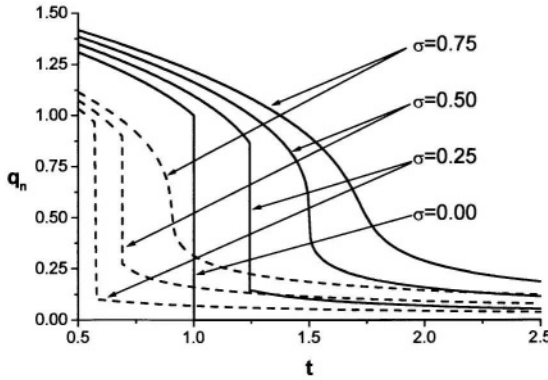


Figure 1. Nematic order parameter q_n as a function of scaled temperature t and surface field σ . Full line: Imry-Ma approach, $t = t^{(n)}$, $\sigma = \sigma^{(n)}$. Dashed line: variational approach, $t = t_n$, $\sigma = \sigma^{(n)} \sqrt{\xi_s / \xi_{\max}^{(n)}}$, $R / \xi_{\max}^{(n)} = 2$, $n_a = 1$.

4. Conclusions

We studied phase behavior of a LC confined to Controlled-Pore Glasses (CPG), focusing ourselves to the I-N and N-SmA phase transition. We considered cases where both transitions are weakly first order as realized in 8CB LC. A simple Landau-type expansion was used in terms of a nematic tensor $\underline{Q} = S(\bar{n} \otimes \bar{n} - \underline{I}/3)$ and smectic complex order parameter $\psi = \eta e^{i\Phi}$.

We took into account that the nematic (S) and smectic (η) order parameters, representatives of “hard” continuum fields, typically respond to locally induced distortions on a length scale given by a relevant order parameter correlation length $\xi^{(i)}$ ($i=n$: nematic, $i=s$: smectic component). On the other hand the “soft” continuum fields $\vec{n}$ and Φ , that suffered loss of continuous symmetry at the relevant phase transition, typically evolve over a length scale ξ_d . This is defined by the geometry of a system that acts as a boundary for the LC phase. For regular geometries ξ_d equals to one of the characteristic linear lengths of the system. In irregular geometries a scale reflecting the disorder characteristics appears.

We took into account specific properties of the CPG void surfaces. For relatively weak void curvatures (with respect to $\xi^{(i)}$) the surface enhances the degree of LC ordering. In this case we assumed that at the void surfaces the degree of ordering is apparently different from that in the central regions. Further random curvature and interconnections of the CPG voids introduce a weak disorder into the system.

We first considered the case in which the validity of the Imry-Ma argument is assumed. According to this argument already an arbitrarily weak degree of disorder breaks the system into a domain-like pattern, provided that a continuous symmetry was broken at the phase transition and that the spatial dimension of the system is less than four. The resulting typical domain length universally depends on the disorder strength.

Taking into account the Imry-Ma domain pattern structure we arrived at an effective free energy density expression in terms of average order parameters of the system and few dimensionless parameters which appropriately scale the system characteristics. In case of a negligible coupling between S and η , average order parameters depend on only two dimensionless quantities: the effective temperature $t^{(i)}$ and the effective surface field $\sigma^{(i)}$. Therefore all mechanisms that can trigger a qualitative change in the temperature behavior of order parameters are assembled in $\sigma^{(i)}$. For $\sigma^{(i)} < 0.5$ the phase transitions remain discontinuous and take place at a critical reduced temperature $t_c^{(i)} = 1 + \sigma^{(i)}$. From this expression one can roughly infer how various mechanisms influence the temperature shift $\Delta T^{(i)}$ of the i -th LC phase transition. Elastic distortions decrease the transition temperature. Elastic variations along long void axes enforce $\Delta T^{(i)} \propto -1/\xi_d^2$ and a bi-component character of the ordering within the cavities introduces $\Delta T^{(i)} \propto -1/R$. The surface “wetting” term tends to increase the transition temperature and its contribution scales as $\Delta T^{(i)} \propto +1/R$. Note that this surface term is relatively negligible in the smectic case because one expects $W^{(\eta)} \gg W^{(s)}$. But in practice the coupling between order parameters is sufficiently strong that both the nematic order (that is directly strongly coupled with the surface) and the smectic one near surfaces are apparently larger than the system average values. If one assumes that $\xi_d \propto R$ then both $\Delta T^{(n)}$ and $\Delta T^{(s)}$ dependencies on R are expected to follow similar trends that are indeed experimentally observed [7]. Note that this rough model also yields a reasonable quantitative prediction on the magnitude of temperature shifts [7].

We next treated the case where ξ_d is not universally determined by the disorder strength, focusing on the I-N transition. We modelled the surface potential that mimics the disorder introduced by the CPG matrix. We introduced the scale ξ_s over which the surface potential apparently changes in a random manner. Further, if $\xi_d > \xi_s$ then the surface contribution is partially averaged out obeying the central limit theorem. In this

approach both S and ξ_d act as variational parameters. This gives a rough insight into how both the degree of order and the average domain size depend on the surface interaction strength and the degree of curvature (i.e. ξ_s). Note that the results in the nematic phase are rather similar to those obtained in the Imry-Ma picture if $\sigma^{(i)} < 0.5$.

We have to stress that the radii of the treated CPG voids are at least comparable to $\xi^{(i)}$. This indicates that finite size effects could be important, masking at least the temperature shift dependence on R . This suggestion is supported by our recent calorimetric study [7], which shows clear finite size dependence of the specific heat maximum height at the N-SmA transition in 8CB LC. However our preliminary studies using semi-microscopic Lebwohl-Lasher interaction and Brownian Molecular Dynamics [14] indicate, that the temperature shifts due to finite scaling are negligible with respect to those enforced by surface interactions or typical elastic distortions.

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5. References

1. De Gennes, P.G. and Prost, J. (1993) *The Physics of Liquid Crystals*, Oxford University Press, Oxford.
2. Crawford, G.P. and Žumer, S. (eds.) (1996) *Liquid Crystals in Complex Geometries Formed by Polymer and Porous Networks*, Taylor and Francis, London.
3. Zeng, H. *et al.* (1999) Effects of quenched disorder on the orientational order of the octylcyanobiphenyl liquid crystal, *Phys. Rev. E* **60**, 5607-5617.
4. Kralj, S. *et al.* (1993) Deuterium NMR of a 5CB liquid crystal confined in a silica aerogel matrix, *Phys. Rev. E* **48**, 340-349.
5. Tripahi, S., Rosenblatt, C., and Aliev, F. (1994) Orientational susceptibility in porous glass near a bulk nematic-isotropic phase transition, *Phys. Rev. Lett.* **72**, 2725-2728.
6. Dadmun, M.D. and Muthukumar, M. (1992) *J. Chem. Phys.* **98**, 4850-4852.
7. Kutnjak, Z., Kralj, S., and Žumer, S. (1993) Calorimetric study of 8CB liquid crystal confined to controlled porous glass, to appear in *Phys. Rev. E*.
8. Iannacchione, G.S. *et al.* (2003) Smectic ordering in liquid-crystal-aerosil dispersions, *Phys. Rev. E* **67**, 011709-13.
9. Kutnjak, Z., Kralj, S., and Žumer, S. (2002) Effect of dispersed silica particles on SmA-SmC* phase transition, *Phys. Rev. E* **66**, 041702-8.
10. Imry, Y. and Ma, S. (1975) Random-field instability of the ordered state of continuous symmetry, *Phys. Rev. Lett.* **35**, 1399-1401.
11. Feldman, D. E. (2000) Quasi-Long-Range order in nematics confined in random porous media, *Phys. Rev. Lett.* **84**, 4886-4889.
12. Anisimov, M. A. *et al.* (1990) Experimental test of a fluctuation-induced first-order phase transition: the nematic-smectic-A transition, *Phys. Rev. A* **41**, 6749-6762.
13. Cleaver, D.J. *et al.* (1996) The random anisotropy nematic spin model, in G.P. Crawford and S. Žumer (eds.), *Liquid Crystals in Complex Geometries formed by polymer and porous networks*, Taylor and Francis, London, pp. 467-481.
14. Bradač, Z., Kralj, S., and Žumer, S. (2002) Molecular dynamics study of isotropic-nematic quench, *Phys. Rev. E* **65**, 021705-10.

EDGE DISLOCATIONS IN SMECTIC-A LIQUID CRYSTALS

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Abstract We study theoretically static structure and annihilation dynamics of edge dislocations in a smectic-A liquid crystal confined to a plan-parallel cell. The Landau-Ginzburg type phenomenological approach is used in terms of a complex order parameter. We investigate a structure of an isolated dislocation that is enforced by boundary conditions. We further follow the annihilation dynamics of a pair of dislocations into a defectless state.

1. Introduction

Defects in ordered media correspond to singular regions where the relevant order parameter field can not be transformed to a homogeneous state via a continuous transformation [1]. Investigations of their behavior have traditionally attracted a lot of attention in almost all branches of physics. In different media they are also referred to as dislocations, disclinations, vortices, etc.. Their universal behavior allows for use of simple models based on basic physical concepts. In this contribution we study an edge dislocation in a smectic-A (SmA) liquid crystal (LC) phase using a simple Landau-Ginzburg phenomenological approach.

The bulk equilibrium SmA LC phase [2] consists of a parallel stack of layers that are displaced for a distance d_0 . The LC molecules within a layer are on average oriented along the layer's normal. The flow of molecules within layers is liquid-like. On contrary in a direction along the layers' normal a crystal-like property appears. Consequently the SmA phase is often referred to as a *one-dimensional crystal* or *two-dimensional liquid* phase.

The undulation of SmA layers is relatively energetically inexpensive. Consequently in "real" SmA structures the layers often exhibit undulations [3] (e.g., chevron structures, zig-zag defects, focal conies). On contrary the layers relatively strongly resist to any changes in layers' separations. As a result edge dislocations can appear. Their appearance enables a global reduction of elastic costs by localizing main energetic expenses to cores of defects. Most often edge dislocations appear if a nematic bend deformation is imposed to a SmA phase. They can also appear if a surface enclosing the SmA phase enforces periodicity [4] $q_s = 2\pi/d_s$ that differs from the equilibrium SmA periodicity $q_0 = 2\pi/d_0$. In this case the smectic layers must be stacked perpendicular to the

surface (or close to this configuration). For a plan-parallel confinement this arrangement is referred to as the *bookshelf structure*.

In this contribution we study the edge dislocation structure and annihilation of a pair of edge dislocations in a bookshelf geometry. We use a Landau-Ginzburg phenomenological approach in terms of a complex order parameter. The advantage of this approach is that it enables description of the fine defect's core structure. The plan of the paper is the following. In Sec. 2 we introduce the model we use. In Sec.3 the static structure of the edge dislocation is analyzed. We show the mapping of our model into the Frenkel-Kontorowa model in the thin cell limit. Different stages of the annihilation dynamics of a pair of edge dislocations are studied in Sec. 4. In the last section we summarize our results.

2. Model

We consider a SmA LC sandwiched between two parallel plates enforcing the planar orientational anchoring to the LC molecules in the *bookshelf geometry* as shown in Fig. 1. The two confining substrates are separated by a distance L_x . We assume that $L_x \ll L_y \approx L_z$, where L_y, L_z describe the surface area of the confining plates.

To describe the SmA structure in the cell we use a simple Landau-Ginzburg type approach. The orientational ordering is given by the nematic director field $\vec{n}(\vec{r})$, pointing along the average uniaxial direction of LC molecules at $\vec{r}$. The layer structure is modeled by the smectic complex order parameter $\psi(\vec{r}) = \eta(\vec{r})e^{i\Phi(\vec{r})}$. The translational order parameter η characterizes the degree of smectic ordering. The phase factor Φ determines the position of smectic layers.

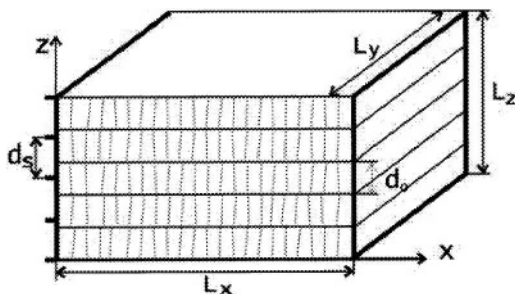


Figure 1. The geometry of the problem.

The free energy F of the confined LC is expressed as $F = \iiint (f_h + f_e) d^3\vec{r} + \iint f_s d^2\vec{r}$, where F consists of the bulk homogeneous (f_h), bulk elastic (f_e) and surface (f_s) free energy density contribution. These terms are approximately expressed as [2,5]

$$\begin{aligned}
f_h &= a_0(T - T_{NA})|\psi|^2 + \frac{b}{2}|\psi|^4, \\
f_e &= \frac{K}{2}((\nabla \cdot \bar{n})^2 + (\nabla \times \bar{n})^2) + C_{II}[(\bar{n} \cdot \nabla - iq_0)\psi]^2 + C_{\perp}[(\bar{n} \times \nabla)\psi]^2, \\
f_s &= \frac{W_p}{2}|\psi - \psi_s|^2.
\end{aligned} \tag{1}$$

Quantities a_0 and b are material constants, T is the temperature and T_{NA} is the temperature of the continuous bulk nematic-SmA phase transition. Below T_{NA} the potential f_h enforces $\eta_0 = \sqrt{a_0(T_{NA} - T)/b}$. The nematic elastic properties are expressed in the equal elastic constant approximation in terms of an average Frank elastic constant K . The smectic elastic properties are described with the compressibility (C_{II}) and smectic bend ($C_{\perp}$) elastic constant. In the SmA phase both constants are positive. They tend to establish the layer structure having the layer separation d_0 and $\bar{n}$ being aligned along the layer normal. For simplicity we henceforth set $C \equiv C_{\perp} = C_{II}$.

In the surface free energy density contribution [6] we write only the smectic positional anchoring term. W_p is the positional anchoring constant and $\psi_s = \eta_s e^{iq_s z}$ is the smectic ordering preferred by the confining plates. We assume that the surface enforces periodicity $q_s = 2\pi/d_s$ along the z -axis that differs from the smectic equilibrium one $q_0 = 2\pi/d_0$, and $\eta_s \approx \eta_0$. In practice this condition is often realized due to memory effects [7].

The most important lengths entering the model are the spacings d_0 , d_s , the cell thickness L_x , the smectic correlation length $\xi \approx \xi_0 / \sqrt{1 - T/T_{NA}}$, where $\xi_0 = C/(a_0 T_{NA})$ is comparable to a typical molecular length of the system, and the surface positional extrapolation length $d_p = C/W_p$.

To study the dynamics of the system we assume that the free energy gained per unit time is entirely dissipated, i.e., the inertial effects are neglected [8]. Accordingly, $-\frac{dF}{dt} = D$, where $D = \iiint g d^3\vec{r}$ stands for the dissipation function. Note that a common problem in non-equilibrium statistical mechanics is the correct identification of D . We model it roughly with the expression

$$g = \gamma \left| \frac{\partial \psi}{\partial t} \right|^2, \tag{2}$$

where γ approximates the effective viscous properties of the system. In g we neglect the contribution from the nematic director field. The characteristic order parameter relaxation time is roughly given by $\tau \approx \xi^2 \gamma / C$.

The symmetry of the problem suggests that the continuum fields of the problem vary only in the (x, z) plane. The nematic director field is parametrized as $\bar{n} = (\sin \theta, 0, \cos \theta)$. Therefore the variational fields are $\theta(x, z, t)$, $\eta(x, z, t)$ and $\Phi(x, z, t)$. For numerical purposes we introduce the phase difference $\varphi = \Phi - q_s z$ to get rid of pronounced spatial variations in

Φ . We further express the smectic order parameter as $\eta e^{i\varphi} = A + iB$, $A(x, z, t)$ and $B(x, z, t)$ are real functions, to avoid non-unique definition of Φ at defect origin, where $\eta = 0$. The corresponding dynamic Euler-Lagrange differential equations for the variational fields were solved numerically. For derivation of these equations and numerical details we refer the reader to ref.[9].

3. Static defect structure

3.1. THICK CELLS

We first consider the case where $L_x \gg \xi$. A lattice of edge dislocations appears in the cell for $d_0/d_s > 1$ and a strong enough positional anchoring strength. For $d_0/d_s < 1$ the system avoids formation of edge dislocations by forming the chevron or tilted structures [4] in which layers are tilted with respect to the confining plates. In this case the edge dislocations can be enforced by imposing an electric field along the z-axis for LC molecules with a positive field anisotropy. By inserting along the z-axis a lattice of edge dislocations with periodicity $2\pi / L_{edge} = 2\pi |d_s - d_d| / (d_s d_p)$ the elastic strain is almost completely removed in the central region of the cell (i.e., the layer separation is close to the equilibrium one). The presence of dislocations enables introduction or removal of a layer in this region for $d_s > d_0$ and $d_s < d_0$, respectively. For $d_0/d_s \neq 1$ the critical condition for the formation of dislocations is roughly given [9] by $\frac{d_0}{d_p |d_0/d_s - 1|} \approx 1$. In Fig.2 we show the formation of the dislocation as the positional anchoring is increased above the critical value $W_c \approx \frac{C}{d_0} \left| \frac{d_0}{d_s} - 1 \right|$ of W_p . Both order parameter and layer profiles are given. For $W_p < W_c$ the depression of the order parameter at the surface appears, marking the site where edge dislocation can be formed. For $W_p = W_c$ (Fig.2a) the dislocation is formed exactly at the surface. By further increasing the anchoring strength the dislocation depins (Fig.2b) from the surface and gradually saturates at the distance roughly given by few ξ . The core structure of the “saturated” edge dislocation does not exhibit the cylindrical symmetry despite the fact that $C_{||} = C_{\perp}$ because of the interaction with the surface. For a common elastic anisotropy $C_{||} > C_{\perp}$ the core is further prolonged along the z-axis. Note also that the director field deviations from the z-axis are negligible small. The maximum value of θ in the study did not exceed few degrees.

3.2. THIN CELLS

In a thin cell limit, where L_x is comparable to ξ , edge dislocations formed at opposite plates interact with each other. For a small enough value of L_x pairs of dislocation annihilate, enabling a smooth transformation into a defect-less state. The critical condition for this event in the strong anchoring limit roughly reads [9] $\frac{d_0}{L_x[d_0/d_s-1]} \approx 1$.

If in addition a weak anchoring limit is assumed, then the mathematics of the problem can be substantially simplified. In these two limits we adopt the following approximations: we neglect (i) variations of the variational fields along the x-axis, and (ii) the order parameter variation along the z-axis. We further set $\theta=0$ based on experiences obtained in the thick cell limit. These assumptions allow us to study the variation of a layer profile analytically as the relevant parameters of model are varied. Note that at the dislocation site melting of the order parameter is expected. But the numerical simulations in the regime of interest show that qualitative picture of the layer profile behavior is not affected by these approximations.

Adopting these approximations, we arrive at the expression for the free energy that

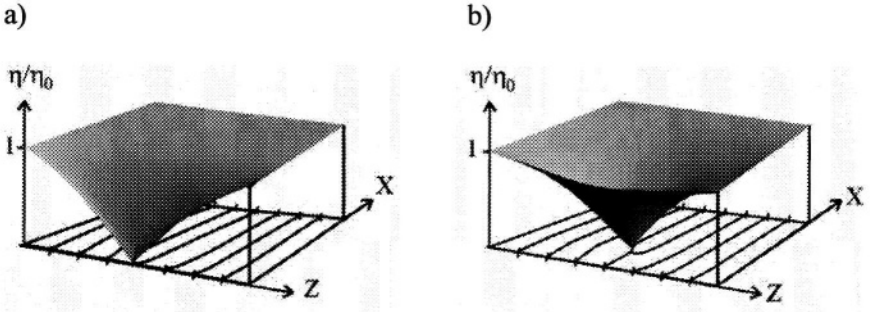


Figure 2. The core structure of the edge dislocation. (a) At the threshold condition $W_p=W_c$ the edge dislocation appears exactly at the surface. (b) Above the threshold ($W_p>W_c$) the dislocation dips from the surface.

maps to the Frenkel-Kontorowa model [10]. This model was originally designed to study commensurate-incommensurate transitions in one-dimensional systems. The Frenkel-Kontorowa form of the dimensionless free energy H_{FK} reads

$$H_{FK} = \Delta F \frac{\varepsilon d_0}{\eta_0^2 C L_x L_y} = \int \left(\left(\frac{d\varphi}{du} + 2\pi\varepsilon \right)^2 + V(1 - \cos\varphi) \right) du. \quad (3)$$

Here the excess free energy $\Delta F = F - F_{bulk}$ is measured relatively to the free energy F_{bulk} of the undistorted SmA phase, $V = d_0^2 / (d_p L_x)$, $\varepsilon = 1 - d_s / d_0$ and $u = z / d_0$.

Solutions of the problem as functions of ε and V are described in detail in Ref.[10]. Here we summarize the main results relevant to our study. Two qualitatively different solutions exist, that are separated by the critical condition $V \equiv V_c = 4\pi\varepsilon^2$. For $V > V_c$ the so called *floating* structure, given by $\varphi(z)=0$, is stable, corresponding to the strained bookshelf structure of layer spacing $d=d_s$. In this regime the smectic layers exactly follow the conditions imposed by the surface: $\Phi=q_s z$. For $V \leq V_c$ a soliton-like solution appears: $\varphi(z) = \pm 4 \arctan\left(e^{u\sqrt{2V}}\right)$. The soliton wall (the site of maximal value of $\left|\frac{d\varphi}{dz}\right|$) is placed at $z=0$, and + (-) branch corresponds to $u>0$ ($u<0$). In this case in the most of the cell the smectic liquid crystal follows the surface tendency (i.e. $\Phi \approx q_s z$) interrupted by relatively steep 2π jumps in φ . This solution corresponds to an insertion of an additional layer for $d_s > d_0$ or to skipping of it in the opposite case.

4. Annihilation dynamics

We next study the simplest annihilation scenario of a pair of edge dislocations. For this reason we consider a thick cell. By using a mathematical ansatz for the edge dislocation layer displacement profile [11], we introduce a pair of dislocations at $z=0$, separated for a distance $L_0 \gg \xi$ along the x -axis. Exactly at the defect site we set $\eta=0$ and $\eta=\eta_0$ in the remaining volume. We study the case $d_s=d_0$, where the annihilation dynamics is driven solely by the layer curvature.

After the equilibration time $t \approx 10\tau_s$, in which the cores adopt the quasi-equilibrium order parameter profile, we begin to follow the annihilation dynamics. Different stages of this process are shown in Fig.3a. Order parameter dependencies $\eta(x,t)$ along the axis through both defects are plotted for the left defect. The second defect is placed symmetrically at the right side of the figure, that is not shown.

A SCHEMATIC DESCRIPTION OF THE DYNAMICS OF GLASS TRANSITION BY THE COUPLING MODEL

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1. Introduction

The research of glass transition has a long history that can be traced back to the Babylonians who documented their recipe of making glasses from desert sand, and to the study of dynamics of alkali silicate glass and a natural polymer by R. Kohlrausch in Göttingen in mid 1800's at the time of Gauss. Since then, glass transition and its phenomena were found in many kinds of materials. Glass transition is a general phenomenon found in many different kinds of materials including inorganic substances with widely different chemical compositions, organic small molecules, synthetic polymers, side chain liquid crystalline polymers, metallic compounds, plastic crystals, and some biomaterials. The thermodynamic and dynamic properties of glass-forming liquids and glasses are similar, falling into well-defined patterns [1,2] to suggest some common fundamental physics are at work. The lure of uncovering the basic physics of glass transition has led many scientists from various disciplines to join in the research. Many modern experimental techniques have been applied to study glass transition in more previously known and newly discovered glass-formers. The explosive increase of research activities has significantly expanded the data and enriched the phenomenology. More anomalous observed properties of the dynamics of glass transition found [2] make the task even more challenging, and helpful in guiding us eventually to a truly satisfactory understanding of glass transition. Here I stress the importance of being constantly aware of *all* the established experimental facts and particularly the anomalous properties, in any attempt to construct theory or explanation of glass transition. It is a much easier task to construct a theory of glass transition if only a subset of the experimental facts and anomalous properties are considered. Certainly this is a reasonable and good start, but the theory is unsatisfactory for one of the following reasons. (1) At the very least, the task is incomplete if the theory does not address or has not addressed the other remaining anomalous properties. (2) The theory is limited in scope because it does not have any prediction to address them. (3) The theory can be brought to address them but unfortunately the predictions contradict them. The last

possibility is catastrophic, because of it the theory has to be rejected. Since the experimental facts and anomalous properties are by now well known and documented, the merit of any theory can be judged immediately. Also a theory is incomplete if it is limited to the description of a special class of model systems but not the mainstream glass-formers, or if it is limited to only a certain time range but not the entire range from microscopic short time to long times. Our requirement for a satisfactory theory is so stringent that it is unsurprising that no existing theory qualifies and probably no theory in the foreseeable future.

However, the situation is not as hopeless as the picture painted here. As I shall show in this work, most if not all factors that determine the evolution of the dynamics from microscopic short times to long times are known. There are a number of different factors, which is the reason why a theory that incorporates all of them is difficult to come by. Conceptually, we know the roles played by these factors. If we are less ambitious, instead of a theory we can have a schematic model by a thoughtful infusion of these factors, which can elucidate all the experimental facts including the anomalous properties. This is the objective of the work. On the other hand, ambitiously looking for a rigorous theory that explains all the experimental facts is an unreachable goal, at least for a long time to come.

Due to space limitation, I shall not redefine the commonly used terms in glass transition.

2. The Determining Factors

Glass transition occurs through the change of temperature, T , or pressure, P . Accompanying the changes in T and P are possibly changes in specific volume, V , and entropy, S , which naturally are related to some factors that determine the rate of all relaxation and diffusion processes in the glass-former. Related to specific volume is the concept of free volume, v_f , of Doolittle [3], which controls the mobility of molecules at any temperature and explains the non-Arrhenius temperature dependence of the viscosity, η , of liquids. The physical basis for free volume can be understood from the theory of Cohen and Turnbull [4]. Related to entropy, is the concept of configurational entropy, S_{cs} , of Gibbs and DiMarzio [5], which also determines the mobility through a theory by Adam and Gibbs [6]. In the past four decades, some workers favor free volume and others configurational entropy as the determining factor. Recent theoretical developments tend to favor configurational entropy. Ironically, recent studies of dynamics by dielectric relaxation under the application of high pressure have shown specific volume is definitely a significant factor in most glass-forming liquids and polymers, except those with mainly hydrogen bonding. This finding dashes the hope that configurational entropy is all that is needed to construct a theory of glass transition, and invalidates the currently popular Adam-Gibbs theory because volume is not in it. Thus, both free volume and configurational entropy have to be considered as the thermodynamic variables that determine the glass transition dynamics.

The glass transition problem is reduced to a simpler problem if T and P are both fixed, and we can legitimately demand any theory to address the remaining properties or anomalies [2]. Some examples of these are listed as follows. (i) The Kohlrausch

stretched exponential time dependence of the correlation function, $\phi(t) = \exp[-(t/\tau_\alpha)^{1-n}]$, where $0 \leq n < 1$ and τ_α is the α -relaxation time. (ii) The heterogeneous nature of the dynamics, rough described as the presence of slow and fast molecules, interchanging their roles at times of the order of τ_α . (iii) τ_α has an anomalous dependence. $\tau_\alpha \propto Q^{2/(1-n)}$, on the scattering wavevector, Q . (iv) Within the same family of glass-formers and for the same τ_α the stretch exponent, $(1-n)$, decreases systematically with increasing intermolecular constraints. (v) There is a faster Johari-Goldstein (JG) relaxation, even if the glass-former is made of rigid molecules. (vi) There is a correlation between the JG β -relaxation time, τ_β and τ_α . Free volume [3,4] and configurational entropy [5,6] give only the averaged or “mean-field” mobility of the molecules but not the complexity in time dependence of the relaxation dynamics. Hence, even a theory that combines free volume and configurational entropy, it is incapable to solve the simpler problem. In particular, any theory based solely on thermodynamic variables is likely to fail to treat a simpler problem of the same materials. This drawback applies to some other proposed theories of glass transition. An important factor is missing

The missing determining factor of dynamics is intermolecular coupling. Glass-forming substances are composed of densely packed and mutually interacting molecular units. The interactions cause the relaxation to be intermolecular coupled, which in simpler words means that motion of one molecule depends on the motions of the other molecules and vice versa. Solution of the problem is difficult because it is a many-body problem and there is no established method to treat many-body relaxation dynamics due to intermolecular coupling. Molecular dynamics simulations [7] and some experimental techniques [8] show directly the motions and their evolution with time, and they are very complex. It is impractical to expect a theory of real glass-formers that can describe all the complex motion to emerge in the foreseeable future. Can we bypass this insurmountable task and still have the means to solve the essential problems in glass transition? The answer is positive, as we shall see by enlisting the coupling model [9-17] to capture the effects due to intermolecular coupling and incorporating the dependence on volume and entropy as well.

The objective of the coupling model (CM) is not to describe the complex motion, which we know is a Herculean task, but to find some general physical principle of coupled many-body relaxations caused by mutual interactions. It is hoped that the general physical principle can help us to bypass the difficulty and yet lead us to solutions of problems. The CM has a long history [9-17]. Here we cite the results of a recent model of coupled arrays of phase-coupled oscillators [10,11], which captures the basic physical principle of the CM and shows the changes with increasing intermolecular coupling. It is remarkable that such a simple model has dynamics that mimic that observed in real glass-formers. Most important is the existence of a crossover time, t_c , from simple independent relaxation to complex many-body relaxation. In the shorter time regime, $t < t_c$, relaxation of any molecule is executed independently, without the influence of other molecules, and the correlation function is thus an exponential function of time,

$$\phi(t) = \exp(-t/\tau_0) \quad (1)$$

where τ_0 is the so-called primitive or independent relaxation time, i.e., it is relaxation time of a molecule without having yet to consider the effect of other molecules on its dynamics due to intermolecular interaction. In the longer time regime, $t \gg t_c$, intermolecular coupling asserts itself and slows down the averaged relaxation rate, and the correlation function assumes the Kohlrausch form,

$$\phi(t) = \exp[-(t / \tau_\alpha)^{1-n}] \quad (2)$$

The coupling parameter, n , and concomitantly, τ_α increase with increasing coupling strength. In the absence of intermolecular coupling, n is identically zero, meaning independent relaxation persists even at long times. This model result suggests that the experimentally observed broadened dispersions of supercooled liquids, usually well fit by the Kohlrausch relaxation function, originate from the intermolecular coupling/constraint. This interpretation of the breadth of the observed broadened dispersion of glass-formers is one of the basic premises of the coupling model.

The crossover in real glass-formers is also supported by experimental data, from which t_c of about 2 ps has been deduced for molecular or polymeric liquids [13]. Evidences of crossover were found in other intermolecularly coupled systems of different kinds, indicating that the crossover is a general result, albeit t_c increases with decreasing interaction strength [13]. At the inception of the CM, I have recognized that this crossover engenders a useful relation between τ_α and τ_0 ,

$$\tau_\alpha = [t_c^{-n} \tau_0]^{1/(1-n)}. \quad (3)$$

Since τ_α is the effective relaxation time of complex many-body relaxations, its magnitude, properties and dependences on various parameters naturally are not easy to comprehend. On the contrary, τ_0 is straightforward and its magnitude and dependences either transparent or known because it is the relaxation time of a simple independent relaxation. Eq.(3) enables us to understand τ_α from τ_0 , which has been repeatedly proven to be extremely useful to solve problems or to explain anomalous properties over the years [9-17]. Such expediency in resolving the often perplexing properties of τ_α is unmatched by any other approaches. One might think that if one knows or visualize how the units move, then all problems can be solved. This expectation turns out to be unfulfilled. Even if one can see the individual motion of each unit as a function of time, like confocal microscopy can do with colloidal particles [8], the anomalous scattering wavevector dependence, $\tau_\alpha \propto Q^{2/(1-n)}$, found by light scattering on the same system [18] cannot be explained from the motion pictures [19]. On the other hand, Eq.(3) immediately takes you to the answer from the well-known dependence, $\tau_0 \propto Q^{-2}$, for independent relaxation [20].

3. A schematic theory that incorporates all the determining factors

We have already shown that both specific volume V and entropy S , or alternatively free volume v_f and configurational entropy S_c , are factors that determine the dynamics of

glass-formers. Intermolecular coupling, the other factor, has been taken into account by the CM. Starting with the CM our next task is to construct a schematic theory by incorporating the dependence on v_f and S_e into it. This is efficiently done by recognizing that v_f and S_e enter into the CM through the explicit dependence of τ_0 on v_f and S_e , because the independent relaxation rate is dictated by thermodynamics and hence the dependence. Also taking into account possible explicit dependence of τ_0 on T and P , we have $\tau_0(T, P, V, S)$ or $\tau_0(T, P, v_f, S_e)$. It would be nice to have a theory that gives the dependences of τ_0 on T, P, V and S , or on T, P, v_f and S_e . None of the existing theories are satisfactory because they consider either v_f or S_e but not both together, which is required by the new result from experiments with the application of pressure [21]. Since the objective of the present paper is limited to construct a schematic model, we do not provide a theory $\tau_0(T, P, v_f, S_e)$. In this spirit, this task is considered as detail, which is left for the future.

3.1 α -relaxation

Numerous experimental data and molecular dynamics simulations have shown at long times the observed correlation functions are invariably well approximated by the Kohlrausch function (Eq.2) of the CM. Thus, we do not need any more theory just to assure us that the correlation function is approximately a Kohlrausch function (Eq.2), or to wait for one that gives us the exact coupling parameter n for a real glass-former. The latter is an impossible task for any theory at the present time. We just shrewdly take what the experiment gives us for the value of n , at any temperature or pressure [22]. Since t_c has already been determined to be approximately 2 ps for molecular liquids and polymers, the relation between the measured τ_α and $\tau_0(T, P, v_f, S_e)$ is complete. We write it out again,

$$\tau_\alpha(T, P, v_f, S_e) = [t_c^{-n} \tau_0(T, P, v_f, S_e)]^{1/(1-n)}, \quad (4)$$

for the purpose of making the following point clear. In Eq.(4), that gives us the answer to τ_α , all determining factors have been accounted for. There are possible implicit dependence of n on T, P, v_f and S_e , which is not written out in Eq.(4). The thermodynamic factors of volume and entropy are incorporated into τ_0 , and the effect of intermolecular coupling is obtained by the manipulation of τ_0 shown on the right-hand-side of Eq.(4). The resultant τ_α has both the dependence on T, P, v_f and S_e , and the effect of intermolecular coupling. The dependence of τ_0 on v_f and S_e is the principal cause of deviation of Arrhenius temperature dependence of τ_α with the assist of possible temperature and pressure dependence n . As demonstrated before in glass-formers and other coupled systems, when used judiciously Eq.(4) can explained the other observed properties of τ_α and the associated transport coefficients such as viscosity, diffusion coefficient and d.c. conductivity, especially the anomalous ones. The origin of several found correlations between n and the properties of τ_α are easily traced to the dependence of τ_α on n in Eq.(4).

3.2 The Johari-Goldstein β -relaxation

Secondary or β -relaxations occur at shorter times or higher frequencies and they are often considered to play no important role in determining the glass transition. This attitude is justified for some β -relaxations that involve motion of only a part of flexible molecules. However, Johari and Goldstein (JG) showed that not all β -relaxations have such trivial intramolecular origin by finding β -relaxations even in glass-formers composed of completely rigid molecules [23-25]. This intriguing finding of JG implies that some β -relaxations does not involve intramolecular motion but instead certain motion of the *entire molecule* as a whole. This is definitely the case of rigid molecular glass-formers, and possibly even in all other kinds of glass-formers as shown by dielectric, mechanical and nuclear magnetic resonance measurements in the last thirty years. To honor their important discovery that has fundamental implication for glass transition, this class of β -relaxations is called the Johari-Goldstein (JG) β -relaxations. However, in the current literature, there is an unfortunate tendency that any observed β -relaxation is referred to as the JG β -relaxation without qualification. We have recently classified observed β -relaxations by their dynamic properties and established criteria for genuine JG β -relaxation [26]. The non-JG β -relaxations have no impact on glass transition, and they will not be further discussed in this work.

From our study of the dynamic properties of JG β -relaxation, the indication is that it involves the entire molecule and no many-body effects. Thus, it bears resemblance to the independent relaxation of the coupling model [14-17,27]. In fact, from dielectric measurements in which we can determine the JG β -relaxation time, τ_β and the CM independent relaxation time, τ_0 , from τ_α and n by using $\tau_0 = (t_c)^n (\tau_\alpha)^{1-n}$ (i.e., the converse of Eq.3), we found that

$$\tau_0(T, P) \approx \tau_\beta(T, P) \quad (5)$$

holds for JG relaxations in many glass-formers [14-17,27]. The finding of the correspondence between the calculated τ_0 and the experimentally observed τ_β of JG β -relaxation add credence to the CM. Note that from Eq.(3), the separation between τ_α and τ_0 given by $(\log \tau_\alpha - \log \tau_0) = n(\log \tau_\alpha - \log t_c)$. Hence Eq.(5) implies that the separation between τ_α and τ_β is approximately given by

$$(\log \tau_\alpha - \log \tau_0) = n(\log \tau_\alpha - \log t_c). \quad (6)$$

For the same τ_α the separation decreases as n becomes smaller, and vanishes when n is exactly equal to zero. This is a remarkable prediction because it is a cross relation between the dynamic property of the α -relaxation (i.e., n) on the one hand and that of the JG β -relaxation (i.e., the location of τ_β) on the other hand. This has been verified for many glass-formers, which have resolved JG β -relaxation peak or shoulder [14-17]. In hindsight, some β -relaxation considered in the first work of this kind [14] are not genuine JG β -relaxation and should not have been included. By eliminating them, the correlation becomes even stronger. The dependence of the separation on n is best demonstrated for glass-formers of the same family [28-30], and it also explains why the

JG relaxation is not resolved in glass-formers with smaller n and instead show the appearance of an excess wing [15,16, 26-30].

Actually τ_β is related to the reciprocal of the frequency, ν_β of the JG β -relaxation loss peak. Traditionally, the peak is modeled by a Cole-Cole distribution. In the extended coupling model [17,27] τ_β is interpreted as merely an indicator of the independent relaxation time τ_0 . With further increase in time, there is increasing independent relaxations and many-body relaxation dynamics becomes increasingly important (or increasing degree of “cooperativity”). This evolution of dynamics accounts for the dispersion on the low frequency side of the JG loss peak and continues until full many-body dynamics (or cooperative dynamics) is reached. From this point onwards, the relaxation becomes the α -relaxation and is amenable to the CM description of subsection (a). Because of the increasing development of many-body dynamics with decreasing frequency (increasing time) in the JG relaxation frequency range, the JG β -relaxation is thus heterogeneous with respect to relaxation time constants as seen from dielectric hole burning experiment [31,32].

3.2.1 Support of the proposed dependence of τ_0 on volume and entropy

At the very start in constructing the schematic theory, we proposed to incorporate the dependence on ν_f and S_c through the explicit dependence of the independent relaxation of the CM on ν_f and S_c . As done previously, the independent relaxation time τ_0 is explicitly dependent on ν_f and S_c , i.e., $\tau_0(T, P, \nu_f, S_c)$. Now, having been identified as the indicator of the independent relaxation, the JG β -relaxation should have some characteristics to reflect its dependence on ν_f and S_c . Evidences of this dependence are found in the relaxation strength, $\Delta\epsilon_\beta$ of the JG relaxation [33-36]. $\Delta\epsilon_\beta$ is found to change on heating through the glass transition temperature in a similar manner as the changes observed in the enthalpy H , entropy S , and volume V . The derivative of $\Delta\epsilon_\beta$ with respect to temperature, $d\Delta\epsilon_\beta/dT$, is raised from lower values at temperatures below T_g to higher values at temperatures above T_g , mimicking the same behavior of the specific heat C_p and the expansion coefficient, which are the derivatives dH/dT and dV/dT respectively. The angle of rotation of the JG relaxation, and hence $\Delta\epsilon_\beta$ likely is dependent on the specific volume and entropy. Thus the rate of change of $\Delta\epsilon_\beta$ is similar to the thermodynamic quantities. For the same reason, the angle of rotation or $\Delta\epsilon_\beta$ is expected to be dependent on the thermal history of the glass. A denser glass has a smaller $\Delta\epsilon_\beta$.

As early as in the study by Johari and Goldstein [23-25], the JG relaxation in the glass was found to be affected by the thermal history including the cooling rate used to vitrify the liquid and the aging time. More recent work confirms this by aging studies of $\Delta\epsilon_\beta$ in the glassy state [34-36]. Another recent detailed study of the JG β -relaxation in dipropyleglycol dibenzoate (DPGDB) [37] demonstrates several effects. Firstly, thermal history of the glass has a strong influence on dispersion of the JG β -relaxation. On aging the glass, τ_β of the JG relaxation increases significantly, mimicking the well-known increase of τ_α with aging. It can be easily verified from Eq.(3) that the increase of τ_0 is smaller than that of τ_α with aging. Thus the moderate increase of τ_β observed in DPGDB with aging is similar to that of τ_0 , thus reaffirming the correspondence between τ_β of JG relaxation and τ_0 from their similar changes with aging and the dependence of

τ_0 on ν_f and S_c . A quantitative test of the correspondence between the increase of τ_0 with that of τ_α with aging is possible if the increase of τ_α with aging were measured together with the increase in τ_β .

3.3 The short time cage dynamics

For glass-formers that have a resolved JG β -relaxation and/or non-JG secondary relaxation, the combined dispersion of the α - and β -relaxation of the equilibrium liquid occupies many decades of frequency, making difficult the characterization of the dynamics at times shorter than the β -relaxation. At higher temperatures, the α - and β -relaxation merge together but the relaxation times becomes short and again does not allow the dynamics to be seen over a broad frequency range. Therefore, the best candidates are those glass-formers that have small n so that the separation between τ_α and τ_β of the JG relaxation is short, and no non-JG β -relaxation. Dielectric data of such glass-formers [15-17,38-40] show the loss at high frequencies can be approximately described by the ν^λ -dependence with a small positive exponent λ , or a logarithmic function of ν , or some other slowly varying function of frequency that increases with decreasing ν . Similar dispersion is found in glassy, molten and even crystalline ionic conductors at temperatures where the ions are not moving from site to site in the experimental frequency range [17,41]. The variation of this dispersion with frequency is very slow and hence it is called the nearly constant loss (NCL) in the field of ionic conductors. A good example is the glass-forming molten salt, $0.4\text{Ca}(\text{NO}_3)_2\text{-}0.6\text{KNO}_3$ (CKN), which is both a glass-former and an ionic conductor at the same time [17,41]. The observation of the NCL in glass-formers is not restricted to dielectric relaxation measurement. Dynamic light scattering measurements on polyisobutylene [42], poly(methyl methacrylate) [43] and glycerol [43] have found the near constant loss in the imaginary part of the depolarized and polarized susceptibility, $\chi''(\nu)$, at high frequencies. The optical Kerr effect studies of several organic glass-forming liquids [44] have found the presence of the near constant from the measured time derivative of the correlation function at temperatures below the critical temperature, T_c , of the mode coupling theory [45].

For glass-formers, the NCL regime is found to start at frequencies (times) higher (shorter) than some ν_{x1} (t_{x1}) which is roughly a decade or more higher (shorter) than the calculated independent relaxation frequency, $\nu_0 \equiv 1/2\pi\tau_0$, (τ_0). The same applies to the ionic conductors, where now τ_0 is the independent ion hopping relaxation time [17,41]. From its very definition, τ_0 , or the corresponding JG relaxation time τ_β is the shortest possible relaxation time of the entire molecule of any amplitude. We have found from experimental data of glass-former in general that t_{x1} is significantly shorter than τ_0 . Because of this empirical relation between t_{x1} and τ_0 and the meaning of τ_0 , whatever the nature of the NCL, the relaxation responsible for it proceeds when essentially all molecules remain caged. The motion within the cage has very limited displacement and the integrated total loss from the onset frequency to ν_{x1} has to be small, and thus the slow increase of the loss with decreasing frequency, i.e., the NCL behavior.

One would like to use the mode coupling theory [45], which is the best-known theory for caged dynamics, to describe the experimental data. Unfortunately, the standard mode coupling theory does not predict the NCL except under very special

potential and condition [44,46], but NCL is found in glass-formers of many chemical forms with different potentials. NCL as a background loss can give rise to a susceptibility minimum having ν^b and ν^p -dependences on the low and high frequency sides. This happens at high temperatures, when τ_α becomes short or the α -loss peak frequency ν_α sufficiently high. Then, the extent of the NCL is shrunk by the encroaching high frequency flank having the $\nu^{(1-n)}$ -dependences on the low frequency side and on the high frequency side by the low frequency flank of the vibrational or Boson peak contribution. The result is a susceptibility minimum as observed by dielectric relaxation, neutron and light scattering experiments at higher temperatures where τ_α becomes short, typically of the order of nanoseconds. On the other hand, it is obvious that a susceptibility minimum predicted by the standard mode coupling theory conversely cannot account for the NCL. Thus, other mechanisms of caged dynamics based on nonlinear Hamiltonian dynamics (e.g., chaos) of caged motion are worth considering. An example is that suggested in Reference 47. A satisfactory theory of caged dynamics is not at hand at this time. But, in the spirit of this work of constructing a schematic theory, we are only concerned with elucidating the properties of the short time caged dynamics, and leaving the theory to be developed in the future.

4. Discussion

There are many factors that determine the dynamics of glass transition. The obvious thermodynamic factors are temperature T and pressure P . The other thermodynamic factors are specific volume V and entropy S or the related free volume ν_f and configurational entropy S_c , the latter two quantities are model-dependent. Recent results of studies at high pressure suggest in many glass-formers *all* these quantities enter into the determination of the mobility of relaxation and diffusion. However, these thermodynamic factors alone can describe neither the many-body relaxation dynamics nor the anomalous properties generated and observed by experiments. Therefore, in addition to the thermodynamic factors, there is the need to include intermolecular coupling and constraints. The strength of intermolecular coupling varies from glass-former to glass-former, dependent on structure, chemical bonding and intermolecular potential. Increase of the intermolecular coupling strength would exacerbate the complexity of the many-body relaxation dynamics and the anomalies. With so many essential factors playing different roles, it is not surprising that the glass transition problem is intractable and not amenable to rigorous theoretical treatment. This is the reason why the problem has already a long history and closure is still not in sight. Improvement of the situation is not helped by theories or models, claiming to have solved the glass transition problem, but have neglected to consider one or more of the essential factors. However, if we do not demand a complete and rigorous solution of the problem, I have shown how all the factors can be incorporated into a schematic description of glass transition with the advantage that *all* the salient features of the dynamics are explained, including the anomalous ones. Of course there is still more detailed theoretical works to be done, but at least we have a good conceptual understanding and explanations, some even quantitative, for the experimental data.

The most commonly neglected factor in extant theories is intermolecular coupling. On the other hand, intermolecular coupling is the heart and soul of the coupling model (CM). It

identifies the stretching of the dispersion, Eq.(2), as due to intermolecular coupling, and n in the stretch exponent is “proportional” to intermolecular coupling strength. To generate predictions, it takes advantage of the crossover from independent relaxation, Eq.(1), to the stretched exponential relaxation, leading to the relation, Eq.(3), between the independent relaxation time τ_0 and the relaxation time τ_α of the complex many-body dynamics. Since τ_0 is understandable and n interpretable as proportional to intermolecular coupling strength, Eq.(3) spawns many predictions and explanations for anomalous dynamic properties. The CM is not a full theory of the many-body relaxation dynamics, and certainly it is far from being a theory of glass transition. However, we can build on it to arrive at a schematic description of glass transition by incorporating the dependence of the dynamics on the thermodynamics factors, T , P , v_f and S_c . This step is facilitated by the explicit dependence of τ_0 on T , P , v_f and S_c . A strong support of this scheme comes from the “universal” genuine Johari-Goldstein β -relaxation, which not only has properties identifiable with the independent relaxation but also similar relaxation times. The relaxation strength and time of the JG β -relaxation are found by experiments to depend on entropy and volume, and these findings in turn supports the proposed dependence of τ_0 on v_f and S_c . There is another recently found property [48] that indicates the dependence on v_f and S_c originates from τ_0 , which gives rise to the dependence of τ_α on v_f and S_c via intermolecular coupling by Eq.4.

We have seen the dynamics in the short time (high frequency) regime is more generally the nearly constant loss (NCL). The upper (lower) bound in time, t_{x1} , (frequency, ν_{x1}) of the NCL regime increase (decreases) with decreasing temperature. There is no restriction on the temperature and it can fall below T_g . At sufficiently high temperatures, the NCL gives rise to susceptibility minima. It is remarkable that for many glass-formers τ_0 is significantly larger than t_{x1} . This relation immediately suggests that in the NCL regime, $t < t_{x1}$, the loss does not come the independent relaxation. All molecules remain caged. Although more theoretical work has to be done because the mechanism of the NCL becomes apparent, a conceptual understanding of the short time dynamics is at hand. The NCL phenomenon is interesting because it is also a general feature. But, it has no impact on relaxation or diffusion dynamics (i.e., glass transition) because it is just the dynamic of molecules when effectively all of them are caged. There is no doubt that NCL is an integral part of the evolution of molecular dynamics from short times to long times, but can be considered as a separate problem from the main theme of relaxation dynamics in glass transition. This view of caged dynamics is in contrast to that taken by the standard mode coupling theory (MCT), which uses its solution of the caged dynamics to deduce glass transition dynamics. MCT only considers susceptibility minima and the temperatures range is restricted to above the critical temperature, T_c . However, experiments have found at lower temperatures that the susceptibility minimum is no longer there and instead the NCL appears [17,41].

By no means this schematic description of glass transition dynamics is the ultimate goal of a theory of glass transition. Nevertheless, it has embodied conceptually the essential determining factors from thermodynamics and intermolecular coupling. None of these factors can be easily incorporated into a rigorous theory, and certainly even

more difficult when required to have all factors included simultaneously. It is therefore impractical to wait for the emergence of such a theory. Instead, if we lower our ambition and accept for the time being the schematic description, at least we can understand all the properties of glass transition including the anomalous ones. Then we have temporarily a closure of the problem of the dynamics of glass transition and not let it drag on indefinitely.

The way intermolecular coupling is treated here for glass transition by the crossover from independent relaxation to stretched exponential relaxation is economical and generally applicable to other systems. Applied to glass transition in amorphous polymers, we have

shown that it can resolve [49] the breakdown of thermorheological simplicity of the viscoelastic responses [50]. There are other applications to problem unrelated to glass transition. An example is the explanation of the dynamics of ions in vitreous, molten and crystalline ionic conductors [51].

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6. References

1. Angell, C.A., Ngai, K.L., McKenna, G.B., McMillan, P.F., and S.W. Martin (2000) *J.Appl.Phys.* **88**,3113.
2. Ngai, K.L. (2000)*J.Non-Cryst.Solids* **275**, 7.
3. Doolittle, A.K. (1951) *J.Appl.Phys.* **22**, 1031.
4. Cohen, M.H. and Turnbull, D. (1959) *J.Chem.Phys.* **31**, 1164.
5. Gibbs, J.H. and DiMarzio, E.A. (1958) *J.Chem.Phys.* **28**, 373.
6. Adam G. and Gibbs, J.H. (1965) *J.Chem.Phys.* **43**, 139.
7. Kob W, Donati C, Plimpton, J., Poole P.H. and Glotzer S.C. (1997) *Phys.Rev.Lett.* **79**, 2827
8. Weeks E.R., Crocker J.C., Levitt A., Schofield A., and Weitz D.A. (2000) *Science* **287**, 627.
9. Ngai, K.L. (1979) *Comment Solid State Phys.* **9**, 127; **9**, 141.
10. Tsang K. Y. and Ngai, K.L. (1997) *Phys. Rev. E* **54**, 3067.
11. Ngai, K.L. and Tsang, K.Y. (1999) *Phys.Rev.E* **60**, 4511.
12. Ngai, K.L. (2001) *IEEE Transactions in Dielectrics and Electrical Insulation* **8**, 329.
13. Ngai, K.L. and Rendell, R.W. (1997) Coupling model explanation of salient dynamic properties of glass-forming substances, in J.T. Fourkas, D. Kivelson, U. Mohanty, and K. Nelson, (eds.), *Supercooled Liquids, Advances and Novel Applications*, ACS Symposium Series Vol. **676**, Am.Chem.Soc., Washington, DC. pp. 45-63.
14. Ngai, K.L. (1998) *J.Chem.Phys.* **109**, 6982.
15. Ngai, K.L.; Lunkenheimer, P.; León, C.; Schneider, U.; Brand, R., and Loidl, A. (2001) *J.Chem.Phys.* **115**, 1405.
16. Paluch, M., Ngai, K.L., Hensel-Bielowka, S. (2001) *J.Chem.Phys.* **114**, 10872.
17. Ngai, K.L. (2003)*J.phys.:Condens.Matter***15**,S1107.
18. Segre, P.N. and Pusey, P.N. (1996) *Phys.Rev.Letters*, **77**, 771.
19. Several years ago, I issued a friendly challenge to Eric Weeks, principal author of Ref.8, to explain the $\tau_\alpha \propto Q^{2/(1-\nu)}$ from the motion of the colloidal particles collected by his confocal microscopy method. So far, I have not been given an answer.
20. Pecora, R., "Dynamic Light Scattering", (1986) Academic, N.Y.

21. Paluch, M., Casalini, R., and Roland, C.M. (2002) *Phys.Rev.B*, **66**, 092202.
22. *Only for a homogenous liquid that is comprised of identical molecules. If the glass-former is mixed with another glass-former, concentration fluctuations cause distribution of coupling parameters. None of coupling parameters in the distribution can be obtained from the measured dispersion. Similar caution applies to glass-formers that has become spatially heterogeneous due to the influence of surfaces or interfaces. See Roland, C.M. and Ngai, K.L. (1992) Macromolecules*, **25**, 363: **24**, 2261.
23. Johari, G.P. and Goldstein, M. (1970) *J. Chem. Phys.* **53**, 2372.
24. Johari, G. P. (1973) *J. Chem. Phys.* **58**, 1766.
25. Johari, G.P. (1976) *Annals New York Acad.Sci.* **279**, 117.]
26. Ngai, K.L. and Paluch, M. (2003) to be published.
27. Ngai, K.L. and Paluch, M. (2003) *J.Phys.Chem.B*, in press.
28. León, C, Ngai, K.L., and Roland, C.M. (1999) *J. Chem. Phys.*, **110**, 11585.
29. Döb, A., Paluch, M., Sillescu, H. and Hinze, G. (2002) *J. Chem. Phys.* **117**, 6582.
30. Mattsson, J., Bergman, R., Jacobsson, P., and Börjesson, L. (2003) *Phys.Rev.Lett.* **90**, 075702.
31. R. Richert, (2001) *Europhys. Lett.* **54**, 767.
32. Duvvuri, K. and Richert, R. (2003) *J.Chem.Phys.* **118**, 1356.]
33. Wagner, H. and Richert, R. (1999) *J. Phys. Chem. B*, **103**, 4071.
34. Johari, G.P., Powers, G., and Vij, J.K. (2002) *J.Chem.Phys.* **116**, 5908.
35. Johari, G.P., Powers, G., and Vij, J.K. (2002) *J.Chem.Phys.* **117**, 1714.
36. Powers, G., Johari, G.P., and Vij, J.K. (2003) *J.Chem.Phys.* **xxx**, yyy
37. Prevosto, D., Bramanti, G., Lucchesi, M., Capaccioli, S., and Rolla, P.A., (2003) paper presented at the 9th International Workshop on Disordered Systems, Andalo, Italy.
38. Hofmann, A., Kremer, F., Fischer, E.W. and Schönhals, A. (1994) *Disorder Effects on Relaxational Processes*, R. Richert and A. Blumen (eds.), Springer, Berlin, pp. 309-325.
39. León, C., and Ngai, K.L. (1999) *J.Phys.Chem.B*, **103**, 4045.
40. Kudlik, A., Benkhof, S., Blochowicz, T., Tschirwitz, C., and Rössler, E. (1999) *J.Mol.Struture*. **479**, 210.
41. León, C. and Ngai, K.L., (2002) *Phys.Rev.B* **66**, 064308.
42. Sokolov, A.P., Kisliuk, A., Novikov, V.N. and Ngai K.L. *Phys. Rev. B* **63**, 172204.
43. Caliskan, G., Kisliuk, A., Sokolov, A.P., and Novikov, V.N. (2001) *J.Chem.Phys.*, **114**, 10189.
44. Cang, H., Novikov, V.N., and Fayer, M.D. (2003) *J.Chem.Phys.*, **118**, 2800.
45. Götz, W., (1999), *J.Phys.:Condens.Matter* **11**, A1.
46. Fabbian, L., Götz, W., Sciortino, F., and Tartaglia, P. (2002) *Phys.Rev.E*, **60**, 2430.
47. Rivera, A., Santamaría, J., León, C., Sanz, J., Varsamis, C. P. E., Chrysikos, G. D., and Ngai, K.L., *J.Non-Cryst.Solids* (2002) **307-310**, 1024.
48. Casalini, R., Ngai, K.L., and C.M. Roland, (2003) *Phys.Rev.B*, **68**, 0142xx.
49. Ngai, K.L., D.J. Plazek, and Rendell, R.W. (1997) *Rheol. Acta*, **36**, 307.
50. Ngai, K.L. and D.J. Plazek (1995) *Rubber Chem.Tech. Rubber Reviews* **68**, 376.
51. Ngai, K.L. and León, C. (2002) *Phys.Rev.B*, **66**, 064308.

TRANSIENT GRATING EXPERIMENTS IN SUPERCOOLED LIQUIDS.

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Abstract. After a brief description of a transient grating experiment, we discuss the detection mechanisms involved in such an experiment. We give the equations of motion for a liquid of anisotropic molecules, which include the relaxation effects typical of the supercooled phase and the sources at the origin of the three effects (thermal, electrostrictive and birefringent) producing the transient grating. Two experimental examples are given, one in which the molecular anisotropy is negligible and the second, in which the effect coming from the molecular anisotropy represents up to twenty percent of the total signal diffracted by the transient grating.

1. Introduction

For several years, supercooled liquids have been the subject of extensive theoretical and experimental studies [1]. The main characteristic of the liquid–glass transition is the structural relaxation which considerably slows down the liquid dynamics at decreasing temperature. This structural relaxation can be characterized by measuring different relaxing variables, and one of the important issues is to describe and understand the interplay between them. This requires to carry out investigations over a very wide domain in time or frequency, which can usually be fully investigated only by combining several experiments : in light scattering, three techniques, Raman and depolarized tandem Fabry-Perot scattering and photon correlation spectroscopy are necessary to measure the orientational correlation function over the whole domain. Transient grating (TG) experiments [2] give a unique insight into the dynamics of supercooled liquids : using a continuous wave beam probe allows to investigate a very wide temporal domain, ranging from nanoseconds to milliseconds, a unique feature in optical measurements. Moreover, the typical wavevectors are located between the wavevectors of an acoustic measurement and of a Brillouin experiment.

In a spontaneous Brillouin experiment, one of the characteristics of the liquid-glass transition is the observation of propagative transverse acoustic modes inside the supercooled liquid or even in the liquid phase. In molecular liquids, these modes are detected through the fluctuations of the molecular orientation, which will scatter the

light only if the molecular polarisability tensor is anisotropic. In a TG experiment, effects due to the anisotropy of the polarisability tensor are also to be expected [3] ; the one investigated here is the dependence of the shape of the measured signal on the polarisation of the laser beams, giving access simultaneously to two relaxing variables. We briefly describe here TG experiments on supercooled liquids : we discuss the detection mechanism and the relevant hydrodynamics equations. After giving the expression of the diffracted signal obtained by solving these equations, we show the results obtain in two different experimental cases.

2. Transient grating experiment and detection mechanisms

2.1 Transient grating experiment

In a TG experiment, two high power laser pulses interfere inside the sample, producing a spatially periodic variation of the refraction index [2]. This transient grating is probed by a second laser beam which is diffracted. The diffracted beam yields the detected signal, which gives information on the dynamics of the relaxing transient grating (Figure 1). The wave vector is given by :

$$(2.1) \quad q = 4\pi \frac{\sin(\theta/2)}{\lambda}$$

where θ is the angle between the excitation beams and λ , the wavelentgh of the excitation pulse. The detected signal is actually very weak so that the detection efficiency is greatly enhanced when a heterodyne detection (HD) is performed, as in the present experiment [4].

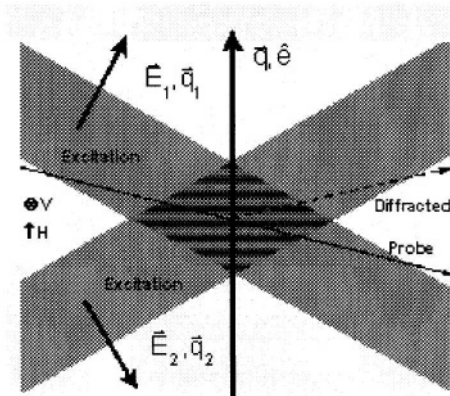


Figure 1

2.2 Detection mechanism

According to Yang and Nelson [2], the transient grating can be described as a pure phase grating generated by two different mechanisms : first, the electric field gradient generates directly a density transient grating by an electrostrictive effect. A weak absorption of the pulse energy in combination or overtones of vibrational levels, which usually thermalizes in a few picoseconds, is at the origin of a second mechanism : the localized heating produces a density grating. The relative magnitude of both contributions depend on the material and on the laser wavelength. Furthermore, as discovered recently [3], in a fluid of anisotropic molecules, i.e. with a non negligible dielectric tensor anisotropy, modification of the molecular orientation due to its coupling to the electric field (Optical Kerr effect) or to alignment induced by translational orientational coupling can give a local anisotropic contribution to the transient grating. The importance of this effect can be obtained by comparing the signal coming from different polarisations of the probe and excitation beams, as seen below. The fluctuations of the dielectric tensor created by density and/or orientational fluctuations can be written [3] as:

$$(2.2) \quad \delta \bar{\bar{\epsilon}}(\vec{r}, t) = a \delta \rho(\vec{r}, t) \bar{\bar{I}} + b \bar{\bar{Q}}(\vec{r}, t)$$

where $\delta \rho(\vec{r}, t)$ is the density fluctuation, a and b are respectively the derivative of the liquid susceptibility with respect to the mass density and the anisotropic part of the polarisability tensor, $\bar{\bar{Q}}(\vec{r}, t)$ is an orientational probability density which has the form of a symmetrical traceless tensor. In the present case, the excitation beams create density and orientation fluctuations, compared to which their thermal fluctuations are negligible. In a HD-TG experiment, the detected quantity is directly proportional to the fluctuation of the dielectric tensor, which is itself the convolution of the response function of the medium by the temporal shape of the excitation beams [4].

The HD-TG experiments described here have been performed with excitation beams with identical amplitude E and polarisation of the electric field, and identical polarisations of the probe and the diffracted beams. Polarisation can be either vertical, V (perpendicular to $\vec{q}_1$ and $\vec{q}_2$) or horizontal, H (practically parallel to $\vec{q}$). The fluctuation of the ii (i being V or H) component of the dielectric tensor, $\delta \epsilon_{ii}(\vec{r}, t)$, is given by:

$$(2-3) \quad \delta \epsilon_{ii}(\vec{q}, t) \approx R_{ii,jj}(\vec{q}, t) E^2$$

where j is the polarisation of the excitation beams, and i , the polarisation of the probe and the diffracted beams.

3. Equations of motion

The fluctuations of density and orientation are obtained by solving a set of hydrodynamics equations including the description of the medium and of the excitation.

3.1 Hydrodynamic equation of a fluid of anisotropic particles in non-forced regime

The Navier Stokes equations describe the dynamics of the fluid. For a liquid, this set is obtained by combining the equations of conservation of mass, momentum and energy and the constitutive equation which describes the mechanical stress of the liquid. The conservation of the mass and of the momentum are given by :

$$(3-1) \quad \dot{\rho}(\vec{r}, t) + \text{div } \vec{J}(\vec{r}, t) = 0$$

$$(3-2) \quad \dot{\vec{J}}(\vec{r}, t) = \text{div } \overline{\overline{\sigma}}(\vec{r}, t)$$

where ρ is the mass density, $\vec{J}$ is the mass current density ($\vec{J} = \rho_m \vec{v}$ with ρ_m the equilibrium mass density and $\vec{v}$ is the mean linear velocity) and $\overline{\overline{\sigma}}$ is the stress tensor. When the dynamics of orientational variables contributing to the total dynamics of a liquid of anisotropic particles must be taken into account, $\overline{\overline{\sigma}}$ is expressed as:

$$(3.3) \quad \overline{\overline{\sigma}} = (-c_i^2 \delta \rho - \rho_m \beta \delta T + \eta_b \text{div } \vec{v}) \overline{\overline{I}} + \eta_s \overline{\overline{\tau}} - \mu \overline{\overline{Q}}$$

where c_i is the isothermal sound velocity, β is the expansion coefficient, η_s , η_b and μ are respectively the shear and bulk viscosities and the translation-rotation coupling coefficient, δT the temperature fluctuation around the mean temperature T , $\overline{\overline{I}}$ and $\overline{\overline{\tau}}$ are the unity tensor and the strain rate traceless second rank tensor:

$$(3-4) \quad \tau_{ij} = \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3} \text{div } \vec{v} \delta_{ij}$$

Furthermore, the equation of motion for $\overline{\overline{Q}}(\vec{r}, t)$ must be included. It reads:

$$(3-5) \quad \ddot{\overline{\overline{Q}}} = -\omega_R^2 \overline{\overline{Q}} - \Gamma \dot{\overline{\overline{Q}}} + \Lambda \mu \overline{\overline{\tau}}$$

where Γ is the orientational relaxation coefficient, ω_R is the libration frequency of the axial molecules, and Λ is the rotation-translation coupling constant [3,5].

The equation of conservation of energy reads as [6]:

$$(3-6) \quad C_v \dot{T} - T \beta \dot{\rho} - \lambda \Delta T = 0$$

where C_v is the specific heat at constant volume per unit volume and λ is the heat diffusion coefficient.

3.2 Retardation effects

The next step is to introduce retardation effects in Eqs 3-3, 3-5 and 3-6. Retardation effects express the fact that some of the motions inside the supercooled fluid become very slow with decreasing temperature, so that the time dependence of the viscosity and of other transport coefficients corresponding to friction forces can no longer be neglected. This means that convolution products (represented by $\otimes$) should be substituted to simple products in these equations. The retardation effects in Eqs 3-3 and 3-5 have been first introduced on purely phenomenological arguments [5a] and have

been since rigorously demonstrated [5b]. Using the same heuristic argument, retardation effects can also be introduced in Eq.3-6 assuming a time dependence on the specific heat C_v and on the expansion coefficient β :

$$(3-7) \quad C_v \otimes \dot{T} - T\beta \otimes \dot{\rho} - \lambda \Delta T = 0$$

3.3 External sources

For $\mathbf{q}_0 = |\bar{\mathbf{q}}_1| = |\bar{\mathbf{q}}_2|$ (see Figure 1), the total electric field associated with the two pumps can be written as:

$$(3-8) \quad \bar{\mathbf{E}}(\bar{\mathbf{r}}, t) = E \hat{\mathbf{e}} \exp(i(q_0 z - \omega t)) \cos(q_0 \theta/2 x) \delta(t)$$

Three different physical effects act as sources and one of them has to be added to each of the Eqs. 3-3, 3-5 and 3-6: (i) The first effect is the energy absorption by the liquid. The absorbed energy is proportional to the density of local electromagnetic energy.

$$(3-9) \quad U(\bar{\mathbf{r}}, t) = E^2 \cos(qx) \delta(t)$$

This absorbed heat acts as an external source so that equation becomes [7]:

$$(3-10) \quad C_v \otimes \dot{T} - T\beta \otimes \dot{\rho} - \lambda \Delta T = HU(\bar{\mathbf{r}}, t)$$

The second effect is the interaction of the space varying electromagnetic energy with the isotropic part of the molecular polarisability tensor. This generates the electrostrictive effect and results in the introduction of an additional term in Eq. 3-3 :

$$(3-11) \quad \bar{\bar{\sigma}} = (-c_i^2 \delta \rho + \eta_b \otimes \text{div} \bar{\mathbf{v}} - \rho_m \beta \otimes \delta T) \bar{\bar{\mathbf{I}}} + \eta \otimes_s \bar{\bar{\tau}} - \mu \otimes \bar{\bar{\mathbf{Q}}} + KU \bar{\bar{\mathbf{I}}}$$

where K is a positive number proportional to a.

Finally, the interaction of the electric field, $\bar{\mathbf{E}}(\bar{\mathbf{r}}, t)$ with the anisotropic part of the molecular polarisability of a linear molecule generates a torque on the molecules. It can be shown that this leads to the appearance of a source term which has to be added to Eq. 3-5. This equation now reads :

$$(3-12) \quad \bar{\bar{\mathbf{Q}}} = -\omega_R^2 \bar{\bar{\mathbf{Q}}} - \Gamma \otimes \bar{\bar{\mathbf{Q}}} + \Lambda \mu \otimes \bar{\bar{\tau}} + FU \bar{\bar{\mathbf{C}}}$$

where F is proportional to b and

$$(3-13) \quad C_{ij}(\hat{\mathbf{e}}) = \hat{\mathbf{e}}_i \cdot \hat{\mathbf{e}}_j - \frac{1}{3} \delta_{ij}$$

The source term in Eq. 3-12 has the same origin and the same role as in an Optical Kerr Effect (OKE) experiment: it tends to orient the molecules along the direction of the field for $b > 0$ and perpendicular to it for $b < 0$.

4-Solution and polarisation dependence

Solving the above equations yields the terms $\delta\rho$ and δQ which appear in Eq 2-2 ; Without entering into the detail of the calculations, which can be found in [7], the response function $R_{ii,jj}(\vec{q}, t)$ is given by :

$$(4-1) \quad R_{ii,jj}(\vec{q}, t) = \frac{1}{2\pi} \int_0^\infty \text{Re} \left[R_{ii,jj}(\vec{q}, \omega) \right] \cos(\omega t) \, d\omega$$

with:

$$(4-2) \quad R_{ii,jj}(\vec{q}, \omega) = R_{ii,jj}^1(\omega) + R_{ii,jj}^2(\vec{q}, \omega)$$

$$(4-3) \quad R_{ii,jj}^1(\omega) = \frac{(1 + 3\varepsilon_p \varepsilon_{ex})}{6} b \, D(\omega)^{-1} \, F$$

$$(4-4) \quad R_{ii,jj}^2(\vec{q}, \omega) = \left[a + \frac{(3\varepsilon_p - 1)}{3} \frac{\Lambda}{\rho_m} r(\omega) b \right] P(\vec{q}, \omega) A(\vec{q}, \omega)$$

$$(4-5) \quad A(\vec{q}, \omega) = - \left[i \frac{\rho_m \beta(\omega)}{\lambda} \frac{H}{1 + i\omega\tau_h} + q^2 \left(K + \frac{(3\varepsilon_{ex} - 1)}{6} r(\omega) F \right) \right]$$

where $D(\omega)$ is a function closely connected to the rotational relaxation function $\Gamma(\omega)$, $r(\omega)$ the translational-rotational coupling function, $P(\vec{q}, \omega)$ is the propagator of longitudinal phonons and τ_h is the thermal diffusion time at wavevector $\vec{q}$; ε takes the value 1 for V polarisation and -1 for H polarisation, ex and p stand respectively for the polarisation of the excitation and of the probe beams.

Each of the three sources, H, heat, K, electrostriction, and F, torque, acts as a source (Eq 4-5). The two first sources launch longitudinal phonons with wave vector $\vec{q}$. The orientational torque orients the molecules, generating the OKE contribution to the signal (Eq. 4-3). Through the orientation-rotation coupling mechanism, this orientational torque also launches a longitudinal phonon through the third term in right-hand side of Eq. 4-5. The three sources appear as origins of the longitudinal phonons which generate an isotropic (term in a) and an anisotropic (term in b) changes in the dielectric tensor.

To summarize, $R_{ii,jj}^1(\omega)$ is the usual Kerr effect term while $R_{ii,jj}^2(\vec{q}, \omega)$ corresponds to all the effects due to the longitudinal phonons. Finally, Eqs. 4-1 to 4-5 make it clear that the four $R_{ii,jj}(\vec{q}, t)$ response functions are all different : the directions V and H are not equivalent because of the symmetry breaking introduced by the standing phonons with wavevector $\vec{q}$; also $R_{VV,HH}(\vec{q}, t) \neq R_{HH,VV}(\vec{q}, t)$ because there is no

symmetry between the excitation, which contains an irreversible heat absorption and diffusion process, and the probe.

5. Experimental results

Eq. 4-2 depends on the excitation and probe polarisations : besides the polarisation independent terms, four terms arise depending respectively on $(1+3\epsilon_p\epsilon_{ex})$, $(3\epsilon_p - 1)$, $(3\epsilon_{ex}-1)$ and $(3\epsilon_p - 1)(3\epsilon_{ex}-1)$. Disentangling these five contributions while we can only measure four independent response functions is not possible except if some contributions are negligible compared to others. We shall see below some examples of such behaviour.

5-1 No polarisation dependence : the case of *O*-Terphenyl

So far, only few case of supercooled liquids have been considered and the polarisation effect has only recently been taken into account [3,4,8]. In the case of *o*-terphenyl [4], experiments with the four polarisations show no difference in the signal. This is in line with the rather globular form of this molecule. The signal depends only on thermal and electrostrictive contributions, which cannot be disentangled as both are polarisation independent. The signal measured at different temperatures is shown in Figure 2 : at short times ($t < 1\mu s$) the longitudinal acoustic mode is present whereas at long time ($t > 50\mu s$), the signal represents the return to thermal equilibrium. The signature of the structural relaxation is clearly visible at $T = 273K$: the signal increases after $1\mu s$, before reaching its maximum value around $25\mu s$.

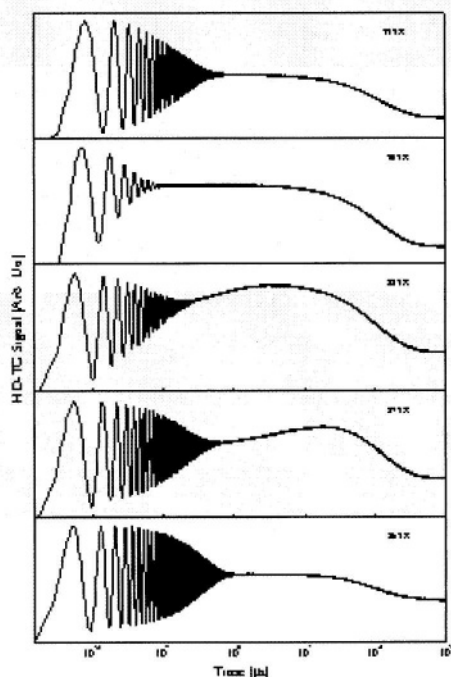


Figure 2. – HD-TG data on *o*-terphenyl for $q=0.338\mu m^{-1}$, at several temperatures. The data show damped acoustic modes at short times and thermal diffusion at long times. At first, the signature of the structural relaxation appears as a strong acoustic damping. At lower temperature, it appears as a gradual rise of the signal in between the acoustic oscillations and the return to thermal equilibrium.

Indeed the density adjusts with its own relaxation time to the local temperature grating that is created instantaneously by the heat absorption ; when this time is long enough, the growth of the density grating is directly detected in the experiments. From an analysis of the signal according to [2], Torre *et al* [4] estimated the structural relaxation time of the density fluctuations as well as the sound velocity and absorption.

5-2 Polarisation dependence : the case of *M-Toluidine*

In *m*-toluidine, the signal is dependent on the polarisation of the probe beam and only on it [3]. This means that the pure OKE contribution is negligible (Eq. 4-3). In figure 3a, the signals detected at different temperatures are shown for two different polarisations of the probe beam. By using the following equations :

$$(5-1) \quad R_{\text{iso}}(t) = \frac{1}{3}(2R_{\text{VVVV}}(t) + R_{\text{HHVV}}(t))$$

$$(5-2) \quad R_{\text{aniso}}(t) = \frac{1}{2}(R_{\text{VVVV}}(t) - R_{\text{HHVV}}(t))$$

it is now possible to disentangle the response functions R_{iso} and R_{aniso} coming from the isotropic and the anisotropic parts of the polarisability (Figure 3b):

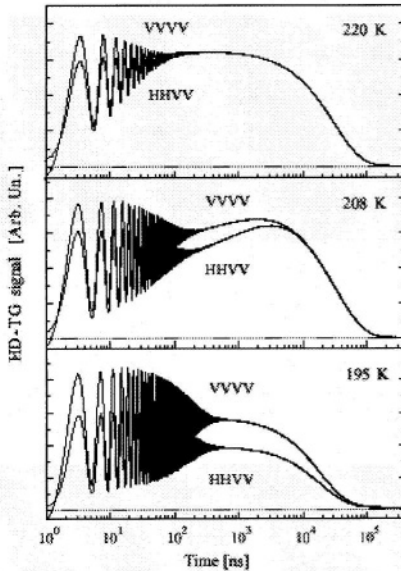


Figure 3a: Diffracted signal in VVVV and HHVV polarisations at 220,208 and 195K and $q=0.68\mu\text{m}^{-1}$ in *m*-toluidine

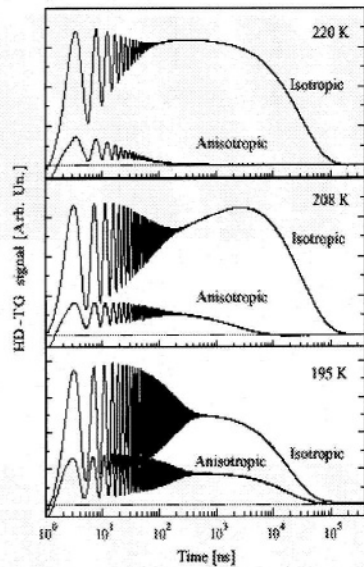


Figure 3b: Isotropic and anisotropic signals at $q=0.68\mu\text{m}^{-1}$ in *m*-toluidine, same temperatures.

Using Eqs 5-1 and 5-2 and writing the phonon propagator $P(\vec{q}, \omega)$ as:

$$P^{-1}(\vec{q}, \omega) = \left[\omega^2 - q^2 \rho_m^{-1} (c_i^2 \rho_m + \omega \eta_L(\omega)) \right] \quad (5-3)$$

and assuming analytical forms for the different relaxation functions, we have performed a fit on the experimental curves of Figure 3b. We assume here Cole-Davidson functions for $\omega \eta_L(\omega)$ and $r(\omega)$:

$$\omega \eta_L(\omega) \rho_m^{-1} = \Delta_L^2 \left[1 - \left(\frac{1}{1 + i\omega \tau_L} \right)^{\beta_L} \right] + i\omega \gamma_L \quad (5-4)$$

$$r(\omega) = \Delta_R^2 \left[1 - \left(\frac{1}{1 + i\omega \tau_\mu} \right)^{\beta_L} \right] \quad (5-5)$$

where τ_L and τ_μ , are respectively the translational relaxation and the translation-rotation coupling times, γ_L represents the acoustic attenuation in the solid phase, β_L is the stretching parameter and Δ_L and Δ_μ , the amplitudes of the relaxation functions associated to the longitudinal viscosity and to the rotation-translation coupling.

We show in Figure 4 the relaxation times τ_L , τ_μ and τ_h obtained in these fits together with the orientational relaxation time, τ_R , obtained in the analysis of the low frequency part of the rotational dynamics by Aouadi *et al.* [9]. Values of β_L were taken from the same authors. We see that τ_h is temperature independent as long as $\tau_L < \tau_h$, while τ_L strongly increases with decreasing temperature. In this temperature domain, $\tau_L / \tau_R < 1$, the ratio increasing up to the temperature at which $\tau_R \approx \tau_h$. At lower temperatures, our fits yield values of $\tau_h(T)$ that are definitely shorter than at higher temperature an effect that has no reason to take place if the specific heat has no frequency dependence, also the analysis suggests that $\tau_L / \tau_R \approx 1$. This “anti-crossing” behaviour of τ_L and τ_h indicates that the role of the frequency dependence of $C_v(\omega)$ and $\beta(\omega)$, which have been neglected so far, have indeed to be explored in more details before a definite conclusion can be drawn on the origin(s) of the effect. Finally, as already suggested in Taschin *et al.* [3], we find that τ_μ is larger than τ_L . A constant ratio of τ_μ / τ_L close to 2.5 seems to describe properly the anisotropic signal in the region 225 K-208 K in which τ_L increases by a factor larger than 10^2 .

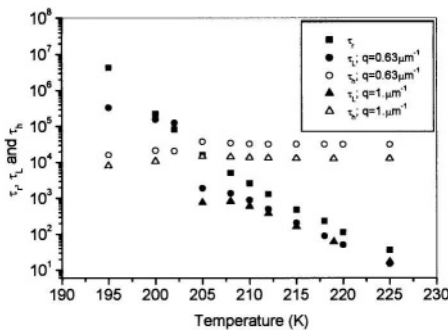


Figure 4. - *m*-toluidine: τ_R (■) from [1], τ_L (○), and τ_h (◇) (—) for $q=0.63 \mu m^{-1}$, τ_L (7), and τ_h (8) for $q=1. \mu m^{-1}$, deduced from the isotropic spectra. See the “anti-crossing” behaviour of τ_L and τ_h around $T=205$ K where $\tau_L \approx \tau_h$.

6. Conclusion

HD-TG experiments are a powerful technique to explore several aspects of the liquid glass transition otherwise difficult to study : the sound velocity and sound absorption are obtained in a range of wave vectors in-between ultrasonics and Brillouin measurements, different relaxation functions and associated relaxation times can be studied and measured simultaneously in a very large range of time. Also progresses in the determination of the relaxational part of thermodynamical quantities like specific heats could be expected by using HD-TG.

7. References

1. W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992); W. Götze; in Liquids Freezing and the Glass Transition, ed. J. P. Hansen, D. Levesque and J. Zinn-Justin, North-Holland, Amsterdam, p.287, (1990).
2. Y. Yang and K. Nelson, J. Chem. Phys. **103**, 7722 (1995). *ibid.*, **103**, 7732 (1995). *ibid.*, **104**, 5429 (1996)
3. A.Taschin, R.Torre, M. Ricci, M. Sampoli, C. Dreyfus and R.M. Pick, Euro. Phys. Lett. **56**, 407 (2001). R.M. Pick, C. Dreyfus, A. Azzimani, A. Taschin, M. Ricci, R. Torre, and T. Franosch, J. Phys.:Cond. Matter, **15**, S825 (2003).
4. R. Torre, A. Taschin and M. Sampoli, Phys. Rev. E **64**, 061504 (2001).
5. a) C. Dreyfus, A. Aouadi, R.M. Pick, T. Berger, A. Patkowski and W. Steffen, Europhys. Lett. **42**, 55 (1998) ; *ibid.*, Euro. Phys. J. B **9**, 401 (1999). b) T. Franosch, A. Latz and R. M. Pick, Euro. Phys.J **B 31**, 229 (2003).
6. J.P. Boon and S. Yip, *Molecular Hydrodynamics* McGraw-Hill, NewYork, (1980)
7. J.P. Hansen and I.R. McDonald, *Theory of Simple Liquids*, 2nd ed., Academic Press, London (1990).
8. R.M. Pick, C. Dreyfus, R. Torre, et al., in preparation.
9. C. Glorieux, K. A. Nelson, G. Hinze and M. D. Fayer, J. Chem. Phys. **116**, 3384 (2002).
10. A. Aouadi, C. Dreyfus, M. Massot, R.M. Pick, T. Berger, W. Steffen, A. Patkowski and C. Alba-Simionesco, J. Chem. Phys. **112**, 9860 (2000).

MEDIUM-RANGE ORDERING IN LIQUIDS APPEARING IN NONLINEAR DIELECTRIC EFFECT STUDIES

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Abstract. Results of nonlinear dielectric effect (*NDE*) studies in supercooling epoxy resin EPON 5, nitrobenzene and menthol are presented. In each case on cooling a non-exponential decay of the *NDE* response after switching-off the strong electric field was found. The obtained "nonlinear" relaxation time is more than 10^6 times longer than the structural relaxation time (alpha relaxation) detected from "linear" broad band dielectric spectroscopy. For EPON 5 it is shown that for the whole tested range of temperatures the *NDE* relaxation time can be well parameterized by the Vogel-Fulcher-Tamman relation. For higher temperatures the *NDE* decay time can also be portrayed by the critical-like dependence, with the power exponent $\gamma = 1$.

Nonlinear Dielectric Effect (*NDE*) describes changes of the static dielectric permittivity caused by the application of an additional strong electric field [1,2]:

$$\varepsilon^E = \varepsilon + \mathcal{E}_{NDE} E^2 + \dots \quad (1)$$

where $\varepsilon, \varepsilon^E$ are the dielectric permittivities for a weak (measuring field) and strong electric field, respectively. $\mathcal{E}_{NDE} = (\varepsilon^E - \varepsilon)/E^2$ is the experimental measure of *NDE*.

The fundamental mechanism giving a contribution to *NDE* is connected with the orientation of permanent dipole moments [2]:

$$\mathcal{E}_{NDE} = -f \frac{N\mu^4}{45k_B^3 T^3} R_S \quad (2)$$

where N denotes the number of permanent dipole moments (μ) per unit volume, k_B is the Boltzman constant, f describes the applied local-field model and R_S is associated with the possible dipole-dipole correlation.

The negative sign of *NDE* is associated with so-called orientational effect, a basic *NDE* contribution in liquids with non-interacting or weakly interacting permanent dipole moments. Relation (1) is a consequence of the application of the Langenvin-type form of polarization. Until recently it was claimed that all other molecular mechanisms, as inter- and intra-molecular interactions and fluctuations related to density, polarizability or pretransitional phenomena, are associated with the positive contribution to *NDE* [2]. Only recently it was shown that on approaching the isotropic – cholesteric phase transition a negative sign of the pretransitional effect is possible [3].

In 1936 A. Piekara was the first to apply *NDE* for the analysis of local structures in liquids. He found a positive sign of *NDE* for pure nitrobenzene [1] and related this to the close-range interactions resulting from the transient structures favoring the antiparallel orientations of permanent dipole moments [2]. Only recently Janssen et al. [4] were able to assess the characteristic of the local field experienced by the nitrobenzene molecules using a molecular dynamics simulation. The obtained local field was found to be largely determined by the antiparallel alignment of neighboring molecules, in agreement with Piekara's suggestions. He was also the first to notice the strong pretransitional rise of *NDE* on approaching the critical point in a homogeneous critical binary mixture [1]. Similar phenomenon was detected in an isotropic mesogens decades later [5].

It was believed that the evidence for local structures in pure liquids or their solutions of unlimited miscibility had no relation to the mentioned pretransitional, critical-like behavior. However, recently Tanaka presented a new, general view of a liquid – liquid phase transition [6]. He assumed, that a single-component liquid may have more than two kinds of isotropic liquid states. He suggested that the resulting model with density related and bond-ordering related local order parameters can be applied to any liquid with no exception, including critical systems and glassforming liquids.

In this contribution results of *NDE* measurements for a glass-forming resin EPON 5 and two "simple" liquids, nitrobenzene and menthol, are presented. Regarding EPON 5 we recall results from ref. [7], supplemented by new measurements and an extended interpretation. *NDE* measurements have been carried out using the modulation-domain single generator apparatus described in detail in the paper by Górny et al. [8] in this volume. The tested compounds were purchased from Fluka. Nitrobenzene was distilled twice prior to measurements.

Figure 1 presents the *NDE* response induced by the rectangular pulse of a strong electric field for liquid epoxy resin EPON 5.

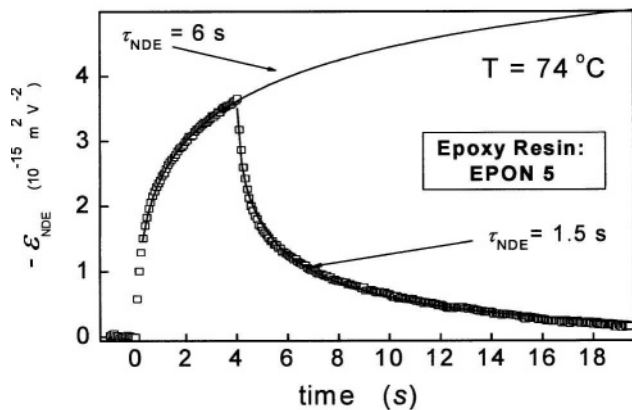


Figure 1 Nonlinear dielectric effect response due to the action a rectangular DC pulse of a strong electric field in liquid epoxy resin EPON 5. Solid curve shows the fit to the *SE* dependence, with relaxation times given in the Figure.

The obtained deformation of the *NDE* response, which reflects the relaxation processes in the sample, can be portrayed by the stretched exponential response dependence [7]:

$$R(t) = 1 - \frac{NDE(t)}{NDE(t \gg \tau)} = \exp \left[- \left(\frac{t}{\tau} \right)^x \right] \quad (3)$$

where t is the elapse time after switching-off the strong electric field, τ is the relaxation time, $NDE(t \gg \tau)$ is the stationary response of *NDE*, well after switching-on the electric field. The exponent $x \leq 1$ describes the stretching of relaxation times.

Tests were carried out using modulation-analyzer, single generator *NDE* apparatus [8]. Figure 2 shows the temperature evolution of relaxation times for EPON 5. In the whole tested range of temperatures it can be well parametrized by means of the Vogel-Fulcher-Tammann function [7]:

$$\tau = \tau_0^{NDE} \exp \left(\frac{DT_0^{NDE}}{T - T_0^{NDE}} \right) \quad (4)$$

where D is a parameter related to the so called fragility. In “linear” BDS studies the temperature T_0 is related to the ideal glass temperature.

The obtained parameters differ essentially from the set received in “linear” BDS dielectric relaxation studies. For BDS the temperature T_0 can be related to the ideal glass temperature. For *NDE* the temperature $T_0^{NDE} = 261 \pm 3 K$ is close to the glass temperature determined in calorimetric studies and with $T_g \approx 260 K$ or from the BDS data. It is noteworthy that $\tau_0^{NDE} / \tau_0 \approx 10^6$ [7].

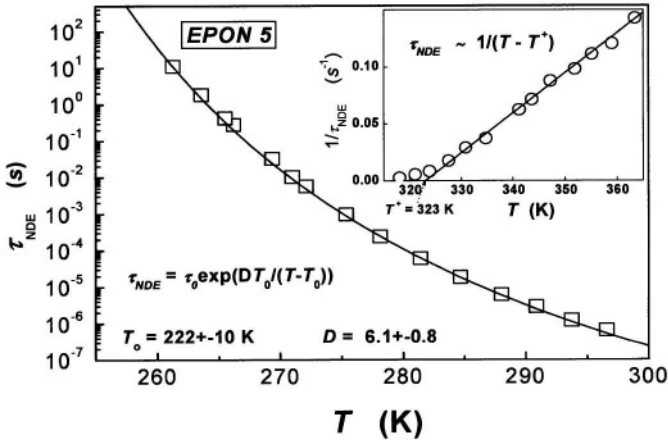


Figure 2 *NDE* decay time in liquid epoxy resin EPON 5. The inset shows reciprocal of experimental data. Fitted functions and obtained parameters are given in the Figure.

The inset in Fig. 2 shows that for higher temperatures the nonlinear dielectric relaxation times can also be portrayed by the dependence:

$$\tau_{NDE} \propto 1/(T - T^+)$$
 (5)

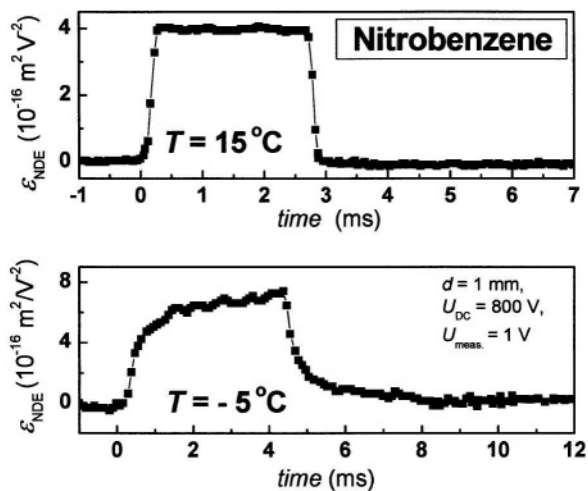


Figure 3 The NDE response to the action of a DC pulse of a strong electric field in a “normal” and supercooled nitrobenzene

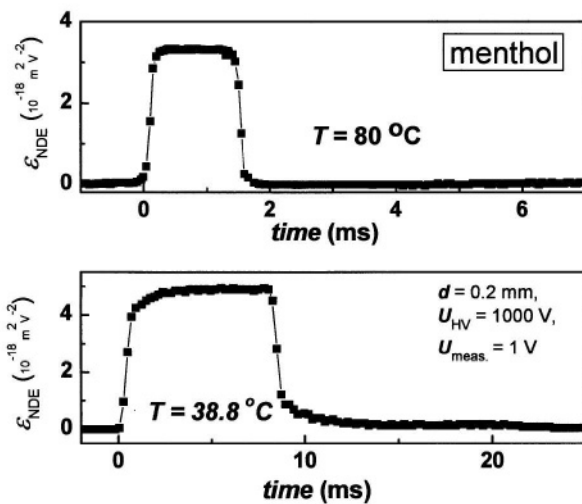


Figure 4 The NDE response to the action of a DC pulse of a strong electric field in menthol

Such types of high temperature behavior were recently suggested for the relaxation time associated with the four-point correlation function or high order susceptibility χ_4 [9] to which *NDE* can be related. The complex “nonlinear” dielectric relaxation may be more general as shown by the preliminary results for pure nitrobenzene in yet unexplored supercooled region below melting temperature ($T_m \approx 278K$).

Fig. 3 shows the typical *NDE* response to the application of the rectangular HV pulse at 15 °C. It is characterized by a positive sign, i.e. $\epsilon^E \gg \epsilon$, in agreement with Piekara's finding [1, 2]. However, on supercooling the *NDE* relaxation after switching off the strong electric field appears. Nonlinear relaxation times are ca. 7 decades longer than the molecular relaxation times from the BDS spectroscopy [2]. A similar behavior, also not noted up to now, was found for menthol as shown in Fig. 4.

Concluding, preliminary time-resolved *NDE* studies put forward the question whether the long-range relaxation time can be associated with the medium range bond-ordering as postulated by Tanaka [6] and consequently with a hidden liquid-liquid spinodal or critical point.

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References

1. Piekara A. (1936) Saturation électrique et point critique de dissolution (présente par Aime Cotton)”, *C. R. Acad. Sci. Paris* **203**, 1058-1059.
2. Chełkowski A (1980) Dielectric Physisc, *PWN-Elsevier, Warsaw*
3. Rzoska S. J., Drozd-Rzoska A., Gömny M., Zioto J. (2002) Nonlinear dielectric effect in superpressed chiral isopentylcyanobiphenyl (5*CB), *J. Non-Cryst. Solids* **307-310**, 311-316
4. Janssen R. H. C., Theodorou D. N., Raptis S., Papadopoulos M. G. (1999) Molecular simulation of static hyper-Rayleigh scattering: calculation of the depolarization ratio and the local fields for liquid nitrobenzene, *J. Chem. Phys.* **111**, 9711-9719.
5. Drozd-Rzoska A. (1999) Quasicritical behavior of dielectric permittivity in the isotropic phase of n- hexyl- cyanobiphenyl in a large range of temperatures and pressures, *Phys. Rev. E* **59**, 5556-5562.
6. Tanaka H. (2000) General view of a liquid-liquid phase transition, *Phys. Rev. E* **62**, 6968-6976.
7. Rzoska S. J. and Zioto J. (1999) Dynamics of glassy clusters appearing by nonlinear dielectric effect studies, *Phys. Rev. E* **59** 2460-2464.
8. Gömny M. and Rzoska S. J. (2004) Experimental solutions for nonlinear dielectric effect studies, *this volume*.
9. Donati C, Franz S., Glotzer S. C., Paris G. (2002) Theory of non-linear susceptibility and correlation length in glasses and in liquids, *J. Non-Cryst. Solids* **307**, 215-224.

THE COOPERATIVE MOLECULAR DYNAMICS AND NONLINEAR PHENOMENA

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Abstract. One of the most widely used theories of the glass forming liquids is the theory of Adam and Gibbs. At the macroscopical level the theory successfully relates the temperature dependence of relaxation times to the configuration entropy. An extension of this theory at molecular level has been discussed here. Two equations for measuring the size of the cooperatively rearranging region are suggested, one from the kinetic and the other from the thermodynamic properties of the liquids. From the thermodynamic equation it follows that the basic molecular units in glass forming liquids are not molecules or monomer segments, but fragment of them, known in thermodynamic as "beads." In polymers with small side-chain groups a bead is formed by one main chain atom with the groups attached to it. The estimated number of the configurations within a cooperatively rearranging region is larger than that in the solid-like Adam-Gibbs cooperatively rearranging region with only two configurations. It follows from this fact that the cooperatively rearranging region is a liquid unit, and that a statistical independence in surmounting the individual potential barriers by the basic molecular units may exist. A molecular interpretation of the Fragility Classification System, the apparent activation energy and the relaxation volume on the basis of the size of the cooperatively rearranging region is given. The relations between the kinetic and the thermodynamic measure of fragility are suggested. A possibility for the existence of analogs of the cooperatively rearranging region in nonlinear dielectric relaxation is discussed. Experimental results for inorganic glasses and polymer are examined.

1 Introduction

A marked success in the phenomenological description of the glass forming liquids in the last decades has been observed [1-5]. The Mode Coupling Theory [1], the Fragility Classification System [2,3], the Coupling model [4] and a new susceptibility function [5] are useful tools for the organization of knowledge for these liquids. Despite this success in the phenomenological description, the glass transition is still regarded as an unsolved problem from a molecular point of view [6]

One of the most widely used theories of glass transition is the theory of Adams and Gibbs [7]. At macroscopical level this theory is supported by experiments for all supercooled liquids for which the configuration entropy has been measured [8-11]. Recently Adam-Gibbs theory has been extended at its molecular level [13-15]. In this paper the evolution of the concept of the cooperativity, related to the Adams-Gibbs theory is reviewed. New thermodynamic expressions for the size of the cooperative rearranging region (CRR) are suggested. The relation between the kinetic and the thermodynamic measures for fragility are obtained.

2 Evolution of the Concept of the Cooperative Molecular Dynamics

2.1 Origin of cooperativity concept

The most simple and widely used equation for the temperature dependence of the relaxation time is Arrhenius equation

$$\tau = \tau_0 \exp(U/RT) \quad (1)$$

where U is the activation energy, R is the gas constant, τ_0 is the vibration time and T is the temperature. The Arrhenius activation energy is measured by the equation

$$U = R \frac{d \ln \tau}{d(1/T)} \quad (2)$$

and if it is a constant, it is interpreted as the height of the potential energy barrier restricting the molecular rearrangement.

In the supercooled temperature range the relaxation time is governed by Vogel-Tamman Fulcher (VTF) equation

$$\tau(T) = A \exp B/(T - T_\infty) \quad (3)$$

where A, B and T_∞ are material constants. If Eq.(2) is applied to the Eq.(3) we obtain

$$R \frac{d \ln \tau}{d(1/T)} = RB \left(\frac{T}{T - T_\infty} \right)^2 = U_{app}. \quad (4)$$

The activation energy obtained is strongly dependent on temperature and it is called apparent, on the other hand, close to the glass transition temperature it exceeds by a large margin the molecular heat of vaporization. To explain this fact it has been assumed that the molecules are rearranging cooperatively. [16,17]

The activation volume is measured from the pressure dependence of the relaxation time by the equation

$$V^* = RT \left(\frac{d \ln \tau}{dp} \right)_T \quad (5)$$

In polymers close to T_g the relaxation volume is estimated to have 10 -20 monomer segments [18-19], In the low molecular liquids V^* above T_g has also been found to be larger than the volume of the molecules and is interpreted as a manifestation of cooperativity. [20,21]. Hence, the concept of cooperativity arise out of the values observed for U_{app} and V^* .

2.2 Adam-Gibbs theory of the cooperative molecular dynamics

Adam and Gibbs obtained that the average transition probability W of a system is

$$W = \bar{A} \exp(-z^* \Delta\mu / kT) \quad (6)$$

where z^* is a critical smallest size of the CRR, $\Delta\mu$ is, largely, the potential energy hindering the cooperative rearrangement per monomer segment, T is the temperature, k is Boltzmann constant and $\bar{A}$ is a frequency factor.. The size of the CRR was defined as the number of molecules, or monomeric segments, which are rearranging cooperatively. The critical size z^* was accepted to have two configurations $w=2$, and in this way, it behaves as solid-like units, in agreement with the assumption that the monomeric units surmount essentially simultaneously the individual barriers restricting their rearrangement.

On the basis of the above definition of cooperativity Adam and Gibbs obtained the following equation for the temperature dependence of the relaxation time

$$\tau = A \exp(C/TS_c) \quad (7)$$

where C is a constant and S_c is the configuration entropy. The configuration entropy is defined as

$$S_c = \int_{T_c}^T \Delta c_p d \ln T \quad (8)$$

where $\Delta c_p = c_{pl} - c_{pc}$ and c_{cl} and c_{pc} are correspondingly the heat capacity of the liquid and the crystal or glass. Eq.(7) has been observed to describe correctly $\tau(T)$ for all substances for which S_c was measured[8-12]. The relaxation time $\tau = W^{-1}$ in accordance of the Eq.(6) can be written

$$\tau = \tau_0 \exp(zU/RT) \quad (9)$$

where $U = \Delta\mu N_A$ is the activation energy per mol basic molecular units. It shall be maintained that Adam and Gibbs assumed $w=2$ as the first approximation.

2.3 Equation for the size of the cooperatively rearranging region. Generalization of the concept for the cooperativity.

In comparing Eqs. (3) and (9) we obtain

$$\tau_0 = A, \quad (10)$$

$$U = RB, \quad (11)$$

and

$$z = T/T - T_{\infty} \quad (12)$$

It was assumed that Eq.(12) measures not the number of the molecules or monomeric segments in polymers, but fragment of them called by Wunderlich “beads”[13-15]. The macroscopical Adam-Gibbs Eq.(7) is compatible with the VTF equation if the Δc_p obeys the hyperbolic dependence[11,22,23.]

$$\Delta c_p = \Delta c_p(T_g) \Gamma_g / T \quad (13)$$

in this case from the Eqs. (8), (12) and (13) we obtain

$$z(T) = \frac{T_g}{T_{\infty}} \frac{\Delta c_p(T_g)}{S_c(T)} \quad (14)$$

This equation may be regarded as the thermodynamic expression for the size of the CRR, as it explicitly includes Δc_p and S_c , the quantity most often related with the Adam-Gibbs theory and used as a thermodynamic measure for fragility. Replacing in this equation the “universal” values of $\Delta c_p(T_g)=11,3$ J/K.mol-bead [24], $S_c(T_g)=2,9$ J/K mol-bead [25], and Adam-Gibbs ratio $T_g/T_{\infty} = 1.29$ we obtain the “universal” size of the CRR to be approximately 5 beads. Indeed the $z(T_g)$ vary around 4-5 beads [13-15], and this is in agreement with the interpretation of Eq.12 as giving the number of the beads.

Eq.(14) can be written as

$$S_c(T) = S_{\infty} / z(T) \quad (15)$$

A similar equation has been used by Takahara et al. [10] for measuring the $z(T)$, estimating S_{∞} by the extrapolation of $S_c(T)$ to $T \rightarrow \infty$. For 3-Bromopentane it was obtained that $z(T_g) \approx 4$. As for this substance $T_g=107.4$ K and $T_{\infty} = 82.5$ K [10.] by the Eq.12 we obtain $z(T_g)=4.31$. Takahara et al. interpreted this number as the number of molecules, while in our interpretation it gives the number of the beads. In some cases the correct interpretation of the basic molecular units in the CRR is not so important but when the physical properties of the CRR itself are estimated naturally, the real basic molecular units are needed. For example, the number of the configurations in the CRR at the T_g by Takahara et al. was estimated at 4000-40000. Estimating this number by $w = \exp(S_c z / nR)$ [14.], where for the molecule of 3-Bromopentane $S_c = 22,36$ J/K mol and the number of beads $n=6$ we obtain $w=6.9$. For the number of the configurations per bead in the CRR we obtain 1.6, a number close to the same number

in polymers and isomeric paraffins [14.]. In Table I the oxide glasses for which the configuration entropy has been measured are listed

TABLE I. The cooperativity in the oxide glasses.

Substance	T_g K	T_∞ K	n	$S_b(T_g)$ J/mol b K	$z(T_g)$	$w(T_g)$	$\frac{w(T_g)}{z(T_g)}$	Ref
B_2O_3	521	263	3	3,6	2,02	2,4	1,19	25,24
69,9%SiO ₂ + 20,4%Na ₂ O+ 9,8% CaO	829	542	1,7	4,27	2,89	4,4	1,52	26
Pyrexglass 7740	823	625	2,1	2,15	4,16	2,9	0,7	26
Ca(NO ₃) ₂ ·4H ₂ O	216	200	10	1,78	13,5	17,9	1,33	27
Cd(NO ₃) ₂ ·4H ₂ O	212	198	10	1,79	15,2	26	1,71	27
H ₂ SO ₄ ·3H ₂ O	162	135	7	4,7	6	29,7	4,95	26,28

For oxide glasses Wunderlich proposed, the number of the beads to be equal to the number of the oxygen atoms in the molecule. The VTF temperatures are listed in the column 3, excluding the last three substances for which Kauzman temperature, where S_c became zero is taken. Adam and Gibbs assumed both temperatures to coincide. From column 8 it may be seen that the number of configurations per bead in the CRR is larger than unit. The fact that in all glass forming liquids the number of configurations in the CRR is higher than the number of beads in the same range implies that every bead surmounts its individual potential barrier, or the transition probability may be presented

$$W = 1/\tau = A \exp\left(-\frac{u_1}{kT}\right) \exp\left(-\frac{u_2}{kT}\right) \dots \exp\left(-\frac{u_z}{kT}\right) = A \exp\left(-\frac{z\bar{u}}{kT}\right) \quad (16)$$

where $u_1, u_2, \dots, u_z$ are the individual potential barriers of the basic molecular units and $\bar{u}$

is the average activation energy per bead into the CRR. The Eq.(16) obtained is in the form of the Adam-Gibbs Eq.(6) but, on the other hand, it suggests that cooperativity, may be a series of statistical overcoming of the individual potential barriers. It shall be mentioned that several new models of the relaxation processes used the model of the random works [29,30], and cooperativity is not identical with simultaneosity[31]. Eq.(16) and the fact that the beads are fragments from molecules or monomeric segments indicates that the intramolecular motion is a substantial property of the glass forming liquids. It is not surprising that the intramolecular degree of freedom has been observed in a variety of simple molecules as toluene, orthoterphenyl, propylene carbonate and salol, which in the past have been regarded as rigid molecules. [32] The β relaxation process, observed in all glass-forming liquids, is often identified as

intramolecular and produced by the species which may be identified as beads.[33,34], Hence the faster relaxations, as $\beta, \gamma \dots \beta_f$ observed in polymers, than the mean- α relaxation, a part of which is also observed in low-molecular weight substances[1,33] are included in the mean relaxation in a natural way accepting beads as basic molecular units. In some polymers and alcohols where the beads are small and nearly equal particles as $-\text{CH}_2-$, $-\text{CH}_3$, $-\text{CCl}$, $-\text{OH}$ the average activation energy measured by Eq.(11) practically coincides with the activation energy for the rotation of these groups [14,35]. It shall be mentioned that β relaxation is regarded to form the primitive relaxation time in Ngai coupling model [36]. .

3. Results Obtained by Measuring the Size of the Cooperatively Rearranging Region

3.1 *The activation energy of the cooperatively rearranging region as a molecular basis of the glass transition temperature.*

From Eq. (9) at the glass transition temperature we obtain

$$\log \frac{\tau(T_g)}{\tau_0} = \frac{z(T_g)U}{2.3RT_g} \quad , \quad (17)$$

and as T_g is usually defined as the temperature where $\tau(T_g) = 100$ sec. and τ_0 in the majority of cases is close to 10^{-14} sec the left hand side of this equation is a constant equal to the “universal” constant $C_1=16$ in the Williams-Landel-Ferry equation [37]. Hence, the right hand side, or Adam-Gibbs factor at T_g appears as a “universal” constant with the value $z(T_g)U/RT_g \approx 37$, or T_g is a linear function of the activation energy of the CRR, $T_g = 3.25 z(T_g)U$ where U is in J/mol. In the Fig.1 this linear dependence is demonstrated for 18 inorganic substances with covalent, ionic and metallic intra- and inter-molecular interactions.

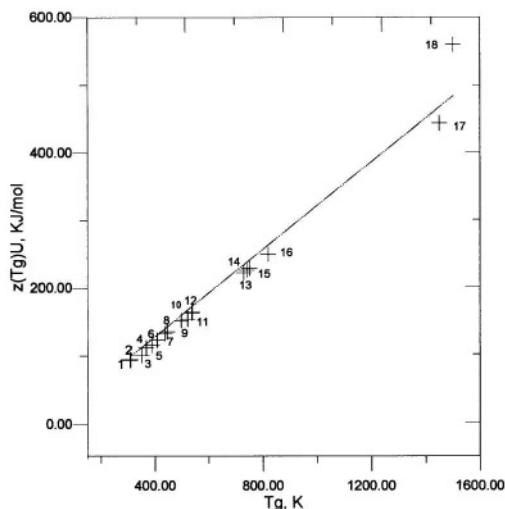


Fig.1 Activation energies of the cooperative units as function of the T_g . 1. AgI, 2. Se (ref.3), 3. $3\text{KNO}_3\cdot 2\text{Ca}(\text{NO}_3)_2$ (ref.38), 4. $\text{Ge}_{6,7}\text{As}_{6,7}\text{Se}_{86,6}$ (ref.27), 5. ZnCl_2 (ref.40), 6. $\text{Ge}_{10}\text{As}_{10}\text{Se}_{80}$ (ref.3), 7. As_2O_3 (ref.40), 8. $\text{Ge}_{13}\text{As}_{13}\text{Se}_{74}$, 9. $\text{Ge}_{17}\text{As}_{17}\text{Se}_{66}$ (ref.3), 10. B_2O_3 (ref.41), 11. soda lime, 12. silicate fl. glass (ref.3), 13. $33\text{Na}_2\text{O}\cdot 67\text{SiO}_2$, 14. $25\text{Na}_2\text{O}\cdot 75\text{SiO}_2$, 15. $20\text{Na}_2\text{O}\cdot 80\text{SiO}_2$ (ref.42), 16. GeO_2 (ref.3), 17. silica (infrasil) (ref.42), and 18. SiO_2 (ref.3).

The linear dependence between the activation energy of the CRR and T_g has been observed also in polymer [14] and it seems to be a fundamental property of the glass forming materials independent of the nature of the molecular forces.

From Eqs.(4),(!!) and (12) we obtain

$$U_{\text{app}} = U z^2 (T) \quad (18)$$

Or, U_{app} is not a linear function in accordance to z . The same dependence is observed for the V^* , indeed, regarding U and z (B and T_∞ in VTF equation) as pressure-dependant, from Eqs.(5), (11) and (12) we obtain

$$V^* = \left\{ \frac{dU}{dp} [T - T_\infty(p)] + \frac{dT_\infty}{dp} U(p) \right\} T^{-1} z^2(T, P) = v_{\text{ba}}(p, T) z^2 \quad (19)$$

where v_{ba} is the activation volume per a basic molecular unit. Hence the estimation of the degree of the cooperativity regarding U_{app} and V^* as linear functions of the z is misleading, and the obtained values as 10 –20 monmeric units [18,19.] is an overestimation. The measurement of the activation volume per basic molecular units seems to give a possibility for identification of this units [15].

It is interesting that VTF equation has been successfully applied to the nonlinear relaxation times [43] and for the liquid crystals [44], which means that analogs of the CRR may be expected to govern the relaxations in these cases.

3.2 The size of the cooperatively rearranging region as a molecular basis of fragility. Relation between the kinetic and the thermodynamic fragility.

The fragility plot, $\log \tau(T)$ as function of T_g/T , the strength parameter $D = B/T_\infty$ and the fragility indices

$$m = \left. \frac{d \log \tau(T)}{dT_g/T} \right|_{T_g} = \frac{BT_g}{\ln 10 (T_g - T_\infty)^2} \quad (20)$$

are widely used parameters for the classification of the glass forming liquids [2,3,12,45-51]. It has been obtained [14] that

$$m = C_1 z(T_g) \quad (21)$$

and as C_1 with a good approximation can be regarded as a “universal” constant [37] it is clear that the molecular basis of fragility is the size of the CRR. Since the time of the introduction of the concept of fragility, many efforts have been made to relate it with the thermodynamic quantities. As a thermodynamic measure for the fragility, $\Delta c_p(T_g)$, c_{pl}/c_{pc} , $S_c(T_g)/S_c(T)$, α_l/α_c , and k_l/k_c , where α_l and k_l are thermal expansion and compressibility coefficients of the liquids, and α_c and k_c are the same coefficients of the crystals it have been discussed [45-51]. Independent of the fact that the above quantities are very important in thermodynamics, no equations to relate them to the kinetic fragility, m or D , have been obtained. Hence it is not surprising that no correlation between the kinetic fragility and these thermodynamic quantities in the majority of cases has been observed [45,47-50]. If in Eq.(14) the “universal” values per beads are replaced we obtain

$$z(T_g) \approx \frac{T_g}{T_\infty} \frac{\Delta c_p(T_g)}{2.93n} \approx \frac{T_g}{T_\infty} \frac{11.5n}{S_c(T_g)} \quad (22)$$

where Δc_p and S_c are per mol and n is the number of beads in the corresponding molecule or the monomeric segment Replacing z in Eq.(21) by Eqs.(14) or (22) we can express the kinetic fragility by the thermodynamic quantities. It will be mentioned that Xia and Wolynes [51] obtained $D_x = 2.3 R / \Delta c_p(T_g)$ and in an empirical way realized, that it is applicable, if Δc_p is taken per mol of beads. The strength parameter D , which from the point of view of Adam- Gibbs theory is Boltzmann factor at VTF temperature $D = U/R T_\infty$ can be related to z by Eq.(17)

$$D = \ln 10 \cdot C_1 \frac{I_g}{T_\infty z(T_g)} \quad (23)$$

In the right hand side of Eq.23 T_g , T_∞ and $z(T_g)$ may be measured in thermodynamic (calorimetric) way, but since C_1 is a kinetic parameter in this case it appears as a hybrid equation and will be marked with D_h . Eq.(23) can be reduced to a pure thermodynamic one if “universal” values of C_1 and $\Delta c_p(T_g)$ and $S_c(T_g)$ per mol of beads are used

$$D \approx 37 \frac{T_g S_c(T_g)}{T_\infty z(T_g)} \approx \frac{108n}{\Delta c_p(T_g)} \approx \frac{3.2 S_c(T_g)}{n}. \quad (24)$$

The first, the second and the third expressions in the above equation will be called thermodynamic, heat capacity and configuration entropy strength parameters and will be marked D_t , D_c and D_s . The relations obtained will be applied to the polymers, since in these substances corrections between the kinetic and the old thermodynamic measures for fragility were not observed [45-48]. In polymers the kinetic and the thermodynamic parameters depend on the degree of polymerization, the degree of crystallinity etc. and a correlation may be observed if both sets of experimental results are measured from one and the same samples [52]. Such kind of results has been obtained by Algeria et al. [23] for the amorphous polymers listed in Table II.

Table I – Kinetic and thermodynamic parameters of polymers

Polymer	D	$T_\infty = T_K$ (K)	T_{gk} (K)	T_{gt} (K)	$C_1(T_{gk})$	$C_1(T_{gt})$	n	$\Delta c_p(T_g)$ (J/mol bead K)	$S_c(T_g)$ (J/mol bead K)
PVME	6.03	205	243	247	14.1	12.8	3	9.74	1.99
PVAc	5.37	266	310.3	315	14	12.7	4	9.92	1.83
PH	2.76	348	376.8	370	14.1	19	6	21.87	1.38

Where PVME – Poly(vinyl methyl ether); PVAc – Poly(vinyl acetate); PH – Poly(2-hydroxypropyl ether of Bisphenol A)

In the Fig. 2 D_h , D_t , D_c , D_s and D_x where Δc_p is per mol-beads are plotted as a function of the kinetic D. As it can be seen from the Figure the hybrid values are exactly equal to the kinetic ones, and this is natural, as in this case all individual properties of the polymers are included.

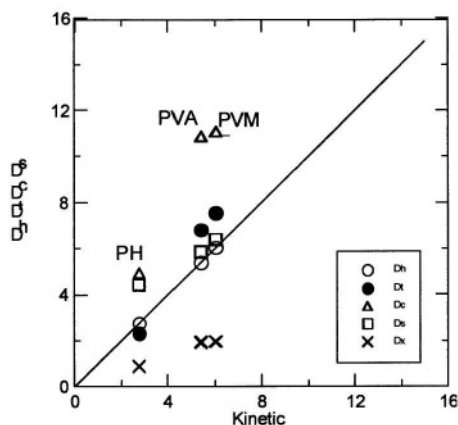


Figure 2. Hybrid D_h , thermodynamic D_t , heat capacity D_c , and configuration entropy D_s strength parameters as well D_x are plotted as a function of the kinetic strength parameter.

Other thermodynamic strength parameters also correlate with the kinetic one and the observed deviations are due to deviations of the individual values from the “universal”, see Table II. The deviations observed between the strength parameters estimated from Δc_p by the expression of Xia and Wolynes and our equation are of one and the same order, but in different directions. These deviations are due to the difference in the constants in both equations

4. Conclusions

A new thermodynamic equation for the size of the cooperatively rearranging region on the basis of the hyperbolic expression for the configuration heat capacity has been obtained. This equation is reduced to express the size of the cooperatively rearranging region only by the configuration heat capacity or the entropy, if the corresponding “universal” values per mol of beads for these quantities are used. On the basis of this thermodynamic expressions for the size of the cooperatively rearranging region the relations between the kinetic and the thermodynamic measures for fragility are suggested. The experimental results have supported the suggested correlation and it can be regarded as additional evidence that beads are basic molecular units in glass-forming liquids.

The Adam-Gibbs molecular equation for the temperature dependence of relaxation times can be obtained assuming, both simultaneous and statistically independent surmountings of the potential barriers, by the basic molecular units in the cooperatively rearranging region. The fact that the number of configurations in the cooperatively rearranging region is larger than two, independent of the nature of the glass-forming liquid, seems to be in favor of the statistical independence. The faster relaxations; $\beta, \gamma, \dots$, than the mean α relaxation, which have always been observed in the

glass-forming substances, seem to be a logical consequence of the beads constructions of their molecules. The nature of the beads, as not strictly identical particles with different interactions between them, seems to be one of the molecular bases for the spectra of the relaxation times.

The “universality” of the Adam-Gibbs factor, at the glass transition temperature, gives prominence to the activation energy of the cooperatively rearranging region among the other activation energies in the cooperative molecular dynamics. The apparent activation energy and the apparent activation volume depend nonlinearly on the size of the cooperatively rearranging region (on the second power) and their interpretation as linear functions leads to the overestimation of the size of the cooperativity.

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6. Reference

1. Gotze W. (1991) Aspects of Structural Glass Transition, in Hansen J. P., Levesques D et Zinn-Justin J.(eds.)*Les Hauches LI 1989 Liquids, Freezing and Glass Transition*, Elsevier Science Publication
2. Angell C. A. (1995) Formation of Glasses from Liquids and Biopolymers. *Science*. **67**,1924-1935
3. Bohmer R., Ngqi K. L., Angell C. A., and Plazek D. J.(1993) Nonexponential relaxations in strong and fragile glass formers. *J. Chem. Phys.* **99**, 4201-4204.
4. Ngai K. L., Rendell R. W., Ragagopal A.K. and Teitler S. (1986) Three Coupled Relations for Relaxations in Complex Systems. *Ann. N. Y. Acad. Sci.* 484, 150-184.
5. Blochowich Th., Tschirwitz Ch. Benkhof St., and Rossler E.A., (2003) Susceptibility functions for slow relaxation processes in supercooled liquids and the search for universal relaxation patterns.. *J.Chem Phys.* **118**,7544- 7555
6. Lunkenheimer P., Schneider U., Brand R. and Lodi A. (2001) Glass dynamics. *Contemporary Physics*, **41**,15-16
7. Adam G. and Gibbs J. H. (1965) On the Temperature Dependence of Cooperative Relaxation Properties in Glass-forming Liquids. *J. Chem. Phys.* **4**, 139-146.
8. Greet R.J. and Turnbull D. (1967) Test of Adam- Gibbs Liquid Viscosity Model with o-Terphenyl Specific-Heat Data. *J. Chem. Phys.* **47**, 2185-219
9. Chang S.S. and Bestul A. B. (1972) Heat Capacity and Thermodynamic Properties of O- Terphenyl Crystal Glass and Liquid, *J Chem Phys.* **56**, 503-516
10. Takahara S., Yamamuro O. and Matsuo T. (1995) Calorimetric Study of 3-Bromopentane Correlation between Structural Relaxation Time and Configuration Entropy. *J. Phys. Chem.* **99**,
11. Richert R., and Angell C A.,(1998) Dynamics of glass-forming liquids. V. On the link between molecular dynamics and configuration entropy. *J. Chem. Phys.* **108**, 9016-9026,
12. Angell C.A.(1997) Entropy and Fragility in Supercooling Liquids. *J. Res. Natl. Inst. Stand. Technol.* **102**,172-185
13. Solunov Ch. (1995). The cooperative Molecular Motion in Liquids. *Balkan Phys. Lett.* **3**, 26-31.
14. Solunov Ch. Cooperative molecular dynamics and strong/fragile behavior of polymers. *Europ. Polym. J* **35**, 1543-1556
15. Solunov Ch.(2002) The apparent activation energy and relaxation volume from the point of view of Adam-Gibbs theory. *J. Phys.:Condens. Matter* **14**, 7297-7309
16. Williams G. (1975) Aspects of the Low Frequency Dielectric Relaxation of Supercooled Non-Associated Liquids and other Viscous Liquids, in Davis M. (eds.) *Dielectric and Related Molecular Process*. Chem. Society, London **2**, 151- 182.
17. Angell C. A. (1988) Perspectives on the Glass Transition. *J. Phys. C.chem Solids.* **49**,863-871

18. Miler A. A, (1969) Analysis of the Melt Viscosity and Glass Transition of Polystyrene. *J. Polm. Sci. A-2* **6**, 1161-1175
19. Tribone J. M., O' Reilly J. M., and Greenner J. (1989) Pressure-jump Volume-relaxation Studies of Polystyrene in the Glass Transition region. *J Polym. Sci.; Polym Phys.* **27**, 837-857 (1989)
20. Fytas G., Dorfmueller Th., and Wang C.H. (1983) Pressure and Temperature Dependent Homogene Photon Correlation Studies of Liquid O-Terphenyl in the Supercooled State. *J. Chem. Phys.* **87**, 5041-5045
21. Leyser H. Schulte A., Doster W. and Petry W. (1995) High- pressure specific- heat spectroscopy at the glass transition in o- terphenyl. *Phys. Rev. E* **6**, 5899-5904.
22. Alba C., Busse L. E., List D. J., and Angell C. A. (1990) Thermodynamic aspects of the vitrification of toluene and xylene isomers and the fragility of liquid hydrocarbons. *J. Chem. Phys.* **92**, 617-624
23. Alegria A., Guerra-Echeverria E., Goitianadia L., Telleria., and Colmenero (1995) **α -Relaxation** in glass Transition Range of Amorphous Polymers. 1 Temperature Behavior Across the Glass Transition *Macromolecules* **28**, 1516- 1527
24. Wunderlich B. (1960) Study of the Change in Specific Heat of Monomeric and Polymeric Glasses During the Glass Transition. *J. Chem. Phys.* **64**, 1052-1056.
25. E. Donth, *The Glass Physics* (Springer, Berlin, 2002)
26. Bestul A. B., and Chang S. S. (1964) Excess Entropy at Glass Transformation, *J. Chem. Phys.* **40**, 3731-3733.
27. Angell C A., (1968) Oxide Glasses in Light of the "Ideal Glass" Concept: I. Ideal and Nonideal Transitions. *J. Am. Cer. Soc.* **40**, 117- 124.
28. Angell C. A. Tucker C. J. (1974) Heat Capacities and fusion Entropies of the Tetrahydrates of Calcium Nitrate, Cadmium Nitrate and Magnesium acetate . *J. Phys. Chem.* **78** 278-281.
29. Angell C. A., (1997) landscapes with megabasins. *Physica. D* **107**, 122-142.
30. Colby R. H. (2000) Dynamic scaling approach to glass formation, *Phys. Rev. E*, **61** 1783-1791
31. Hinze G (1998) Geometry and time scale of the rotational dynamics in supercooled toluene, *Phys. Rev. E* **57**, 2010-2018. See also Coffey T. W., Anomalous dielectric relaxation and continuous time random walks. *in this volume*
32. Donth E. (1996) Characteristic Length of the Glass Transition. *J. Polym. Sci. Part B Polym. Physics* ; **34**, 2881-2892.
33. Sillescu H Bohmer R., Doz A., Hinze G., Jorg Th. And Qi F., (2002) Intramolecular Motions in Simple Glass-Forming Liquids Studied by Deuteron NMR. In Fourkas J. (eds) *Liquid dynamics: experiment, simulation and theory.*" (ACS, Washington, 2002), Chp. 19, 256-266.
34. McCrum N. G., Read B. E. and Williams G., (1967) Anelastic and Dielectric Effects in polymeric solids, Wiley, London.
35. Floudas G., Higgins J. S. and Fytas G. (1992) Dynamic of Glass-Forming Liquid di-2-ethylenhexyl phthalate (DOP) as studied by liquid scattering and neutron scattering *Chem. Phys.. J.* **96**, 7672-7682.
36. Solunov Ch. (1997) On the Spectra of Relaxation Times in the Cooperative Motion of Supercooled Liquids. *Bulgarien J. Phys.* **24**, 32-38.
37. Ngai K. L., Lunkenheimer, Leon C., Schneider U., Brand R. and Loidl A., (2001) Nature and properties of the Johari- Goldstain **β - relaxation** in the equilibrium liquid state of a class of glass- formers. *J. Chem. Phys* **115**, 1405-1413.
38. Angell C. A. (1997) Way **$C_1=16-17$** in the WLF equation is physical and the fragility of polymer. *Polymre* **38**, 6261-6266.
39. Pavlatou F. A., Rizos A.K., Papatheodorou and Fytas G. (1991) Dynamic light scattering study of ionic **$\text{KNO}_3\text{-Ca(NO}_3)_2$** mixtures. *J. Chem. Phys.* **94**, 224-232.
40. Pavlatou E. A., Yannopoulos S. N., Papatheodorou G.N. and Fytas G. (1997) Dynamics of Density and Orientation Fluctuations in Supercooled Zinc Halides. *J Phys Chem. B* **101**, 8748-8755.
41. Yannapoloulos S. N., Papatheodorou G.N and Fytas G. (1997) Ligth-scattering study of slow and fast dynamics in a strong inorganic glass former. *Phys. Rev. B* **60**, 15136-15142
42. Grimsditch M and Torell L. M., (1989) Opposite Extreme Structural Relaxation Behaviour in Glassformers; a Brillouin Scattering Study of **B_2O_3** and **$\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$** . in Richter et al. (edis.) *Springer Proseding in Physics* . Springer- Verlag, Berlin **37**, 196-210.
43. Mills J. J. (1974) Low Frequency Storage and Loss Modula of Soda-Silica Glasses in Transformation range. *J.Non-Cryst. Solids* **14**, 255-266.
44. Sylwester J. Rzoska A, and Ziolo J. (1999) Dynamics of clusters appearing by nonlinear dielectric effect Studies. *Phys. Rev. E* **59**, 2460-2463.

45. Rzoska S. J., Paluch M., Drozd-Rzoska A., Ziolo J. Janik P., and Czuprynski K. (2002) Glassy and fluidlike behavior of the isotropic phase of n-cyanobiphenyl in broad-band dielectric relaxation studies. *Eur. Phys. J. E* **7**, 387-392
46. Roland C. M., Santangelo P. G. and Ngai K. L. (1999). The application of the energy landscape model to polymers. *J. Chem. Phys.* **111**, 5593-5598.
47. Ngai K. L. and Yamamuro O. (1999) Thermodynamic fragility and kinetic fragility in supercooled liquids: A missing link in molecular liquids. *J. Chem. Phys.* **111**, 104043-10406.
48. Martinez L. M., and Angell C. A. (2001) A thermodynamic connection to the fragility of Glass-forming liquids. *Nature* **410**, 663-667.
49. Huang D., McKeenna B., (2001) New insights into the fragility dilemma in liquids. *J. Chem. Phys.* **114**, 2990-2994.
50. Huang D., Colucci D. M., and McKenna G. B., (2002) Dynamic fragility in polymers: A comparison in isobaric and isochoric conditions *J. Chem. Phys.* **16**, 3925-3933.
51. Wang L. M., Velikov V., and Angell C. A. (2002) Direct determination of kinetic fragility indices of glass-forming liquids by differential scanning calorimetry: Kinetic versus thermodynamic fragilities. *J. Chem. Phys.* **117**, 10184-10192.
52. Xia X. and Wolynes P.G.,(2000) Fragilities of liquids predicted from the random first order transition theory of glasses *PNAS*, **97**,2990-2994.
53. Yannapoloulos S. N. and Solunov Ch. On the Relation between Kinetic and Thermodynamic Fragility. to be published.

ANNIHILATION RESPONSE OF THE ORTHO - POSITRONIUM PROBE FROM POSITRON ANNIHILATION LIFETIME SPECTROSCOPY AND ITS RELATIONSHIPS TO THE FREE VOLUME AND DYNAMICS OF GLASS - FORMING SYSTEMS

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Abstract. Positron annihilation lifetime spectroscopy (PALS) becomes gradually a standard technique for detecting the local regions of reduced electron density of condensed systems via the formation and annihilation behaviour of ortho - positronium (o-Ps). First we give a short overview of the free volume concept and the principles of PALS method. Then, we present typical o-Ps annihilation responses of organic small molecular and simple polymer systems and their operational classification with a discussion of the microscopic origin of the distinct features between the Type I and Type II glass formers. Further, we give a free volume interpretation of o-Ps annihilation behavior by means of two model dependent treatments of the annihilation parameters, i.e., the o-Ps lifetime, τ_3 , and the relative o-Ps intensity, I_3 , in terms of free volume hole size, R_h , or free volume hole fraction, f_h , respectively. Finally, an example of correlation between effective free volume hole characteristics and macroscopic dynamics will be demonstrated on the case of dielectric relaxation data of *glycerol*.

1. Introduction

1.1. FREE VOLUME CONCEPT OF CONDENSED MATTER

Free volume concept of condensed systems belongs for its physical simplicity and intuitive plausibility to the oldest and most popular ideas about the structure and dynamics of disordered materials [1]. Until recently, however, a potential of this pseudomolecular concept has suffered from the existence of several approaches to quantification of the free volume as well as from the absence of experimental method for straight detecting and quantification of this quantity. Thermodynamic approaches [2] based on the $V - T$ state diagram can be expressed by the generalized equation:

$V_f(T) = V(T) - V_{ref}(T)$, where $V(T)$ is the total macroscopic volume from dilatometry (DIL) and $V_{ref}(T)$ is the appropriately chosen reference volume. Thus, e.g., if $V_{ref}(T) \equiv V^w$, i.e., van der Waals volume of constituents, we obtain the maximal static empty free volume, $V_f^{empty}(T)$, or if $V_{ref}(T) \equiv V(0K)$, i.e., the extrapolated volume to zero temperature, we have the expansion free volume, $V_f^{expansion}$. The dynamic approach is represented by the heuristic Doolittle equation linking viscosity, $\eta(T)$, with the independently determined free volume fraction $f(T)$ from DIL data [3]: $\eta(T) = \eta_\infty \exp[B_\eta/f(T)]$, where B_η is the empirical coefficient and $f(T)$ was originally defined as the expansion free volume fraction $f^{expansion}(T) = [V(T) - V(0K)]/V(T)$. Later, a functional form of this equation has found a significant utilization in free volume interpretation of the empirical Williams - Landel - Ferry (WLF) equation for dynamics of supercooled liquids, but now with $f(T)$ as a fitting parameter [4]:

$$\log a(T_{ref}) = \log \eta(T)/\eta(T_{ref}) = -C_{1,ref}(T - T_{ref})/[C_{2,ref} + (T - T_{ref})] = B_\eta[1/f(T) - 1/f(T_{ref})] \quad (1)$$

where $a(T_{ref})$ is the shift factor and $T_{ref} \geq T_g$ is the reference temperature, e.g., the glass transition temperature T_g . Comparing the outputs from both the approaches one arrives to diametrically different values for the free volume fraction $f^{therm} \cong 30$ or 15% versus $f_g^{dyn} \cong 2 - 4$ %. This rather undesirable situation given by the existence of several operational definitions emphasizes the need of independent determination of free volume and its correlating to various dynamic and transport properties. One solution offers *positron annihilation lifetime spectroscopy (PALS)* [5-7].

1.2. POSITRON ANNIHILATION LIFETIME SPECTROSCOPY (PALS)

PALS is a structural - dynamic method of probing the condensed materials based on measurement of the annihilation behaviour of various forms of positrons e^+ [5-7]. In conductive systems such as metals or semiconductors, thermalized positrons annihilate via direct interaction with electrons of a matrix. On the other hand, in most of non-conducting materials such as organic systems, positronium (Ps), i.e., a bound system of positron e^+ and electron e^- can also be created. Depending on the mutual orientation of the positron and electron spins, a singlet para-positronium (p-Ps), or a triplet ortho-positronium (o-Ps) are formed. All the three positron annihilation modes are characterized by the corresponding lifetime, τ_i , and a relative probability of their occurrence called the relative intensity, I_i , where $i = 1-3$. The p-Ps lifetime, τ_1 , and the "free" positron lifetime, τ_2 , being nearly temperature independent, reach the values of 0.1 - 0.2 ns or 0.3 - 0.4 ns, respectively. On the other side, the o-Ps lifetime, τ_3 , varies significantly with temperature and reaches the values from ~ 0.8 ns up to ~ 5 ns range.

The latter is practically instantaneously stabilized and lives for a certain time period, τ_3 , in the local regions of reduced electron density such as vacancies in crystalline materials and free volume holes in amorphous ones. In the final step, the o-Ps annihilates by the so-called pick-off mechanism via interaction with an excess electron in surrounding of cavity under emitting γ photons which are analysed. Since τ_3 and I_3 reflect the fluctuating local electron distribution in a given material, they are intimately related to the *effective* free volume situation in a matrix under given external conditions. Subsequently, the *effective* free volume information can be extracted by means of physically reasonable models in terms of free volume holes size and free volume hole fraction as it will be presented after presentation of phenomenological features.

2. Experimental

2.1 MATERIALS

In our systematic PALS studies we have used the two series of organic materials. The first group consists of small molecular compounds containing systems of van der Waals type such as *meta*-tricresyl phosphate (*m*-TCP) ($T_g^{DSC} = 210K$) and of hydrogen-bonded type such as *glycerol* (GL) ($T_g^{DSC} = 190K$), *propylene glycol* (PG) ($T_g^{DSC} = 170K$), *dipropylene glycol* (DPG) ($T_g^{DSC} = 185K$), *tripropylene glycol* (TPG) ($T_g^{DSC} = 195K$). The other class of amorphous materials includes a series of structurally simple polymers, i.e., elastomers with $T_g^{DSC} < RT$ of diene type such as *cis* - *trans* - 1,4 - *polybutadiene* (*c*-*t*-1,4-PBD), - $[CH_2-CH=CH-CH_2]_n$ - with $T_g^{PALS} = 178K$, *cis* - 1,4 - *polyisoprene* (*cis*-1,4-PIP), - $[CH_2-CH=C(CH_3)-CH_2]_n$ -, ($T_g^{DSC} = 201K$), of vinylidene type, i.e., *polyisobutylene* (PIB), - $[CH_2-C(CH_3)_2]_n$ -, ($T_g^{DSC} = 203K$) and finally, of vinyl type such as *atactic polypropylene* (*a* - PP), - $[CH_2-CH(CH_3)]_n$ -, $T_g^{DSC} = 259K$ and *1,2-polybutadiene* (1,2-PBD), - $[CH_2-CH(CH=CH_2)]_n$ -, with $T_g^{DSC} = 272K$. PALS results on several polymers have been already published in several papers e.g. [7,9].

2.2. PALS MEASUREMENTS

The positron annihilation lifetime spectra were obtained by the conventional fast - fast coincidence method using plastic scintillators coupled to Phillips XP2020 photomultipliers. The time resolution of prompt spectra was about 320 ps. The radioactive positron ^{22}Na source plus samples assembly was kept in rotary vacuum pump. During the low temperature measurements from 15K up to 310K samples in holder were fixed at the end of cold finger of a closed-cycle helium gas refrigerator Leybold with automatic temperature regulation. The high temperature measurements from 290K up to 390K were performed with home - made heater with temperature stabilization. In this case the source - samples assembly was kept in air atmosphere.

The positron lifetime spectra were analyzed using well known the PATFIT - 88 software package in terms of three above-mentioned annihilation modes.

3. Results and Discussion

3.1. PHENOMENOLOGICAL PALS RESULTS

Typical o-Ps annihilation responses from our set of glass - formers differing in their fragilities, i.e., the steepness of temperature dependencies of primary α relaxation time or viscosity in the vicinity of glass transition T_g [8], are presented in *Figures 1a* and *1b*. *Figure 1a* shows the o-Ps lifetime, τ_3 , and the relative o-Ps intensity, I_3 , as a function of temperature normalized on the respective glass transition temperature (T/T_g^{PALS}) for two members from our group of small molecular systems: a representative of strong systems: *glycerol (GL)* and of fragile substance: *meta - tricresyl phosphate (m - TCP)*. *Figure 1b* gives a similar comparison between two members of our series of structurally simple amorphous polymers: one of fragile type: *cis-trans-1,4-polybutadiene (c-t-1,4-PBD)* and the other of strong character: *polyisobutylene (PIB)* over an extraordinary wide temperature range.

3.1.1. General and specific features of PALS response in our investigated systems and characteristic PALS temperatures

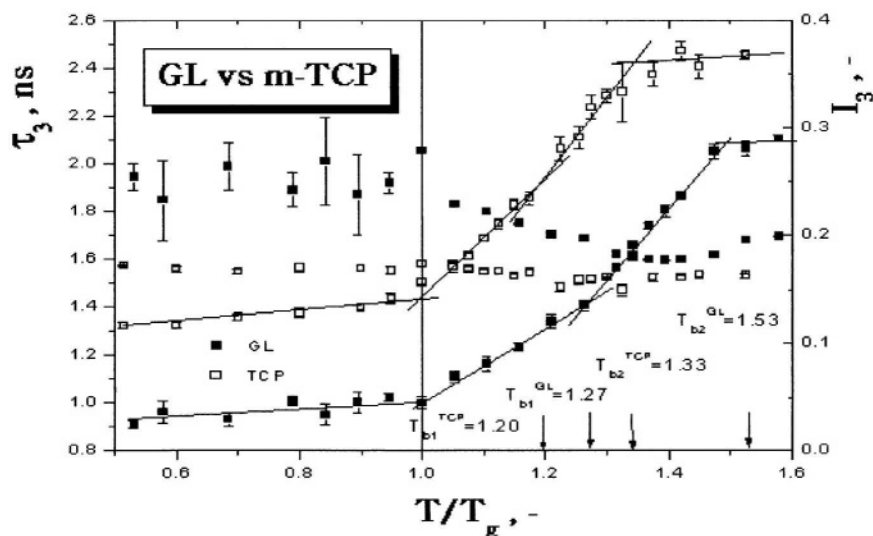
All the o-Ps annihilation responses in our set of small and high molecular systems studied exhibit certain common features independently of the chemical composition of the material as well as some specific ones characterizing a given system.

The first o-Ps annihilation parameter, the o-Ps lifetime, τ_3 , shows four or sometimes five regions of different thermal behavior marked by three or sometimes four characteristic PALS temperatures. The most pronounced characteristic effect lies in the vicinity of the thermodynamic glass to liquid transitions determined from dilatometry T_g^V or calorimetry T_g^{DSC} and for this reason it defines the PALS glass transition temperature T_g^{PALS} . In general, their values lie in the close vicinity a few Kelvins of the glass transition temperatures from standard thermodynamic DSC method.

The second most characteristic effects, i.e., a plateau - like zone or in some cases a sharp decrease in the slope are situated at higher temperatures and they define the second liquid bend temperature at $T_{b2}^{\text{liq}} \cong (1.3 - 1.75)T_g^{\text{PALS}}$. Recently, we have revealed that this strong bend effect is characterized by the equality between the o-Ps lifetime, τ_3 , and the primary α relaxation time, τ_α [9]. This can be demonstrated by comparison of the corresponding τ_3 values with the relaxation times of the primary process, τ_α , from two different types of phenomenological analysis of the DS spectra of *glycerol* – see Figs. 3 and 4 from Refs. 10 or 11, respectively. Moreover, in some cases T_{b2}^{liq} can be correlated with certain characteristic temperatures from recent detailed dynamic studies. Thus, for *glycerol* [12,13] $T_{b2}^{\text{liq}} = 290 \text{ K}$ is close to the characteristic temperature, $T_B^{\text{DS}} = 285 \text{ K}$ [14] marking a boundary between the two VFTH equations accounting for the different motional regimes of the relevant data from DS studies. However, the $T_{b2}^{\text{liq}} \cong T_B$ relation has no general validity for all the systems studied, as it will be demonstrated for the case of *m-TCP* below. In other cases, e.g., of *PIB*, $T_{b2}^{\text{liq}} = 347 \text{ K}$ agrees with $T_A^\eta = 350 \text{ K}$, at which a crossover from the VFTH regime to the Arrhenius one appears [15].

In addition to these the two most pronounced effects, in some systems, especially polymers, further slight change in the slope of $\tau_3 - T$ plot can be revealed in the glassy

state at T_{b1}^{gl} as it is evident for the case of *c-t-1,4-PBD* in Figure 1b. These glassy PALS temperatures, T_{b1}^{gl} , coincide with occurrence of the slow secondary β processes of Johari - Goldstein (JG) type [16] as it has already been demonstrated previously for some thermoplastics, e.g., *polymethyl methacrylate* with $T_g^{DSC} > RT$ [17].



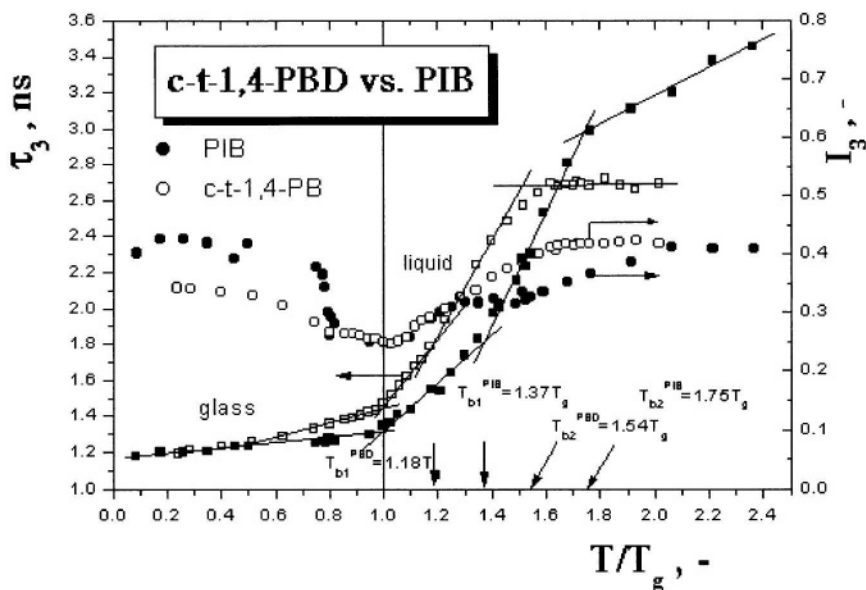


Figure 1 o-Ps lifetime, τ_3 , and relative o-Ps intensity, I_3 , as a function of temperature normalized on T_g^{PALS} on (a) small molecular glass formers: glycerol (GL) and m-tricresyl phosphate (m-TCP) and (b) simple polymers: cis-trans-1,4-polybutadiene (c-t-1,4-PBD) and polyisobutylene (PIB).

Finally, the last change in the liquid state above T_g^{PALS} defines the first liquid PALS temperature at $T_{b1}^{\text{liq}} \cong (1.2-1.5) T_g^{\text{PALS}}$ in the systems investigated - see also [9]. This effect seems to suggest the presence of two types of supercooled liquids from the point of view of PALS, at least: one slightly supercooled liquid from T_{b2}^{liq} down to T_{b1}^{liq} which is characterized by a large slope of the $\tau_3 - T$ dependence and the other being deeply supercooled one from T_{b1}^{liq} down to T_g^{PALS} with a reduced slope of τ_3 vs T dependence. Similarly as in the previous case of T_{b2}^{liq} , T_{b1}^{liq} can be found to coincide with some characteristic temperatures from numerous dynamic studies as performed by means of various spectroscopic and scattering techniques [9]. Specifically, T_{b1}^{liq} agrees sometimes with characteristic temperature T_B^{DS} . Thus, for *m-TCP* $T_{b1}^{\text{liq}} = 241\text{K}$ from our data agrees with $T_B^{\text{DS}} = 245\text{K}$ [14] which lies below $T_{b2}^{\text{liq}} = 270\text{K}$. Clearly, this coincidence is not valid for *glycerol* where $T_{b1}^{\text{liq}} = 241\text{K}$ is essentially lower than the dielectric $T_B^{\text{DS}} \cong 285\text{K}$. Despite these differences, the presence of the first bend liquid effect in our set of systems studied appears to be a universal phenomenon because the characteristic α relaxation time from DS method at T_{b1}^{liq} lies at around 10^{-6} s as already reported in [9] and confirmed on further compounds: *PG*, *DPG*, *TPG* and *m-TCP*. It is interesting to note that for *glycerol*, at least, the o-Ps lifetime $\tau_3(T_{b1}^{\text{liq}})$ is quite close to the average β relaxation time $\tau_\beta(T_{b1}^{\text{liq}})$ as obtained from a specific analysis of the DS spectra [11]. Consequences of this finding will be discussed later.

As for the second annihilation parameter, the relative o-Ps intensity I_3 vs. T dependencies exhibit two basic types of their thermal behavior in our series of the system studied, at least. From Figure 1a it can be seen that for *glycerol* and *m-TCP* in

the glassy state I_3 holds practically constant value up to T_g^{PALS} followed by a more or less pronounced decreasing trend through some minimum above T_g^{PALS} which is ended up by nearly constant value or slightly increasing trend at high temperatures that coincides with the plateau - like effect. On the other hand, *Figure 1b* shows that for *c-t-1,4-PBD* and *PIB* the onset of this decreasing trend is relatively deeply in the glassy state below the respective T_g^{PALS} 's and that the minimum is situated just in the vicinity of glass to liquid transition temperature T_g^{PALS} .

3.1.2. Classification of the *o* - Ps annihilation responses of studied systems and its connection to the secondary processes

On the basis of our so far quite extensive and detailed database of the *o*-Ps annihilation results on a series of five relative simple amorphous small molecular compounds and five simple amorphous polymer systems we can present a classification of simple organic systems according their characteristic annihilation behavior in dependence on temperature. Thus, our systems can be divided into two classes:

- i) *Type I glass-forming systems* is characterized by the general $\tau_3 - T$ course with three or four bend effects and the $I_3 - T$ dependence of the first specific kind for the relative *o*-Ps intensity I_3 as a function of temperature, i.e., a decreasing trend starts after crossing the respective T_g^{PALS} , so that possible inversion effect is situated in the liquid state. To this class of glass-formers belongs not only *glycerol* and *m-TCP* from *Figure 1a*, but also *PG* and its dimer *DPG* and trimer *TPG* [to be published].
- ii) *Type II glass formers* is characterized by the similar general $\tau_3 - T$ dependence but with the specific dependence of the second type. As mentioned above, this decreasing effect starts already in the glassy state and its corresponding minimum lies at around the glass to liquid transition temperature T_g^{PALS} . This class includes simple amorphous polymers besides *c-t-1,4-PBD* and *PIB* shown in *Figure 1b* also *PIP*, *a-PP* and *1,2-PBD*.

Thus, the only difference between both the types of PALS responses in our series of glass formers appears to consist in a distinct thermal behavior of the relative *o*-Ps intensity. At first sight, this main feature appears to be connected with the molecular vs. polymer nature of the systems investigated, because the Type I includes all our small molecular systems and the Type II all our simple polymers. However, this identification seems to be oversimplified and insufficient for our detail understanding of the classification because it does not indicate the possible origin for such a distinct behavior. In our search for the microscopic origin of such a difference we accept the so - called physical hypothesis of the I_3 reduction based on an idea that any motion having appropriate frequency as well as amplitude parameters might reduce the number of free volume holes and subsequently, I_3 being proportional to the formation probability of *o*-Ps formation [18]. In this connection it may be useful to recall some degree of resemblance our PALS classification with Rössler's operational division of glass formers according to their dielectric behavior over very wide frequency range from 10^3 up to 10^9 Hz [10]. Two groups of glass formers are distinguished on the basis of the features of the excess relaxation losses besides the primary α relaxation one: Type A systems are characterized by the absence of the secondary relaxation process of J-G type and they contain both the primary α relaxation peak and the so-called high-

frequency wing (HFW), while Type B systems exhibit a well discernible β relaxation peak in addition to the main one. Indeed, in our recent detailed PALS studies on *glycerol* [12] as a typical representative of Type A glass formers and on *c-t-1,4-PBD* [9] - a member of Type B systems - we have revealed the existence of the high - frequency dynamics on nanosecond scale in the corresponding temperature ranges of the I_3 reduction. Specifically, in the case of *glycerol*, the emergency of decreasing trend above T_g correlates with the presence of dielectric losses at 10^8 Hz in the DS spectrum [10, 12]. On the other hand, the onset of I_3 reduction already in the glassy state in *c-t-1,4-PBD* can be related to the short time tail of the distribution of slow secondary β relaxation times [9, 19]. By comparing, three compounds from Type A group, namely *glycerol*, *PG* and *m - TCP* [10], match into our Type I systems. On the other hand, *DPG* and *TPG* from our Type I class are known to exhibit weak secondary relaxation peaks [20] in apparent disagreement with the characteristic dielectric loss features of Type A systems.

At present, a large debate continues concerning the microscopic origin of a wing on the high-frequency side of the primary α relaxation peak. The current hypotheses can be divided into two groups. One hypothesis argues that the HFW is an intrinsic feature of the main process [10, 21], while the other gives phenomenological as well as theoretical arguments within the coupling model in favor of the notion that the HFW is simply the high - frequency flank of the secondary β relaxation process lying in the vicinity of the primary α process [22-26]. It follows from special aging experiments on *glycerol*, *PG* and other systems [22, 23] and high-pressure studies on *glycerol* [25, 26]. The above - mentioned agreement between the DS and PALS features for *glycerol*, *PG* and *m - TCP* might be interpreted as an argument in favor of the first possibility of the coupled processes. However, the clear inconsistency for dimer *DPG* and trimer *TPG* exhibiting the weak secondary peaks [20] might be considered rather as a support for the second idea about the high - frequency contribution from the usual secondary β relaxation submerged under the much more intense α peak [11]. At the present level of our knowledge, further argument supporting rather the latter hypothesis will be presented in the next section dealing with free volume analyses of the o - Ps annihilation response 3.2.2. In any case, regardless of the microscopic nature of the excess wing on the high - frequency side of the primary relaxation, our finding of the I_3 reduction can be considered as an experimental evidence for the existence of some kind of mobility on the nanosecond time scale as well as on the mesoscopic length scale, which may eliminate some portion of free volume holes for the subsequent o - Ps localization and annihilation events.

We conclude this part by noting that further studies, especially on small molecular systems are requested in order to confirm the degree of validity of our classification scheme based on the results on the ten relative simple glass - forming compounds so far measured in detail by our PALS group. In addition, the present experimental situation in the DS field becomes more complicated due to the recent finding that in some systems such as fluoraniline (FAN) besides the primary process both additional secondary processes, i.e., the HFW contribution as well as the slow secondary β relaxation peak occur [10].

3.2 FREE VOLUME INTERPRETATION OF o - Ps ANNIHILATION BEHAVIOR

3.2.1. Models for free volume characterization

On the basis of numerous experimental observations, namely i) the absence of o-Ps in almost perfect crystals, ii) the presence of o-Ps in common defective (vacant) crystals, especially in the vicinity of their melting temperatures and iii) the similarity of the τ_3 - T dependencies in crystals or deeply supercooled liquids with the corresponding V - T diagrams exhibiting the pronounced bends at T_m or T_g , respectively, the temperature dependencies of o-Ps lifetime are interpreted in terms of vacancy or more generally, free volume holes size. This is based on a vacancy concept of crystal expansion and its melting or a free volume hypothesis for the case of expansion of macroscopic volume of amorphous solids.

Two aspects of free volume characterization of any disordered material, i.e., free volume hole size, V_h , and free volume hole fraction, f_h , can be obtained from o-Ps annihilation behavior by means of two physically plausible models. The former quantity can be determined by using a standard quantum - mechanical model of o-Ps in a spherical hole giving the following relationship between the o-Ps lifetime, τ_3 , and the free volume hole radius, R_h [27-29]:

$$\tau_3 = \tau_{3,0} \left\{ 1 - \frac{R_h}{(R_h + \Delta R)} + \left(\frac{1}{2\pi} \right) \sin[2\pi R_h / (R_h + \Delta R)] \right\}^{-1} \quad (2)$$

where $\tau_{3,0}$ is the lifetime of Ps^- anion being 0.5ns and ΔR is the thickness of electron layer about hole obtained as a calibration parameter from fitting the observed o-Ps lifetimes to known vacancy or free volume hole sizes in molecular crystals or zeolites. In fact, the shape of free volume entities is not strictly spherical because of the non - spherical form of constituent's particles, so that the standard model is currently used in the sense of an equivalent spherical hole size $V_h = (4\pi/3)R_{h,eq}^3$. Recent paper [30] has shown that some parameters derived from PALS such as the free volume hole fraction are not strongly influenced by the choice of the free volume hole geometry.

As for the second basic free volume characteristic of the integral nature, i.e., free volume hole fraction, f_h , several models for its quantification have been formulated [31-36]. All of them are based on a combination of the thermal expansion behavior of the macroscopic volume $V(T)$ from dilatometry with that of the microscopic free volume hole size $V_h(T)$ via eq. (2). At present, two groups of these models have been developed differing in the definition expression for the free volume hole fraction: a) $f_h(T) = K_{Vh} \cdot V_h(T)$ [34,35] b) $f_h(T) = K_{VhI_3} V_h(T) \cdot I_3(T)$ [31-33,36]. Whereas the former approaches neglect the role of I_3 due to complicated processes in radiation track in some specific systems, the latter ones are based on the rather plausible hypothesis that the relative intensity of o-Ps, being proportional to its formation probability, is a measure of the number density of free volume hole entities: $I_3(T) \propto C_h(T)$ [31,32]. Here, we present the most developed version of model for free volume hole fraction [36] which generalizes the most acceptable features of the previous ones [31,33,34,35] into a generalized two-state model (GTSM). In contrast to our previous models [33,34], it is based on more realistic assumptions concerning i) the temperature dependence of the so-called occupied volume $V_o(T)$ and ii) the incorporating of the I_3 term. Detailed derivation of the GTSM will be presented elsewhere [36] so that here, we give the resulting equations for important free volume characteristics:

$$T_i = T_g - 1/\alpha_{vh,13,g}^q \quad (3)$$

$$f_{h,g} = (\alpha_v^{gl} - \alpha_v^{lq}) / (\alpha_{vh,13,g}^{gl} - \alpha_{vh,13,g}^{lq}) \quad (4)$$

$$\alpha_o = (\alpha_v^{lq} \cdot \alpha_{vh,g}^{gl} - \alpha_{vh,13}^{lq} \cdot \alpha_v^{gl}) / (\alpha_{vh,13}^{gl} - \alpha_{vh,13}^{lq}) \quad (5)$$

where T_i is the initial temperature of the dynamic free volume, $f_{h,g}$ is the free volume hole fraction at T_g , α_o is the expansion coefficient of the occupied volume, α_v^{gl} , α_v^{lq} are the thermal expansion coefficients of macroscopic volume in glassy and liquid state from DIL and finally, $\alpha_{vh,13,g}^{gl}$, $\alpha_{vh,13,g}^{lq}$ are the corresponding thermal expansion coefficients of free volume hole fraction in both the physical states $x = gl$ or lq defined as $\alpha_{vh,13,g}^x = (1/V_{h,13})_g \cdot [(\Delta V_{h,13})^x / \Delta T]$.

In the context with previous discussion, it is important to note that both the free volume quantities extracted from the above -mentioned models have an effective character for the geometric or/and dynamic reasons. The former is connected with the finite size of o-Ps probe, being $R_{o-Ps} = 0.53 \text{ \AA}$, so that only a relevant part of the total free volume distribution accessible to o-Ps probe can be sampled. The latter one is linked to the mutual relationship between the o-Ps lifetime, τ_3 , and the characteristic time, τ , and the related displacement of any molecular motion giving the possibility to detect the free volume holes that have a lifetime higher than the o-Ps lifetime, at least.

3.2.2. Effective free volume microstructure of a typical glass former from PALS

As a representative example of the effective free volume characterization, we display the case of *glycerol*. Figure 2 shows both the effective free volume characteristics as a function of temperature. Several regions of different thermal behavior, one below T_g and three in the liquid state are obvious. At low temperatures o-Ps is trapped in local free volume of the glass, so that τ_3 and hence, V_h reflect the mean size of pre-existing quasi - static free volume holes. The slight increase of V_h with temperature can be attributed to the thermal expansion of the glass due to the weak anharmonicity of vibrations of the constituent's particles. On crossing $T_g = 190K$, generally, molecular motion increases and the free volume holes begin to have an increasingly dynamic character. Some, especially the small holes can be eliminated for o-Ps localization due to certain motion of constituent's particles having sufficient displacement and high frequency. This results in the increase in the mean o-Ps lifetime, τ_3 , and hence, in the mean hole size, V_h , and the decrease of $I_3 \sim C_h$ as discussed in section 3.1.2. On further increasing the temperature, the relative large changes in both the slopes of the free volume hole size and fraction begin to occur at around 240 - 250K which suggest apparently the presence of two qualitatively different supercooled liquid phases. The physical origin of this bend effect is unclear and we outline two hypotheses. The first, being of the dynamic nature, may consists in a releasing some rapid mobility. As already mentioned in section 3.1.1, the β relaxation time as obtained from specific analysis of the DS spectra of *glycerol* [11] becomes comparable with τ_3 . Consequently, a part of the total free volume distribution might be eliminated for o-Ps formation and annihilation process due to elimination of smaller holes and possible creation of larger ones, so that τ_3 will increase with sharper slope. Another reason may consist in a change

of the structural nature, e.g., a release of dense packing of group of particles or a decay of certain specific cluster formations with increasing temperature. This possibility will be discussed later in section 3.2.3. All these structural - dynamical reorganizing processes suggest the possibility of a qualitative change of the free volume distribution. Consequently, it will lead to the increase in the thermal expansion of o-Ps lifetime in deeply supercooled liquid on continuing heating to higher temperatures. Finally, at very high temperatures above $T_{b2}^{lq} = 290K$, where the structural relaxation time, τ_α , becomes comparable or shorter than the mean o-Ps lifetime, τ_3 , o-Ps probe “feels” a rapidly fluctuating surrounding, i.e., a homogeneous liquid on the time scale of o-Ps, at least [9]. Consequently, o-Ps probe is able to reflect the effective free volume microstructure of a heterogeneous liquid only below T_{b2}^{lq} [9].

For our idea about a range of the typical mean effective free volume hole sizes, van der Waals volume of *glycerol* molecule $V_{mol}^W = 86.5 \text{ \AA}^3$ is marked in *Figure 2*. While below ca 260K, where a minimum in I_3 occurs (*Figure 1a*), the mean free volume hole size V_h reaches a certain portion of this molecular volume, above this temperature $V_h > V_{mol}^W$ and at the plateau level $V_h \cong 1.2V_{mol}^W$; a quite reasonable value. This last finding seems to be consistent with the idea about molecules rapidly exchanging their positions and consequently, a rather homogeneous character of a liquid [9]. It is also interesting to note that T_{b2}^{lq} in our amorphous sample of *glycerol* lies close to the melting temperature, T_m , of the crystalline form of *glycerol* [37]. It implies that the supercooled state of *glycerol* below $T_m \cong T_{b2}^{lq}$ is characterized by the existence of local spatial heterogeneities with the reduced electron density whose the mean lifetime becomes progressively longer in comparison to the o-Ps lifetime with decreasing temperature.

The free volume fraction as a function temperature has been determined using the GTSM (eqs.3 - 5) with the following input parameters: $\alpha_v^{gl} = 2.4 \times 10^{-4} \text{ K}^{-1}$, $\alpha_v^{lq} = 4.8 \times 10^{-4} \text{ K}^{-1}$ [37], $T_g^{PALS} = 190K$, $\alpha_{vh,I3,g}^{gl} = 3.03 \times 10^{-3} \text{ K}^{-1}$ and $\alpha_{vh,I3,g}^{lq} = 1.58 \times 10^{-2} \text{ K}^{-1}$. The corresponding output quantities are as follows: $T_i = 127K$, $f_{h,g} = 1.9\%$ and $\alpha_0 = 1.82 \times 10^{-4} \text{ K}^{-1}$. For comparison and subsequent discussion, we summarize also the outputs data from the previous models, namely the one-state model (OSM) using a simplified eq.5 (SOSM) $T_i = 155K$ and its generalized version with eq.6 (GOSM) [12] $T_i = 137K$ as well as from the two recent simplified two-state models (STSM)[34,35]: $T_i = 153K$, $f_{h,g} = 1.1\%$ and $\alpha_0 = 2.1 \times 10^{-4} \text{ K}^{-1}$. The outputs parameters from all these models can be discussed in relation to the various characteristic temperatures within the glassy state and the thermal behavior of *glycerol* as obtained by independent techniques. Thus, the starting temperatures T_i from the present GTSM as well as from the GOSM compare well with the numerous determinations of the Vogel temperature, $T_0 = 124 - 137K$, from the VFTH equation describing many dynamic measurements [11,38] as well as with the Kauzmann temperature, $T_K = 135$ from calorimetric study [38]. On the other hand, both simplified versions of one-state and two-state model provide

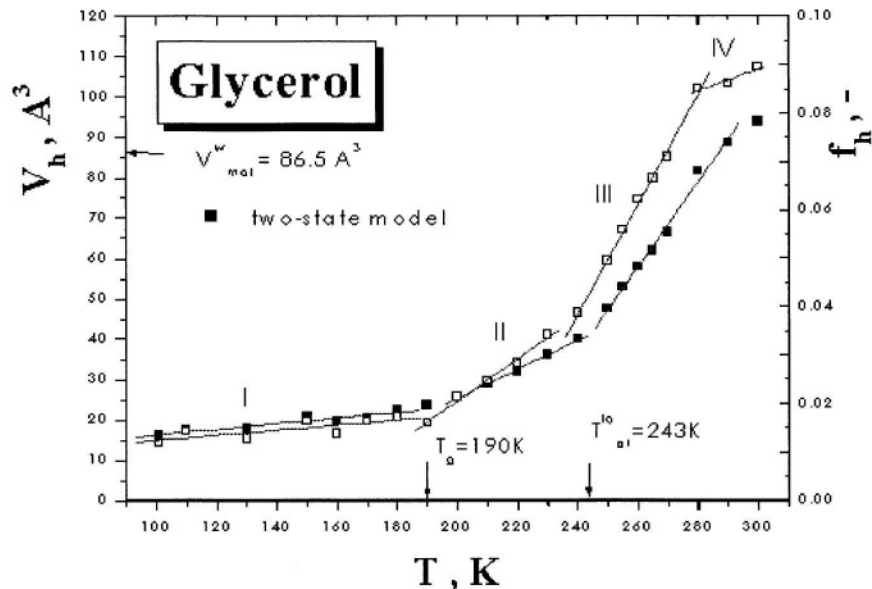


Figure 2 Free volume characteristics as a function of temperature for *glycerol* from the generalized two-state model.

essentially higher $T_i = 154 \pm 1\text{K}$ indicating the preference of the definition $f_h(V_h, I_3)$ over $f_h(V_h)$. Further, two-state models (GTSM as well as STSM) in contrast to one-state ones (GOSM or SOSM) are able to provide a unique property, i.e., the thermal expansion coefficient of the occupied volume that is inaccessible by other means. The values of $1.82 \times 10^{-4} \text{ K}^{-1}$ from the GTSM and $2.1 \times 10^{-4} \text{ K}^{-1}$ from the STSM are consistent with a general expectation: $\alpha_V^{gl} = 2.4 \times 10^{-4} \text{ K}^{-1}$ [37] $> \alpha_0 = 1.82$ or $2.1 \times 10^{-4} \text{ K}^{-1} > \alpha_V^{crystal} = 1.8 \times 10^{-4} \text{ K}^{-1}$ [37] supporting the physical picture which includes the concept of temperature dependent occupied volume [4,37]. Globally, from these comparisons we can make conclusion about the preference of the present generalized two-state model (GTSM) over the simplified two-state one (STSM) [34,35] on the basis of more favorable agreement between T_i and T_0 and also the GTSM over the GOST[33] because of the incorporating the $\alpha_0 \neq 0$ assumption.

In connection with our classification of glass formers according their o-Ps annihilation response in section 3.1.2. it is of interest to discuss further connections between the T_i value from the GTSM with the results from the two phenomenological analyses of the dielectric spectra of *glycerol* [10,11]. Phenomenologically, the DS spectra of *glycerol* have been accounted for using the generalized Cole-Davidson function that is able to describe the peak from the primary α relaxation, where the imaginary part of dielectric susceptibility $\epsilon'' \propto \nu^{-\beta}$ as well as a wing on the high - frequency side of the α peak $\epsilon'' \propto \nu^{-\gamma}$ [10]. Extrapolation of the temperature dependence of the γ parameter of the wing from the liquid state down to zero value leads to $T_{\gamma,0} = 134\text{K}$ also in good agreement with $T_i = 127\text{K}$ from the GTSM analysis as well as $T_i = 137\text{K}$ from our previous one

using the GOSM[12]. Alternatively, the authors [11] have performed extensive aging experiments on *glycerol* which demonstrate that the original flat course of a high - frequency side of the primary relaxation develops into a shoulder resembling the secondary β relaxation peak. Subsequently, they have been able to fit the DS spectra over a wide frequency range by a superposition of the KWW function for the main relaxation and the Cole - Cole (CC) function for the secondary β relaxation. The main α process can be accounted for by the VFTH equation:

$$\tau_{\alpha}(T) = \tau_{\alpha 0} \exp [B_{\alpha} / (T - T_{0,\alpha})] = 2.5 \times 10^{-16} \exp [2567 / (T - 124)] \quad (6)$$

Concerning the β relaxation, in contrast to the usual Arrhenius behavior in the glassy state, the non - Arrhenius temperature dependence above T_g has been found from a KWW + CC superposition analysis:

$$\tau_{\beta}(T) = \tau_{\beta 0} \exp [B_{\beta} / (T - T_{0,\beta})] = 2.5 \times 10^{-15} \exp [1850 / (T - 125)] \quad (7)$$

Evidently, both the relaxation processes are characterized by the similar Vogel's temperatures $T_{0,\alpha} \cong T_{0,\beta}$ and moreover, they are in acceptable agreements with the initial temperature of the dynamic free volume T_i from the present GTSM analysis. This consistency means that not only a certain generic connection could exist between both the processes, but also that their courses appear to be linked with the onset of the dynamic free volume from PALS method.

Thus, the two quite different phenomenological analyses of the DS spectra of *glycerol* provide practically the same characteristic temperature parameters ($T_{0,\beta}$ or $T_{\gamma,0}$) for the additional relaxation process, both being commensurable with our T_i from PALS. Hence, regardless of interpretation of the origin of this additional effect on the high - frequency side of the primary relaxation the onset of all the processes in *glycerol*, i.e., the main relaxation and the HFW or the secondary β relaxation, appears to be connected with the occurrence of the dynamic free volume detectable by PALS technique.

3.2.3. Relationship between effective free volume fraction and macroscopic dynamics

From the above - mentioned it follows that we are able to obtain the effective free volume information from the PALS data after their plausible model treatments. This opens up the possibility to verify various expressions proposed to relate the macroscopic dynamics with the free volume fraction f [3,4,39]. However, in contrast to these previous equations based either on the phenomenology such as the Doolittle free volume formula [3] or on its combination with the Arrhenius thermal activation term in the hybrid Macedo - Litovitz expression [39], our approach is based on using the directly obtainable effective free volume hole fraction, f_{h_e} , from a combination of independent PALS and DIL measurements.

Figure 3a displays an example of such a test for the case of dielectric relaxation dynamics in *glycerol* in a form of the shift factor $a_{\tau}(T_{ref})$ from the very recent DS study [11]. The dielectric relaxation times of the primary relaxation, $\tau_{\alpha}(T)$, were obtained from a phenomenological analysis of the dielectric loss spectra under assumption of

a sum of the primary α process and the secondary β relaxation. It is evident that the α relaxation time can be related to the effective free volume hole fraction from *Figure 2* at the choice of $T_{ref} = 243K$ in the vicinity of T_{b1}^{lq} from *Figure 1a* via the WLF - Doolittle - type equation (1) with the $\langle B_{\tau} \rangle$ coefficient equal to 0.125 ± 0.009 . This correlation is satisfactory in the region III of the $f_h - T$ dependence of slightly supercooled liquid state where the relaxation time varies over two decades. Deviations can be observed outside this region III. At the high temperatures above T_{b2}^{lq} , this departure is connected with the intrinsic limitation of PALS method as mentioned above, while the deviation at low temperatures below T_{ref} can be fitted by the generalized WLF – Macedo - Litovitz type equation:

$$\log a(T_{ref}) = (E_{act}/2.303R)[1/T - 1/T_{ref}] + (B/2.303)[1/f(T) - 1/f(T_{ref})] \quad (8)$$

based on sequential probability condition for the dynamics of supercooled liquids [39]. This postulates that two events, i.e. local energy fluctuation (E_{act}) and free volume one ($f \equiv f_h$), are necessary for a successful course of motional act. Hence, after subtraction of the free volume term from the experimental shift factor in eq.8, we can determine the activation energy term, E_{act} , from the slope of this difference with the zero intercept. *Figure 3b* indicates that it is the case for *glycerol*. The value of E_{act} reaches almost the three-fold of typical cohesive energy of intermolecular H – bond $E_{coh}^H \approx 20$ kJ/mol. This finding strongly suggests that the course of primary α relaxation in the region II of a deeply supercooled liquid is very probably connected with a local breaking up of the extended H bonded network of *glycerol* molecules participating in a moving event. On the other hand, the validity of the special case of eq. 8 without activation - energy term in the slightly supercooled liquid state indicates that this thermal contribution to the relaxation dynamics appears to be less significant, although the H-bonded molecules will certainly persist also at higher T's in the region III. This seems to suggest that at higher temperatures the primary α process takes place in local regions of the more released microstructure where subsystems of non-bonded molecules through

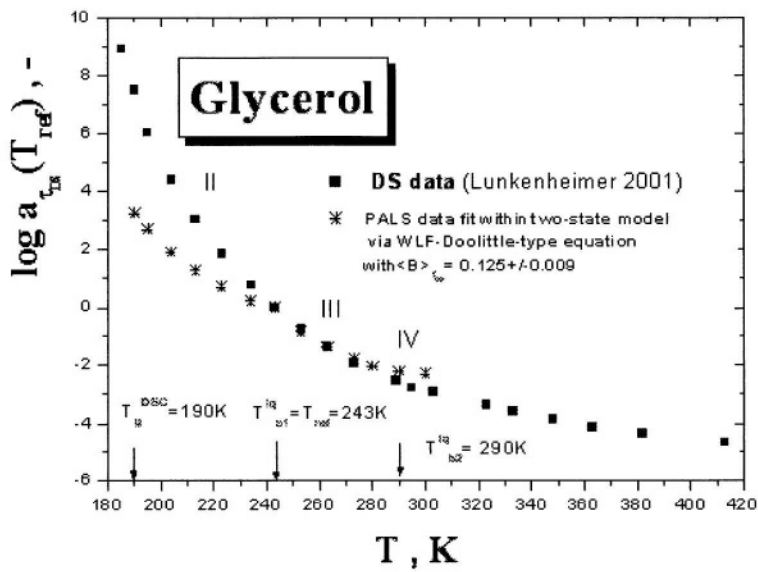


Figure 3a Correlation between the dielectric shift factor and free volume hole fraction for glycerol

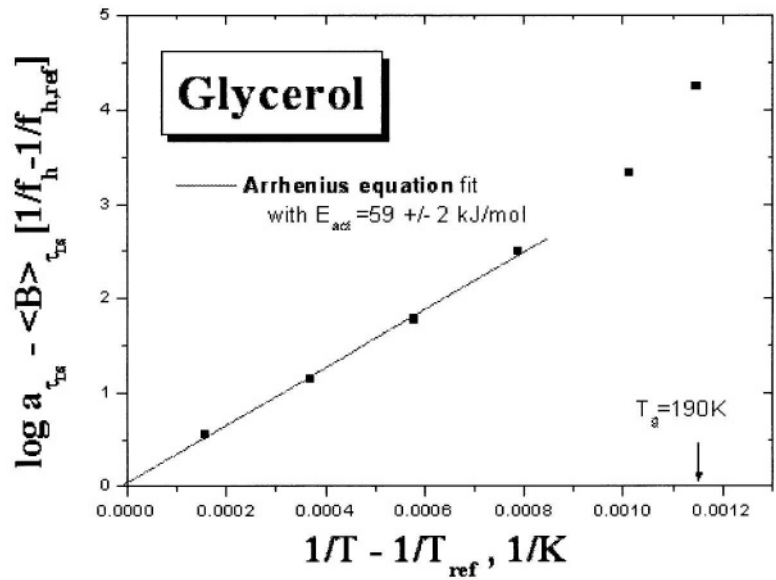


Figure 3b Test of the WLF-Macedo-Litovitz-type equation for glycerol

intermolecular H bonds dominate in the relevant motional act. This picture seems also to be consistent with the restructuring hypothesis behind the bend effect at the first liquid PALS temperature $T_{b1}^{iq} = 241\text{K}$. Accordingly, the slope change in $\tau_3 - T$ plot in *Figure 1* could be connected with relative rapid releasing the densely packed regions - H-bonded clusters - in microstructure of bulk *glycerol* [12]. Thus, both the structural and dynamic concepts of the first bend effect might be of the relevance in *glycerol*, at least.

Summary

Operational classification of a series of small molecular and simple polymer systems into two groups Type I and Type II glass formers based on their o-Ps annihilation behavior is presented. The origin of this division is discussed within the present knowledge situation in the field of dynamics of supercooled liquids. Effective free volume characterizations and an example of its utilization in correlating with the macroscopic dielectric relaxation on *glycerol* are shown.

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References

1. Fox, T.G., Flory, P.J. (1950) *J. Appl. Phys.* **21**, 581 - 591
2. Bondi, A. (1968) *Molecular Crystals, Liquids and Glasses*, Wiley, New York.
3. Doolittle, A.K. (1951) *J. Appl. Phys.* **22**, 1471 - 1475
4. Ferry, J.D. (1980) *Viscoelastic Properties of Polymers*, Wiley and Sons, New York.
5. Brandt, W., Dupasquier, A. eds. (1983) *Positron Solid State Physics*, North-Holland, Amsterdam.
6. Jean, Y.C. (1995) Characterizing Free Volume and Holes in Polymers by Positron Annihilation Spectroscopy in Dupasquier, A. (ed) *Positron Spectroscopy of Solids*, IOS, Ohmsha, Amsterdam, pp. 563 - 580.
7. Bartoš, J. (2000) Positron Annihilation Spectroscopy of Polymers and Rubbers in R.A. Meyers (ed) *Encyclopedia of Analytical Chemistry*, Wiley & Sons, Chichester pp. 7968-7987.
8. Angell, C.A. (1985) Strong and fragile liquids in Ngai, K., Wright (eds) *Relaxations in Complex Systems*, NTIS, Springfield, p. 1 - 11.
9. Bartoš, J., Šauša, O., Bandžuch, P., Zrubcová, J., Krištiak, J. (2002) *J. Non-Cryst. Solids* **307-310**, 417-425.
10. Kudlik, A., Benkhof, S., Blochowicz, T., Tschirwitz, C., Rössler, E. (1999) *J. Mol. Struct.* **479**, 201-218.

11. Ngai,K., Lunkenheimer,P., Leon,C., Schneider,U., Brand,R., Loidl, A. (2001) *J. Chem.Phys.* **115**, 1405 - 1413.
12. Bartoš,J., Šauša,O., Krištiak,J., Blochowicz,T., Rössler, E. (2001) *J.Phys. - Cond.Matter* **13**, 11473 –11484.
13. Ngai,K.L., Bao,L.R., Yee,A.F., Soles,Ch.L (2001) *Phys.Rev.Lett.* **87**, 215901-1 –215901-4.
14. Stickel,F. (1995) *Thesis* , Shaker, Aachen.
15. Wang, J., Porter, R.S. (1995) *Rheol. Acta* **34** , 496 - 503.
16. Kudlik.A., Tschirwitz,Ch., Blochowicz,T.,Rössler,E. (1998) *J.Non - Cryst. Solids* **235-237**, 406-411.
17. Millan,S., Geckle,U., Levay,B., Ache,H. (1980) *Ber.Bunsen-Ges.Phys.Chem.* **94**, 781-785.
18. West,D.H.D., McBrierty,V.J., Delaney,C.F.G. (1975)*Appl.Phys.***7**,171-174.
19. Arbe,A., Richter,D.,Colmenero,J., Farago,B.(1996) *Phys.Rev.* **E54**, 3853-3869.
20. Leon,C., Ngai,K., Roland,C.M. (1999) *J.Chem. Phys.* **110**, 11585-11 591.
21. Leheny, R.L., Nagel.S.R.(1998) *J.Non-Cryst.Solids* **235 - 237**, 278-285.
22. Schneider,U., Brand,R., Lunkenheimer,P., Loidl,A.(2000) *Phys.Rev.Lett.* **84**, 5560 - 5564.
23. Lunkenheimer,P., Wehn,R., Riegger,Th., Loidl, A. (2002) *J.Non -Cryst.Solids* **307-310**, 336-344.
24. Döss,A., Paluch,M., Sillescu,H., Hinze,G. (2002) *Phys.Rev.Lett.* **88**, 095701-1-095701-4.
25. Johari,G.P., Whalley,E. (1972) *Faraday Symp.* **6**, 23–41.
26. Paluch, M., Casalini,R., Hensel -Bielowska,S., Roland ,C.M. (2002) *J.Chem. Phys.* **116**, 9839 - 9844.
27. Tao, J. (1972) *J.Chem.Phys.* **56**, 5499-5510.
28. Eldrup.M., Lightbody,D., Sherwood,J.N. (1981) *Chem.Phys.***63**, 51-58.
29. Nakanishi,H., Wang, S.J.,Jean,Y.C. (1988) in S.C.Sharma (ed), *Positron Annihilation Studies of Fluids*, World Science, Singapore , pp.292 - 298.
30. Consolati,G. (2002) *J.Chem.Phys.* **117**,7279-7283.
31. Kobayashi,Y., Zheng, W., Meyer, E.F., McGervey, J.D., Jamieson,A.M., Simha,R. (1989) *Macromolecules* **22** 2302 - 2306.
32. Wang,Y.Y., Nakanishi,H., Jean,Y.C., Sandrecki,T.C. (1990) *J.Polym.Sci.B Polym.Phys.* **28**, 1431-1441
33. Bartoš,J., Krištiak,J. (2000) *J.Phys.Chem.* **B 104**, 5666 - 5673.
34. Bandžuch,P.,Krištiak,J., Šauša, O., Zrubcová,J. (2000) *Phys.Rev.* **B61** 8784- 8787.
35. Consolati,G., Levi,M., Messa,L., Tieghi,G. (2001) *Europhys.Letts* **53** ,497-503.
36. Bartoš,J., Račko,D. to be published
37. Kovacs ,A. (1963) *Adv.Polym.Sci.* **3**, 394 -507.
38. Angell,C.A. (1997) *J.Res.Natl.Inst. Stand.Technol.* **102**, 171 – 185.
39. Macedo,P.B., Litovitz,T.A. (1965) *J.Chem.Phys.* **42**, 245 - 256.

INFLUENCE OF MOLECULAR STRUCTURE ON DYNAMICS OF SECONDARY RELAXATION IN PHTHALATES

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Abstract

Dielectric relaxation measurements have been used to study influences of the molecule topology on the secondary relaxation process in three phthalate derivatives. The measurements were performed over ten decades in frequency and a broad range of temperature and pressure. The isobaric data show thermally activated relaxation time in all cases, but with different activation energies. The isothermal measurements confirm that the secondary relaxation is insensitive to pressure in the vicinity of glass transition temperature. The relaxation strength, $\Delta\epsilon$, decreases on lowering temperature below the glass transition temperature.

Introduction

In dielectric spectra of supercooled liquids several types of relaxation phenomena can be observed [1,2,3,4]. The slowest and the most prominent is the α -relaxation, that is responsible for the relaxation of the structure of the liquid. It has a characteristic broad and asymmetric peak, with the maximum moving towards the lower frequencies with decreasing temperature. Both the shape of the peak and the temperature dependence of the relaxation times of the supercooled liquids are distinctly different from the normal liquids above the melting point [5]. The α -relaxation time usually has non-Arrhenius temperature dependence and there are several formulae, which model this behavior. One of them is the Vogel-Fulcher-Tammann [6] (VFT) law in the form:

$$\tau = \tau_{\infty} \exp \frac{DT_0}{T - T_0} \quad (1)$$

where D is a strength parameter and T_0 is the temperature of the ideal glass transition.

The shape of the α -relaxation peak can be well described in the term of the Havriliak-Negami [7] (HN) function, which accounts well the data in a region about two decades below and above the peak maximum, and is given by

$$\epsilon^*(\omega) = i \frac{\sigma}{\omega \epsilon_0} + \epsilon_{\infty} + (\epsilon_s - \epsilon_{\infty}) \left[1 + (i\omega\tau_{HN})^{\alpha} \right]^{\beta} \quad (2)$$

However, two decades above the maximum of the α -relaxation peak a systematic deviation from the HN-function can be observed. This deviation is caused by another relaxation process called the β relaxation. This process appears in the temperatures not far from the glass transition temperature (about $1.2T_g$). It has a very characteristic: broad and symmetric shape, and its strength is of some decades weaker than that of the α -process. The temperature evolution of the β -relaxation times, unlike the α -process, follows the Arrhenius law:

$$\tau_{\beta} = \tau_0 \exp(E/k_B) \quad (3)$$

In the last few years the occurrence and behavior of the β -relaxation became one of the most discussed topics in the dynamics of the supercooled liquids [8,9,10,11,12,13]. However the nature of the β -relaxation still remain unclear. One of the most often considered issue is whether the β -relaxation is intramolecular or intermolecular in origin. Initially the β -relaxation of polymer was assigned to motion of flexible side chains [14]. In the seventies Johari and Goldstein [15,16] carried out a systematic observation of the β -relaxation in the mixtures of the small rigid molecules as well as in some one component liquids. They concluded that the β -relaxation is intermolecular in origin and further suggested that it occurs in some loosely packed regions in the glass called "islands of mobility"[17] and is an inherent feature of the deeply supercooled and the glassy state. This kind of secondary relaxation differs from those which arise from the internal motions within the molecule, occurring usually at higher frequencies. To distinguish them from others, they are called the Johari-Goldstein (JG) relaxation.

However, this point of view is not generally accepted. It often becomes matter of discussion if given molecule can be regarded as rigid. In some cases, it was shown that the internal motions of the molecule could cause the β -process [18]. It is not clear what origin such slow β -relaxation is of but under the isobaric conditions of ambient pressure it reveals all features characteristic for the JG-relaxation [1]. Majority of the studies on the dynamics of the supercooled liquids are carried out by use of the broadband dielectric spectroscopy with temperature as a parameter under ambient pressure. It is advantageous to introduce pressure also as a variable for the purpose of resolving problems [19,20,21, 22,23]. By changing pressure, only the density of the probed substance changes, thus interesting results can be gained. One of such remarkable observations is that the β -process in some cases turns out to be completely pressure independent [2]. Such a behavior can be explained on the basis of the Vogel and Roessler statement[24], that the β -relaxation is a highly restricted motion on a cone of a very small open angle. However, on the other hand, it can serve as a proof that the β -process is merely intramolecular in origin, because that the latter is also pressure independent.

In this paper we would like to discuss some features of the β -relaxation in a series of phthalates. It should be noted that phthalates belongs to that group of compounds in which the origin of the β -relaxation is still unclear. The substituents to the phenyl ring in studied samples are flexible and can be potentially a source of the secondary relaxation process. At first sight, the β -process of the sample liquids reveals all the features of the JG-relaxation. The situation become more uncertain when one takes into account analysis of the pressure dependence of the relaxation times, τ_{β} , or on

comparing τ_β with the primitive relaxation times, τ_0 , predicted by the coupling model of Ngai [25,26,27]. Insensitivity of τ_β on compression as well as lack of agreement between τ_β and τ_0 suggest that the secondary relaxation peak observed in dielectric spectra could not be true JG process [].

We have chosen three phthalates, which differ only slightly by the substituents. These are diethyl phthalate (DEP), dibutyl phthalate (DBP) and diisobutyl phthalate (DIBP). The first two of them have the same type (chain) substituents, which differ with two $-\text{CH}_2-$ groups. The last two of them have the same summaric formula, but differ in the topology. We would like to compare the similarities as well as differences that can be observed for the β -relaxation in the series.

Experimental

Diethyl phthalate (99.5%) dibutyl phthalate (99%) and diisobutyl phthalate (99%) were supplied by Aldrich Chemicals and used as purchased. The molecular structures of the samples are displayed in inset to fig 4. From temperature dependence of the α -relaxation we have determined the $T_g(\tau_\alpha=100\text{s})$ which amounted 184K, 177K and 191K respectively and are in a good agreement with the results obtained by others[28].

The temperature-dependent dielectric measurements were carried out using the experimental set-up made by Novocontrol GmbH. This system was equipped with a Novocontrol GmbH Alpha dielectric spectrometer (10^2 - 10^7 Hz) and Agilent 4291B impedance analyzer (10^6 - 1.8×10^9 Hz) for measurement of the complex dielectric permittivity $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$. The sample was placed in a parallel plate cell (diameter 20 mm, gap 0.1 mm). The temperature was controlled using a nitrogen-gas cryostat, with temperature stabilization better than 0.1 K.

For high-pressure measurements we used a pressure system constructed by UNIPRESS with a home-made flat parallel capacitor. The pressure was exerted on the sample by steel piston up to the 1.8 GPa. The measured samples was in contact only with stainless steel and Teflon. The temperature was controlled within 0.1K by means of liquid flow provided by a thermostatic bath.

Results and discussion

In fig.1 we have shown the representative dielectric loss spectrum of the phthalates. Three different relaxation modes are present in the spectrum. At low frequencies the loss is due to dc-conductivity of mobile ions commonly present in the dipolar liquids. In the middle range of the spectrum one can observe the α -relaxation peak with its characteristic asymmetric shape. As the spectrum is taken in temperatures above the glass transition, the α -relaxation dominates the spectrum, however about two decades above the α -peak maximum another process can be observed. This is the β -relaxation, which becomes more and more clearly visible at lower temperatures by moving the α -relaxation peak towards the lower frequencies. When the α -relaxation

moves totally out of the experimental window, the β peak becomes the dominating relaxation process in the spectrum. The dotted lines are the best fits to the sum of the HN, function, the conductivity term and a Cole-Cole-functions for the α , the dc-conductivity and the β -modes respectively.

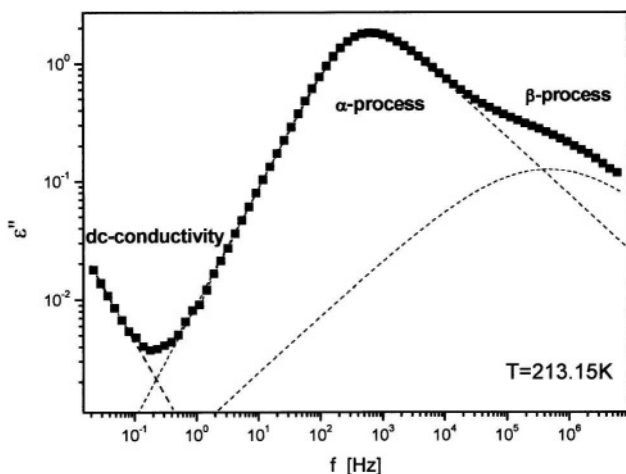


Figure 1. Sample spectrum for DIBP for $p=1$ bar and $T=213$ K. Dashed lines and curves represent three different relaxation processes in the sample: dc-conductivity, α -relaxation and β -relaxation

In the fig. 2 we present the temperature evolution of the β -process below T_g at atmospheric pressure. This set of data is obtained for diisobutyl phthalate. However the same pattern of behavior for the β -relaxation is also observed in of the two other compounds. As was mentioned above, below the glass transition temperature the influence of the α -process is negligible. The maximum of the β -relaxation peak also move towards the lower frequencies with the lowering temperature according to eq.3. In fig. 2 another important features of the β -relaxation can be recognized. The first is the lowering of the strength of the β -process and the second is the broadening of the spectra. The first effect can be well seen in the fig. 3 where the dependence of $\Delta\epsilon$ on T is depicted. The relaxation strength $\Delta\epsilon$ was obtained by the fitting the Cole-Cole function to the experimental data. The CC function can be obtained from eq.2 when assume the parameter $\beta=1$. In figure 3 we depicted the data for all three phthalates. It is now evident that the value of the $\Delta\epsilon$ of the β -relaxation decreases significantly approaching the glass transition temperature for all studied compounds. However, the change of dielectric strength with lowering temperature is very weak below T_g [29].

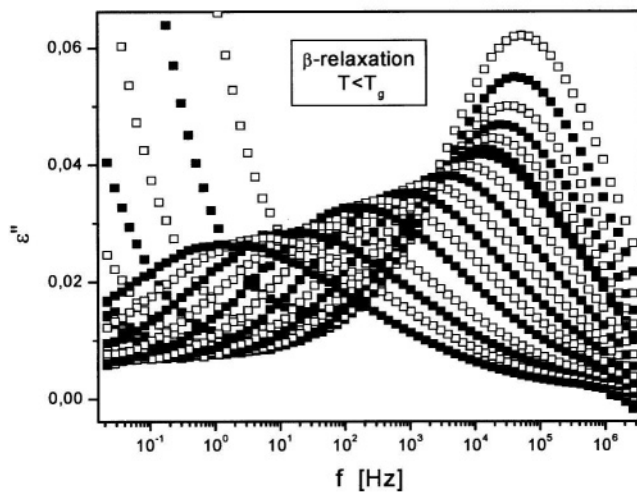


Figure 2. The frequency dependence of the dielectric loss ϵ'' for DIBP at different temperatures below T_g .

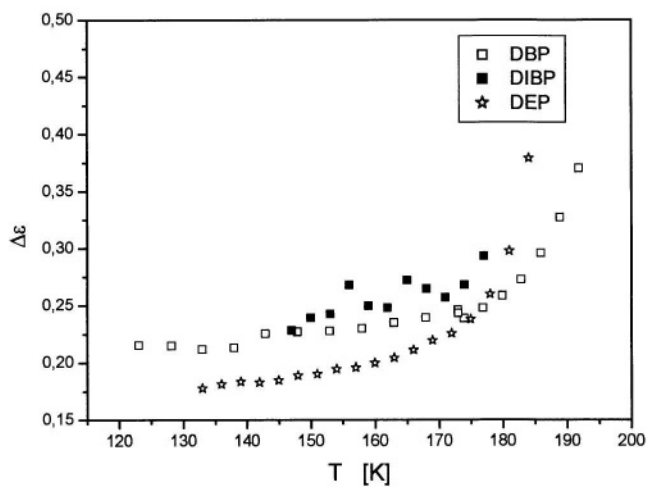


Figure 3. Temperature dependence of the secondary relaxation strength $\Delta\epsilon$ for all phthalate derivatives.

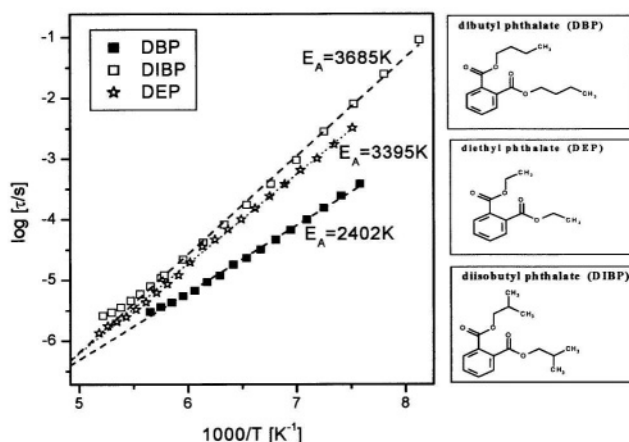


Figure 4. Arrhenius plot of β -relaxation times for DEP, DBP and DIBP. Right panel present chemical structures of investigated substances

In this figure it is also visible that while the ΔE of the DBP and DIBP are on the same level, the strength of the DEP β -relaxation is somewhat weaker. Consequently, it means that for the behavior of this parameter the molecular structure is of the lesser importance. From the fit of the secondary relaxation peak by means of the CC function we determined the value of secondary relaxation times. The obtained dependences of the β -relaxation times on temperature both above and below T_g are presented in fig.4. In all cases the relaxation times τ_β obey the Arrhenius law. It is somewhat surprising that the results for the diisobutyl and diethyl phthalates are very similar, while the dependence obtained for the dibutyl phthalate is somewhat weaker. From fitting the eq.3 to the temperature dependence of $\tau_\beta(T)$ we determined the mean activation energies for DIBP, DEP and DBP, which are equal to 3685K, 3395K and 2402K respectively. These values are typical of JG-relaxation in other glass formers. For instance $E_\beta = 3043K$ for toluene []. Dashed lines are for the best fit using eq.3. The apparent deviation from the Arrhenian behavior for the highest temperatures in all three cases might be caused by the influence of the α -relaxation as these results are obtained above respective T_g . In fig. 5 the shapes of the whole spectra of three phthalates are compared. In panel (a) and (b) we compare the spectra with almost the same α -relaxation time, to see how the relation between the α and β -relaxations changes with the change in substituents. The results presented in the graph (a) come from the isobaric experiments under the atmospheric pressure. The heights of the spectra were scaled to the α -relaxation peak maximum of DIBP.

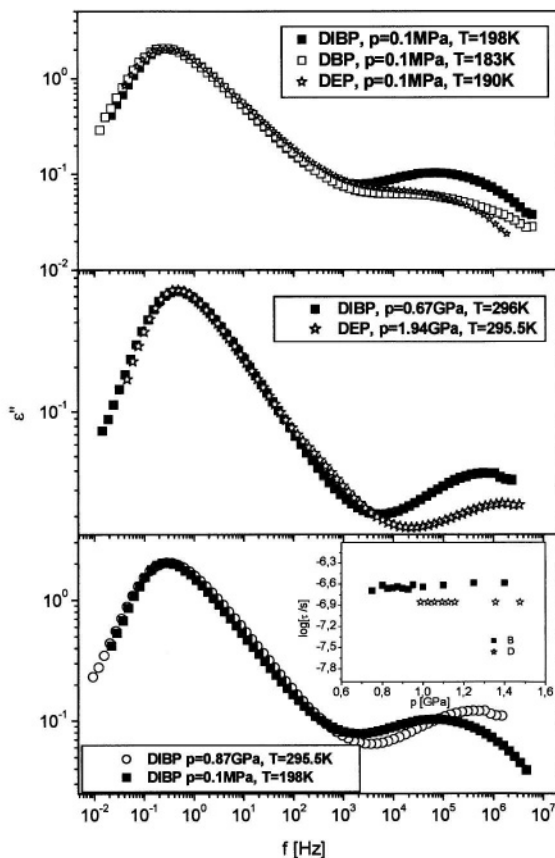


Figure 5. Upper panel show comparison of the dielectric loss spectra obtained from isobaric measurements. Central panel present a comparison of the spectra obtained from isothermal measurements for DEP and DIBP. And lower panel show a comparison of the spectra obtained from isothermal and isobaric measurements for DEP. Inset in this panel shows pressure dependence of the secondary relaxation times for DEP and DIBP.

Scaling the spectra to the α -peak maximum may seem a bit arbitrary but we believe that nevertheless it is a suitable point of reference to compare spectra for different compounds and obtained under different thermodynamic conditions. The striking fact is that the shape of the α -relaxation is the same for all three cases, and this holds also under high pressure (graph (b)). Moreover, α -relaxation in all three

phthalates turns out to obey temperature–pressure superpositioning, which can be observed in the lowest panel by the example of the spectra of DIBP.

The only changes visible in fig. 5a and 5b are in the β -relaxation. It means that the molecule topology and slight difference in the length of the substituents are of no consequence for the α -relaxation. But it influences significantly the β -relaxation which is non cooperative and the geometry of the molecule plays leading role in this kind of motion. The reciprocal relation between the heights of the β -relaxations in phthalates is apparent, as one should remember that the spectra were scaled to the α -peak maximum. The relation between the heights of these peaks can be seen from the fig. 3 and was discussed earlier. A real effect is the larger splitting between α and β -relaxation under high pressure (fig. 5c). It is caused by the fact that the β -relaxation in all three studied materials is basically pressure independent in vicinity of glass transition. To emphasize this fact we collected the β -relaxation times obtained for DEP and DIBP in the inset of fig. 5c. Thus, the β -relaxation in phthalates is thermally activated[30].

From some recent works it turns out that although phthalates are not the sole glass formers in which such effect can be observed [.,]. It is not a rule that pressure doesn't influence the β -relaxation at all. In some cases the β -mode reveals a slight pressure dependency [31]. The problem whether this feature can be a determinant of the true JG-relaxation is a matter of the lively discussion.

The β -relaxation in phthalates possesses also another characteristic feature, which should be mentioned herein. In the frame of the coupling model (CM) by Ngai [25,26,27] a primitive relaxation is postulated. The relaxation time of this relaxation is related to the α -relaxation time via Ngai relation:

$$\tau_0 = t_c \tau_\alpha^{1-n} \quad (4),$$

where the τ_0 is the primitive relaxation time, t_c ($\approx 2\text{ps}$ for molecular liquids) is a crossover time from primitive to cooperative relaxation and $(1-n)$ is the KWW stretch exponent. It was recently established that the primitive relaxation time from CM agrees well with the one of the JG-relaxation in many different materials[32,33]. However, for the phthalates the real τ_β is much shorter then the estimated value of the respective primitive relaxation. For the DEP it was found that the KWW fit gives $n=0.36$ [.]. The same value can be assumed for other phthalates as we have seen in fig. 5 that the differences in substituents do not influence the shape of the α -relaxation. The comparison of the calculated values of τ_β and τ_0 are collected in Table 1.

TABLE 1. The comparison between values of primitive and secondary relaxation times for studied compounds.

Name of material	T [K]	$\log_{10}\tau_\beta$	$\log_{10}\tau_0$	$\log_{10}\tau_0 - \log_{10}\tau_\beta$
DEP	190.14	-5.75	-4.57	1.18
DBP	179.97	-5.60	-3.68	1.92
DIBP	194.82	-5.65	-3.82	1.83

Recently the last two features of the β -relaxation, i.e. the independence of the β -relaxation on pressure and discrepancy between the τ_0 from CM and τ_β are considered as to be crucial in distinguishing the β -relaxation which originates in the

intramolecular motions from the true JG-relaxation with the intermolecular origin[34,35].

Conclusions

We analyzed the β -relaxation in three phthalates. Two of them have the same molecular weight but different geometry, while another two of them have very similar (chain) substituents and very similar topology. It turns out that the differences in topology influences many features like the ΔE activation energy, the position of the β -peak in comparison to the fixed α -peak position. The comparison of the influence of temperature on relaxation times is very interesting in its own right as similarity can be observed in the behavior of the DEP and DIBP, while the DBP behave clearly different. From the comparison of the shape of the whole spectra (including the α and β -relaxations) we notice that the different substituents influence only the non-cooperative β -relaxation while the cooperative α -relaxation remains unchanged.

Although the shape and the temperature behavior of the β -relaxation reveals features typical for the JG-relaxation, from the total independence on pressure of this process in the range of measurement, one can conclude that the origin of the β -relaxation in these glass formers may be not intermolecular in origin, but arises from the motion of the internal degrees of freedom and consequently it is not the true JG-relaxation.

Acknowledgments

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References

1. Kremer, F. (2002) Dielectric spectroscopy - yesterday, today and tomorrow, *J. Non-Crys. Solids* **305**, 1.
2. Wu, L. (1991) Relaxation mechanisms in benzyl chloride-toluene glass, *Phys. Rev.B* **43**, 9906.
3. Pawlus, S., Paluch, M., Sekula, M., Ngai, K.L., Rzoska, S.J. and Ziolo, J. (2003) Changes in dynamic crossover with temperature and pressure in glass-forming diethyl phthalate, *Phys. Rev.E* **68**, 021503.
4. Hansen, C., Stickel, F., Berger, T., Richert, R. and Fischer, E.W. (1997), Dynamics of glass-forming liquids. III. Comparing the dielectric α - and β -relaxation of 1-propanol and o-terphenyl, *J. Chem. Phys.* **107**, 1086.

5. Boehmer, R., Ngai, K.L., Angell, C.A. and Plazek, D.J. (1993) Nonexponential relaxations in strong and fragile glass formers, *J. Chem. Phys.* **99**, 4201.
6. Vogel, H. (1921) Das Temperaturabhängigkeitsgesetz der Viscosität von Flüssigkeiten, *Phys. Z.* **22**, 645; Fulcher, G. S. (1923) Analysis of recent measurements of the viscosity of glasses, *J. Am. Ceram. Soc.* **8**, 339
7. Havriliak, S. and Negami, S. (1966) A complex plane analysis of α -dispersions in some polymer systems, *J. Polym. Sci. Polym. Symp.* **14**, 99.
8. Kudlik, A., Benkhof, S., Blochowicz, T., Tschirwitz, C. and Roessler, E. (1997) The dielectric response of simple organic glass formers, *Europhys. Lett.* **40**, 649.
9. Olsen, N.B. (1998) Scaling of β -relaxation in the equilibrium liquid state of sorbitol, *J. Non-Cryst. Solids* **235-237**, 399.
10. Wagner, H. and Richert, R. (1998) Spatial uniformity of the β -relaxation in D-sorbitol, *J. Non-Cryst. Solids* **242**, 19.
11. Kudlik, A., Tschirwitz, C., Benkhof, S., Blochowicz, T. and Roessler, E. (1999) Slow secondary relaxation process in supercooled liquids, *J. Mol. Struct.* **479**, 201.
12. Doess, A., Paluch, M., Sillescu, H. and Hinze, G. (2002) From Strong to Fragile Glass Formers: Secondary Relaxation in Polyalcohols, *Phys. Rev. Lett.* **88**, 095701; A. Doess, Paluch, M., Sillescu, H. and Hinze, G. (2002) Dynamics in supercooled polyalcohols: primary and secondary relaxation, *J. Chem. Phys.* **117**, 6582.
13. Schneider, U., Brand, R., Lunkenheimer, P. and Loidl, A. (2000) The Excess Wing in the Dielectric Loss of Glass-Formers: A Johari-Goldstein beta Relaxation?, *Phys. Rev. Lett.* **84**, 5560; Lunkenheimer, P., Wehn, R., Riegger, Th. and Loidl, A. (2002) Excess wing in the dielectric loss of glass formers: further evidence for a β -relaxation, *J. Non-Cryst. Solids* **307-310**, 336.
14. Williams, G. and Watts, D.C. (1971) Analysis of molecular motion in the glassy state, *Trans. Faraday Soc.* **67**, 1971.
15. Johari, G. P. and Goldstein, M. (1970) Viscous Liquids and the Glass Transition. II. Secondary Relaxations in Glasses of Rigid Molecules, *J. Chem. Phys.* **53**, 2372; (1971) Viscous Liquids and the Glass Transition. III. Secondary Relaxations in Aliphatic Alcohols and Other Nonrigid Molecules, *J. Chem. Phys.*, **55**, 4245.
16. Johari, G. P. (1976) Glass transition and secondary relaxations in molecular liquids and crystals, *Ann. N. Y. Acad. Sci.* **279**, 117.
17. Goldstein, M. (1969) Viscous Liquids and the Glass Transition: A Potential Energy Barrier Picture, *J. Chem. Phys.* **51**, 3728; Johari, G. P. (1973) Intrinsic mobility of molecular glasses, *J. Chem. Phys.* **58**, 1766.
18. Meier, G., Gerharz, B., Boese, D. and Fischer, E.W. (1990) Dynamical processes in organic glassforming van der Waals liquids, *J. Chem. Phys.* **94**, 3050.
19. Paluch, M. and Ziolo, J. (1998) Dynamical processes in a superpressed glass-forming liquid studied by dielectric spectroscopy, *Europhys. Lett.* **44**, 315.
20. Paluch, M., Ngai, K.L. and Hensel-Bielowka, S. (2001) Pressure and temperature dependences of the relaxation dynamics of cresolphthalein-dimethylether: Evidence of contributions from thermodynamics and molecular interactions, *J. Chem. Phys.* **114**, 10872.

21. Hensel-Bielowka, S., Ziolo, J., Paluch, M. and Roland, C.M. (2002) The effect of pressure on the structural and secondary relaxations in 1,1'-bis (p-methoxyphenyl) cyclohexane, *J. Chem. Phys.* **117**, 2317.
22. Paluch, M., Casalini, R., Hensel-Bielowka, S. and Roland, C.M. (2002) Effect of pressure on the α -relaxation in glycerol and xylitol, *J. Chem. Phys.* **116**, 9839.
23. Hensel-Bielowka, S. and Paluch, M. (2002) Origin of the High-Frequency Contributions to the Dielectric Loss in Supercooled Liquids, *Phys. Rev. Lett.* **89**, 025704.
24. Vogel, M. and Roessler, E. (2000) On the nature of Slow β -Process in Simple Glass Formers: A 2H NMR Study, *J. Phys. Chem. B* **104**, 4285; Vogel, M. and Roessler, E. (2001) Slow β process in simple organic glass formers studied by one- and two-dimensional 2H nuclear magnetic resonance, *J. Chem. Phys.* **114**, 5802.
25. Tsang, K.Y. and Ngai, K.L. (1997) Relaxation in interacting arrays of oscillators *Phys. Rev E* **54**, 3067.
26. Ngai, K.L. and Tsang, K.Y. (1999) Similarity of relaxation in supercooled liquids and interacting arrays of oscillators, *Phys. Rev. E* **60**, 4511.
27. Ngai, K.L. (2001) Coupling model explanation of salient dynamic properties of glass-forming substances, *IEEE Trans. Dielectr. Elec. Insul.* **8**, 329.
28. Paluch, M. (1998) PhD thesis, Silesian University, Katowice
29. Blochowicz, Th., Tschirwitz, Ch., Benkhof, St. and Roessler, E.A. (2003) Susceptibility functions for slow relaxation processes in supercooled liquids and the search for universal relaxation patterns, *J. Chem. Phys.* **118**, 7544.
30. Ferrer, M.L., Lawrence, C., Demirjian, B.G., Kivelson, D., Alba-Simionesco, C. and Tarjus, G. (1998), *J. Chem. Phys.* **109**, 8010.
31. Hensel-Bielowka, S., Paluch, M., Ziolo, J. and Roland, C.M. (2002) Dynamics of Sorbitol at Elevated Pressure, *J. Phys. Chem. B* **106**, 12 459.
32. Ngai, K. L. (1998) Relation between some secondary relaxations and the α relaxations in glass-forming materials according to the coupling model, *J. Chem. Phys.* **109**, 6982
33. Leon, C., Ngai, K.L. and Roland, C.M. (1999) Relationship between the primary and secondary dielectric relaxation processes in propylene glycol and its oligomers, *J. Chem. Phys.* **110**, 11585.
34. Ngai, K.L. and Paluch, M. (2003) Inference of the Evolution from Caged Dynamics to Cooperative Relaxation in Glass-Formers from Dielectric Relaxation Data, *J. Phys. Chem. B* **107**, 6865.
35. Ngai, K. L. and Paluch, M. (2004) Classification of secondary relaxation in glass-formers based on dynamic properties, *J. Chem. Phys.* **109**, 8010.

ELECTROSTRICTION AND CRYSTALLINE PHASE TRANSFORMATIONS IN A VINYLIDENE FLUORIDE TERPOLYMER

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Abstract. Substantial electrostrictive strains can be obtained from terpolymers of vinylidene fluoride, trifluoroethylene, and chlorotrifluoroethylene. The mechanism of the electromechanical response was investigated using x-ray diffraction and infrared absorption measurements on the polymer under an electric field. While application of the field is found to induce changes in the crystal phase structure, the phase transition that can effect dimensional changes is too small to account for the magnitude of the electrostriction. Thus, the origin of the exceptional electromechanical properties of this material remains to be fully elucidated.

1. Introduction

Electroactive materials convert electrical energy into mechanical energy (and vice versa for piezoelectrics), and thus are attractive when low weight and minimal power consumption are important. Potential fields of application include sensors, actuators, loudspeakers, sonar transducers, artificial muscles, and robotics. Existing commercial and military devices are based on ceramics and, to a more limited extent, poly(vinylidene fluoride) (VDF) or its copolymer with trifluoroethylene (TrFE). However, these polymers require high electric fields to achieve significant strains, restricting their utility. Current research and development work with polymers focuses on the electrostrictive response, which refers to the strain quadratic in the polarization (and also quadratic in the field for linear dielectrics below the saturation limit). While electrostriction represents a source of error in sensors [1] and nonlinear dielectric measurements [2], it offers the potential to realize large strains at low fields.

Recent progress has been made using various VDF copolymers, with reported electrostrictive coefficients as large as $1.6 \times 10^{-15} \text{ m}^2/\text{V}^2$ [3,4,5,6]. We have been investigating terpolymers of VDF with trifluoroethylene (TrFE) and chlorotrifluoroethylene (CTFE) [7,8], which exhibit electrostrictive properties rivaling the best obtained to date. The terpolymers are produced using a combination of bulk polymerization and oxygen-activated

free radical initiation [9]. The controlled monomer addition results in non-blocky terpolymers.

To optimize and best utilize these terpolymer materials, it is necessary to understand the origin of their electrostriction. In general, various mechanisms can give rise to electric-field-induced strains. These include dipole reorientation (requiring anisotropy or inhomogeneities), ionic displacements (which perturb the unit cell), a change in crystal structure (melting or phase change), the Maxwell effect (Coulombic attraction of the electrodes), charge injection, and interfacial polarization (space charge effects). There are five possible crystalline forms (polymorphs) of polyvinylidene fluoride homopolymer, the relevant ones herein being the anti-polar α , the all-trans polar β phase (which is only stable below the Curie point), and the polar δ structure [10,11]. The latter has the same conformation as the α form, but with the dipoles of adjacent chains rotated 180 degrees, resulting in a net dipole moment. For the VDF-TrFE-CTFE terpolymers, conversion of the anti-polar α crystal phase to the polar β phase is a possible mechanism for electrostriction, since the unit cell of the latter is 10% smaller in the direction transverse to the chain dimension [12]. This implies that field-induced phase conversion might yield substantial macroscopic strains. The α form has no net dipole moment due to the antiparallel packing of the crystal dipoles; however, there is a moment normal to the chain which allows strong interaction with applied fields [13]. Piezoelectricity and pyroelectricity in VDF homopolymer have been ascribed to a phase-conversion mechanism [13,14]. In this work, we describe experiments probing the possible contribution of a field-induced phase change to the electromechanical response of the terpolymer.

2. Experimental

The terpolymers, having a compositions of 58 to 68% VDF, 28 to 34 % TrFE, and 4 to 8% CTFE, were synthesized T.C. Chung. Films of the terpolymer were prepared from 5% dimethylformamide solutions. For the x-ray diffraction measurements, films (220 μm thick) supported on an aluminum substrate were used. The sample was scanned from $2\theta = 17$ to 23° at two deg per min, with six scans averaged. For the FTIR experiments, 5 μm thick films were cast directly on a germanium electrode. The spectra were obtained using a Nicolet 750 spectrometer. Sixteen scans were averaged at a resolution for 2 cm^{-1} , with all absorbances falling within the limits of Beer's law. Electric fields were obtained using a Trek 610-D amplifier, with an alternating input wave (typically triangular) generated with a Solartron 1254. Electrostrictive strains were determined using an MTI 1000 Fotonic Sensor, with the polarization simultaneously measured by a Sawyer-Tower circuit. Differential scanning calorimetry (DSC) employed a Perkin-Elmer DSC-7. The scan rate was at 10 deg per min.

3. Results and Discussion

Representative electrostrictive strains measured parallel to the electric field are shown in Figure 1. The response is second-order in the field, occurring at twice the applied frequency and independently of the field direction. By fitting the data to a second order polynomial, we obtain $10^{-16} \text{ m}^2/\text{V}^2$ for the electrostrictive coefficient. The frequency response is shown in Figure 2 for a field of 10 MV/m.

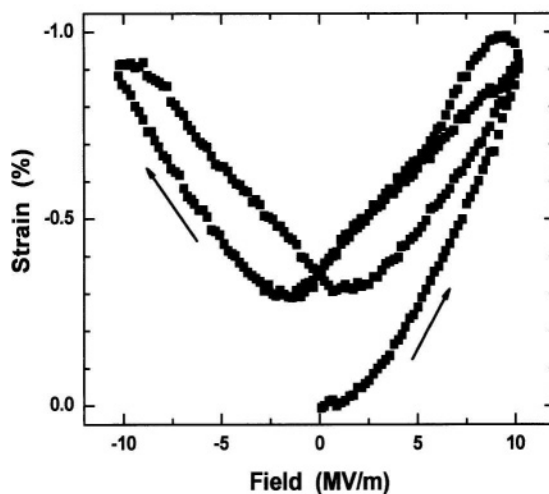


Figure 1. Thickness strain measured at RT as a function of the electric field. There is an offset after the initial cycle, equal to roughly one-third the maximum strain.

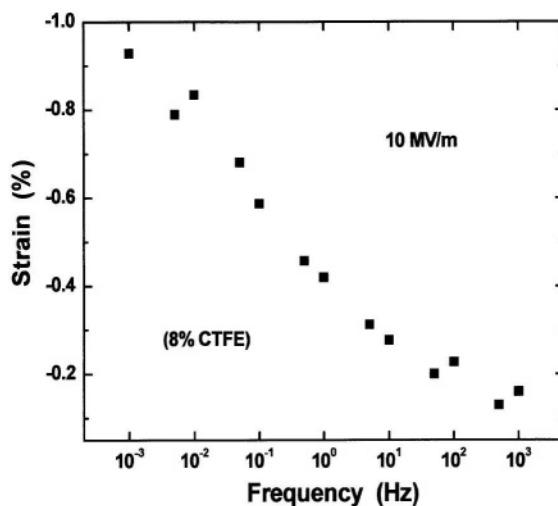


Figure 2. Frequency dependence of the electrostrictive strain in the terpolymer at room temperature.

The data in Figs. 1 and 2 were measured at room temperature, which is below the Curie transition. This transition, which varies with chemical composition of the terpolymer [7], can be seen in the DSC curve in Figure 3. Clearly, there is a significant amount of the polar β structure present at room temperature.

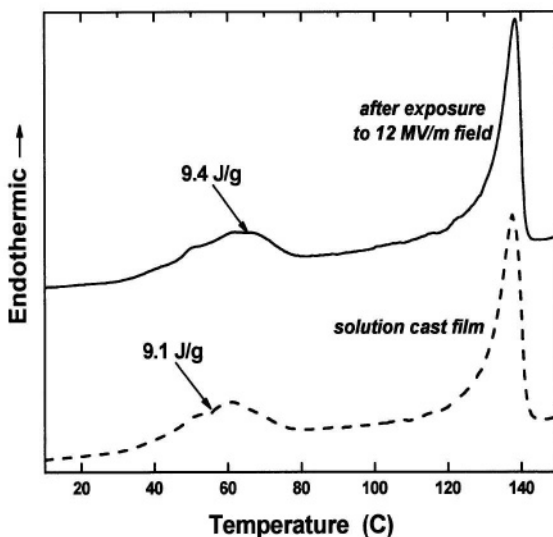


Figure 3. Differential scanning calorimetry for the terpolymer as Cast from solution (dashed Curve) and after poling with a 12 MV/m electric field.

X-ray diffraction data for the terpolymer is shown in Figure 4. In the vicinity of $2\theta \sim 19$ degrees, there are unresolved reflections from the $110\ \alpha$ planes and, at slightly higher angle, from the combined $(110)+(200)\ \beta$ planes [12]. These peaks correspond to distances primarily perpendicular to the chain axes. The diffraction pattern indicates a loss of intensity of the α peak, with an increasing intensity of the β peak. Clearly, the electric field induces changes in the crystal morphology. However, it is well-known [15,16] that strong fields cause rotation along the c -axis of alternate chains in the α crystallites. This brings the dipole moments into parallel alignment with the electric field, forming the δ crystalline phase. The α and δ crystals diffract at the same angles, but have different form factors, thus yielding different peak heights. Given the overlapping of the peaks in Fig. 4, resolution of the various crystalline forms from the diffraction pattern is difficult. This is especially the case since the bulky CTFE disrupts the crystal structure, changing the interchain spacing [17]; thus, precise unit cell information is unavailable for the terpolymer.

One of the x-ray scans in Fig. 4 was obtained roughly 15 hours after removal of the electric field. As can be seen, the phase conversion is partially stable. This corresponds to the offset strain seen after the first cycle in Fig. 1. DSC of this poled sample revealed a 3% increase in the magnitude of the Curie transition, consistent with some conversion of the α or δ phases to the β crystal form.

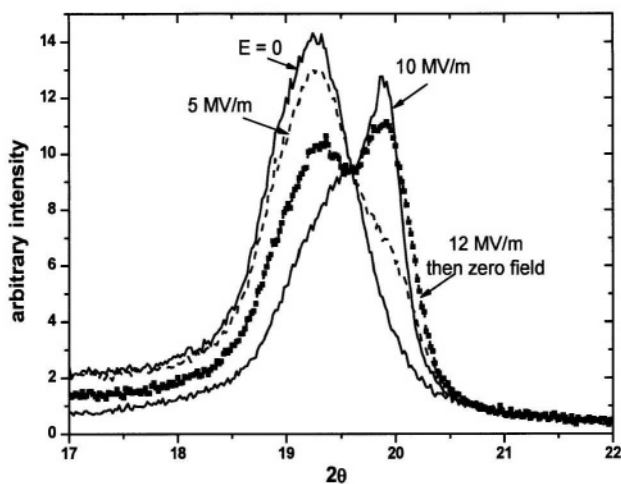


Figure 4. X-ray diffraction pattern of the terpolymer under electric fields of the indicated strength. The measurement for 12 MV/m was obtained 15 hrs after removal of the field. All data obtained at room temperature.

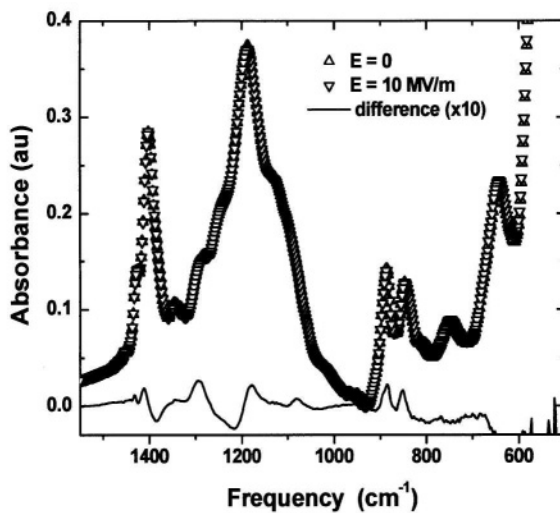


Figure 5. Room temperature FTIR spectra of the terpolymer unpoled (Δ) and under an electric field of 10 MV/m (∇). The solid line is the difference spectrum ($E=10$ MV/m subtracted from $E=0$ MV/m) multiplied by a factor of ten for clarity.

To better quantify the extent of this conversion, we measured the effect of an electric field (10 MV/m) on the FTIR spectrum of the terpolymer (Figure 5). As seen from the almost flat difference spectrum, the field causes an almost negligible change in the absorption spectrum, indicating that the conversion from the α to the β crystal form is quite small. On other hand, when the FTIR spectrum is measured as a function of temperature, there is an easily discerned decrease in the β absorption peaks, and concomitant increase in the intensity of the α peaks, upon heating through the Curie transition. This shows that the β to α phase change, as induced by temperature, is observable. However, the electric field conversion at constant (room) temperature is minimal. The main effect is a very small decrease in the all-trans intensities due to some orientation parallel to the applied field.

4. Conclusions

The origin of the large electrostriction in poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) was investigated. Application of an electric field to the terpolymer causes conversion of the anti-parallel α form into the polar δ and, to a lesser extent, β structures. The form factor for x-ray scattering of the δ conformation differs from that of the α , while the β crystals have a different unit cell. Consequently, the crystal phase conversions are reflected in changes in the x-ray diffraction pattern. However, the observed electrostrictive strains cannot be due primarily to this mechanism, since the transverse crystal dimension is unchanged for the α to δ conversion, and reduced only 10% by the α to β transition. For a degree of crystallinity of 30% [8], electrostrictive strains of 1% (Figs. 1 and 2) would require a 33% change of the α to the β form. This is much more than observed experimentally.

5. Acknowledgements

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6. References

1. Yuki, T., Yamaguchi, E., Koda, T., and Ikeda, S. (1999) Electrostriction Phenomena Associated with Polarization Reversal in Ferroelectric Polymers, *Jpn. J. Appl. Phys.* **38**, 1448-1453.
2. Furukawa, T. and Matsumoto, K. (1992) Nonlinear Dielectric Relaxation Spectra of Polyvinyl Acetate, *Jpn. J. Appl. Phys.* **31**, 840-845.
3. Cheng, Z.-Y., Olson, D., Xu, H., Xia, F., Hundal, J.S., Zhang, Q.M., Bateman, F.B., Kavarnos, F.B., Ramotowski, T. (2002) Structural changes and transitional behavior studied from both micro- and macroscale in

- the high energy electron-irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer, *Macromolecules* **35**, 664-672.
4. Lu, X., Schirokauer, A., Scheinbeim J. (2000) Giant Electrostrictive Response in poly(vinylidene fluoride-hexafluoropropylene) copolymers, *IEEE Transactions on Ultrasonics, Ferroelectric, and Frequency Control* **47**, 1291-1295.
 5. Casalini, R., Roland, C.M. (2001) Highly electrostrictive poly(vinylidene fluoride-trifluoroethylene) networks *Appl. Phys. Lett.* **79**, 2627-2629.
 6. Casalini, R., Roland, C.M. (2002) Electromechanical properties of poly(vinylidene fluoride-trifluoroethylene) networks, *J. Polym. Sci. Polym. Phys. Ed.*, **40**, 1975-1984.
 7. Buckley, G.S., Roland, C.M., Casalini, R., Petchsuk, A., Chung, T.C. (2002) Electrostrictive Properties of Poly(vinylidene-trifluoroethylene-chlorotrifluoroethylene) *Chem Materials* **14**, 2590-2593.
 8. Garrett, J.T., Roland, C.M., Petchsuk, A., Chung, T.C. (2003) Electrostrictive Behavior of Poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene), *Appl. Phys. Lett.*, in press.
 9. Chung T.C., Petchsuk A. (2002) Synthesis and properties of ferroelectric fluoroterpolymers with Curie transition at ambient temperature, *Macromolecules* **35**, 7678-7682.
 10. Lovinger, A.J. (1982) Annealing of poly(vinylidene fluoride) and formation of a 5th phase, *Macromolecules* **15**, 40-44.
 11. Kepler, R.G., Anderson, R.A. (1992) Ferroelectric polymers, *Adv. Phys.* **41**, 1-57.
 - Hasegawa, R., Takahashi, Y., Tadokoro, H., Chatani, Y. (1972) Crystal-structure of 3 crystalline forms of poly(vinylidene fluoride), *Polym. J.* **3**, 600-610.
 12. Davis, G.T., McKinney, J.E., Broadhurst, M.G., Roth, S.C. (1978) Electric-field-induced phase changes in poly(vinylidene fluoride), *J. Appl. Phys.* **49**, 4998-5002.
 13. Newman, B.A., Yoon, C.H., Pae, K.D., Scheinbeim (1979) Piezoelectric activity and field-induced crystal structure transitions in poled poly(vinylidene fluoride) films, *J. Appl. Phys.* **50**, 6095-6100.
 14. Naegele, D., Yoon, D.Y., Broadhurst, M.G. (1978) Formation of a new crystal form (α_p) of poly(vinylidene fluoride) under electric field, *Macromolecules* **11**, 1297-1298.
 15. Takahashi, Y. (1998) Molecular mechanisms for structural changes in poly(vinylidene fluoride) induced by electric field., *J. Macromol. Sci. - Phys.* **B37**, 421-429.
 16. Haisheng, X., Cheng, X.-Y., Olson, D., Mai, T., Zhang, Q.M., Kavamos, G. Ferroelectric and electromechanical properties of poly(vinylidene-fluoride-trifluoroethylene-chlorotrifluoroethylene) terpolymer (2001) *Appl. Phys. Lett.* **78**, 2360-2362.

SELF-ASSEMBLY AND THE ASSOCIATED DYNAMICS IN PBLG-PEG-PBLG TRIBLOCK COPOLYMERS

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1. Introduction

Peptides of poly(γ -benzyl-L-glutamate) (PBLG) are known to form two secondary structures: α -helices stabilized by intra-molecular hydrogen bonds and β -sheets stabilized by inter-molecular hydrogen bonds [1][2]. The α -helical structure, in particular, is thought to give rise to a rigid rod structure and PBLG is used as a model rigid-rod polymeric system. In the present report we review our recent work on (i) the structure and dynamics of BLG oligopeptides [3], (ii) the hierarchical self-assembly of poly(γ -benzyl-L-glutamate)-poly(ethylene glycol)-poly(γ -benzyl-L-glutamate) (PBLG-PEG-PBLG) triblock copolymers [4], and (iii) provide new results on the effect of interfacial mixing on the dynamics in the same triblock copolymers. We find that (i) the helical structures have low persistence length caused by structural defects, (ii) the incorporation of PEG next to the peptide blocks provides the means of controlling the stability of a specific peptide secondary structure. The latter has consequences on the local/segmental dynamics investigated by dielectric spectroscopy.

2. Self-assembly and dynamics of oligopeptides

The structure and the associated dynamics have been investigated in a series of oligopeptides of γ -benzyl-L-glutamate using DSC, PVT, WAXS, FTIR, NMR and dielectric spectroscopy, rheology, respectively. The peptides with degrees of polymerization below 18 are mixtures of a lamellar assembly of β -sheets and of columnar hexagonal arrangement of α -helices whereas for longer chains the intra-molecular hydrogen bonds stabilize the α -helical conformations. Figure 1 gives a schematic of the monomer and polymer structure in an "idealized" 18/5 helical conformation. Our work, however, have shown that this is a very crude approximation of the real structure adopted by BLG oligopeptides (see below). Figure 2, gives the results from differential scanning calorimetry (DSC) and pressure-volume-temperature (PVT) for two oligopeptides with emphasis on the first-order transformation from a 7/2 to an 18/5 helical conformation, by increasing temperature. This transformation is irreversible in the oligopeptides and a stable 18/5 helix exists in the second heating run of the DSC experiment (Figure 2).

We have employed NMR, FTIR and WAXS to identify the peptide secondary structure. Especially, WAXS patterns from oriented samples issued for this problem.

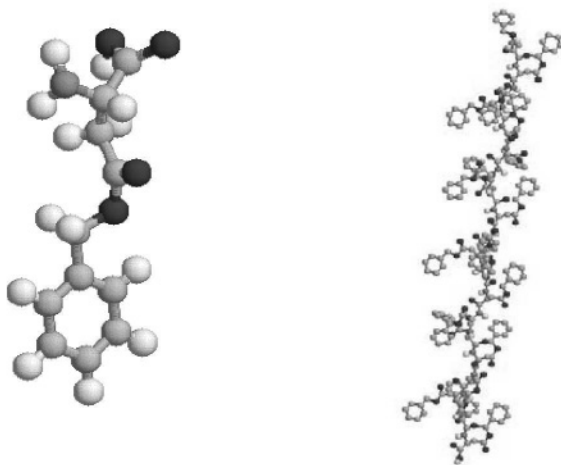


Figure 1. Schematic representation of the monomer and 20mer of Poly(γ -benzyl-L-glutamate) (PBLG) the latter at its "idealized" 18/5 helical conformation.

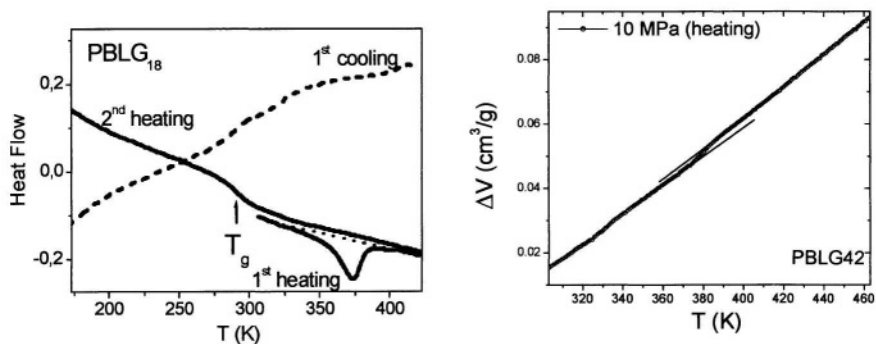


Figure 2. DSC thermogram (left) and relative change in specific volume (ΔV) (right) for two oligopeptides with $x=18$ and $x=42$, respectively. Notice in the DSC curve, the first order transition during the first heating run that is absent in the second heating run. The transition associates with the transformation from a 7/2 to 18/5 helical transformation. Within the same temperature range the specific volume displays a discontinuous increase expected for a first-order transformation.

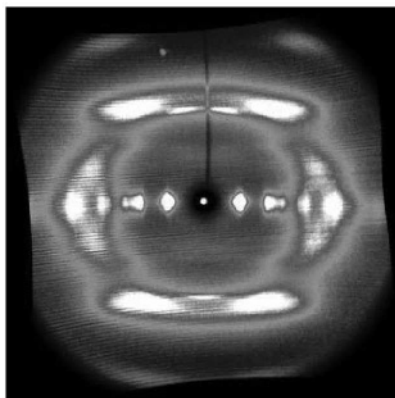


Figure 3. Wide-angle X-ray image from a PBLG₄₂ fiber extruded at T=353 K, and subsequently annealed (for 2 days) at T=373 K and measured at 303 K. The fiber axis is along the vertical direction [3].

A macroscopically oriented PBLG₄₂ sample was prepared using a micro-extruder at T=353 K and was subsequently examined with X-rays using a 2-dimensional detector at 303 K. Figure 3 depicts the pattern from the fiber sample measured at T=303 K. Annealing substantially improves the orientation and the sample displays a set of strong equatorial reflections with positions reflecting hexagonal packing together with some layer lines. This form of PBLG, with continuous scattering on the layer lines and reflections in the equator is known as form C [5]. The positions of the lines can be accounted for by a normal α -helical conformation of 18 residues in 5 turns (i.e., 18/5 helix) with a repeat unit of $c=2.7$ run. The structure has been described as a nematic-like paracrystal with a periodic packing of α -helices in the direction lateral to the chain axis ($a=1.5$, $b=1.45$, $c=2.7$ nm and $\gamma=118$ -120°C), while along the chain axis the mutual levels of chains are irregular.

The same oligopeptides were investigated with dielectric spectroscopy, a technique very sensitive not only to the presence but also to the persistence of the helical structures. The latter structures give rise to a large dipole moment parallel to the helical axis. The dipole moment results from the C=O and N-H bonds which for helical amino acids are hydrogen bonded to form a peptide group: $N-H\cdots O=C$ with a net dipole moment of about 3.4 D. This large dipole moment along the chain is used as a probe of the persistence of helical structures. It is therefore not surprising that dielectric studies have been employed both in solution [6][7] and in the melt [8][9]. The solution studies were able to identify the large dipole moment per peptide residue (3.46 D).

In our melt studies, the dynamics were investigated, for the first time, as a function of the degree of polymerization. Multiple dielectrically active processes were found. Starting from low temperatures, the Arrhenius process (γ -process, to distinguish from the more cooperative β -process associated with motions of the side chain dipoles sensitive to the 7/2 helical packing), with an apparent activation energy of about 21 kJ/mol, associate with the local relaxation of the side-chain methylene units. The glass transition is manifested in the thermal properties with a step in the heat capacity (Figure 2) and with an intense dielectric process bearing characteristics (molecular weight

dependence, temperature and pressure-dependence of relaxation times) known from amorphous polymers. Based on these findings the α -process in the oligopeptides is attributed to the relaxation of amorphous segments located within and the ends of the helices. Two slower processes were identified with opposite molecular weight dependence. The weak intermediate mode with an M^2 molecular weight dependence of the characteristic relaxation times suggests amorphous-like chains, whereas the strong slower process originates from the loss of dipole orientational capacity caused by structural defects and reflects the migration of helical sequences along the chains. This identifies the helices as structures of low persistence length. The viscoelastic response indicated that the structural defects arise from locally aggregated chains that inhibit the flow of these oligopeptides. As a result of this investigation, the highly schematic structure of Figure 1 indicating perfect 18/5 helices should be abandoned [3].

3. Self-assembly in PBLG-PEG-PBLG rod-coil-rod triblock copolymers

Recently [4] we have examined the hierarchical self-assembly of poly(γ -benzyl-L-glutamate)-poly(ethylene glycol)-poly(γ -benzyl-L-glutamate) (PBLG-PEG-PBLG) triblock copolymer melts. This system combines the basic ingredients favoring self-assembly (crystallization, hydrogen bonding, liquid crystallinity and microphase separation). We have shown that interfacial mixing is a key factor in controlling the appearance of β -sheets in low molecular weight peptides. More specifically, the tandem molecular interactions in PBLG-PEG-PBLG triblock copolymers give rise to structural changes for both blocks:

- Three levels of organization exist in the copolymers: first, the hydrogen bonds present in the peptide blocks stabilize the peptide secondary structures (α -helices and β -sheets) and, in addition, chain folding occurs in PEG; second, the α -helical and β -sheet secondary structures are packed in a hexagonal and orthogonal unit cells, respectively and third, the repulsive interactions between the unlike blocks give rise to nanostructures typical of phase separated block copolymers.
- Based on the peptide volume fraction two cases were found: for low peptide fractions, microphase separation results in PBLG and PEG phases rich in all secondary structures (α -helix, β -sheet and chain folded PEG). However, for the PEG mid-block large undercooling ($\Delta T \approx 50$ K) is necessary as a result of the confinement. Increasing the peptide volume fraction results in interfacial mixing of the two blocks. Under such conditions only the more coherent peptide secondary structure (α -helices) can survive. These structural effects are schematically depicted for low (left) and high (right) peptide fractions in Figure 4.

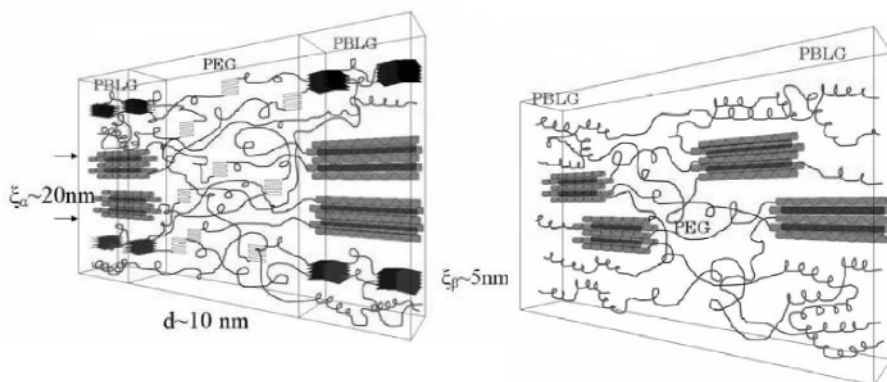


Figure 4. Schematic model of the phase state in the PBLG-PEG-PBLG triblock copolymers. Left: low peptide volume fraction, right: high peptide volume fraction. For low peptide volume fractions phase separation prevails. At high peptide volume fraction ($f_{\text{pep}} > 0.4$) phase mixing results in the destruction of the less ordered peptide secondary structures (β -sheets) [4].

4. Dynamics of PBLG-PEG-PBLG triblock copolymers

The local/segmental dynamics of the same triblock copolymers have been investigated with DS aiming in exploring the effect of interfacial mixing (Figure 4) on the segmental dynamics. The results for the relaxation times from all examined copolymers are summarized in Figure 5 together with the PBLG and PEG homopolymers and the respective dielectric intensities are shown in Figure 6. At low temperatures, in both homopolymers, a local (β -process) exists with an Arrhenius T-dependence:

$$\log \tau = \log \tau_0 + \frac{E}{2.303RT} \quad (1)$$

where τ_0 is the characteristic time at high T and E is the apparent activation energy (21.2 kJ/mole for PBLG₁₄). In the copolymers a mixed β -process was found comprising characteristics of both PBLG and PEG local processes with intermediate activation energies (~30 kJ/mole). This process reflects the local side-chain dynamics below the calorimetric glass temperature and its position and activation energy implies mixing at a very local scale. At higher T, in the vicinity of the PBLG T_g , the PBLG segmental (α -) process has a stronger T-dependence and conforms to the Vogel-Fulcher-Tammann (VFT) equation:

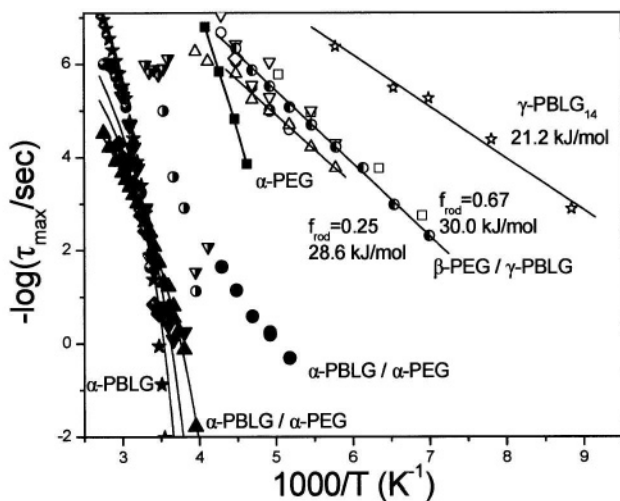


Figure 5. Relaxation map of the different dynamic processes in pure PBLG₁₄ (stars), pure PEG (squares) and the different triblock copolymers: (circles): $f_{rod}=0.064$, (up triangles): $f_{rod}=0.25$, (down triangles): $f_{rod}=0.43$, (rhombus): $f_{rod}=0.53$, (half-filled circles): $f_{rod}=0.67$. The different processes correspond to the α -relaxation (filled and half-filled symbols) associated with the glass transition and a more local β -process associated with the PEG and PBLG local relaxations.

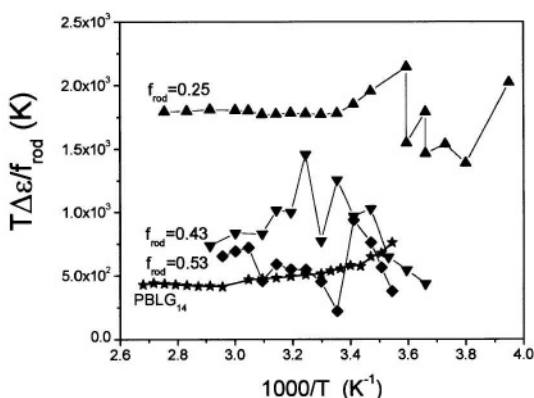


Figure 6. Reduced dielectric strength for the α -process in PBLG₁₄ (stars) and three copolymers with PBLG volume fractions of 0.25, 0.43 and 0.53.

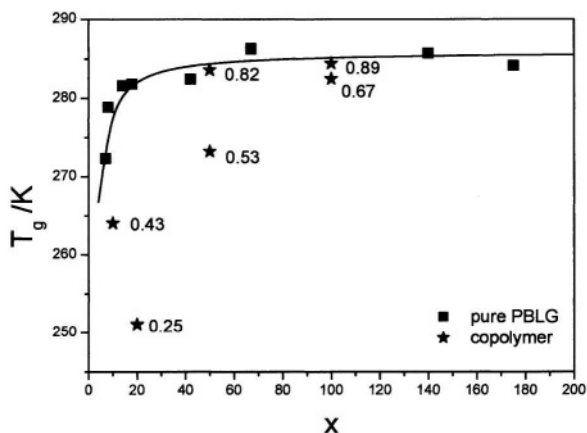


Figure 7. Glass transition temperatures obtained from DS (we use here the operational definition of T_g as the temperature where the α -process relaxation time is 100 s) for PBLG homopolymers and the corresponding copolymers as a function of the degree of the peptide degree of polymerization (x). The line is the result of the fit to the homopolymer T_g dependence on x : $T_g = 285.9 - 83.7/x$. Notice the lower PBLG glass temperatures in the copolymers with $f_{rod}=0.25$, 0.43 and 0.53 suggesting mixing of the PBLG segments with the more mobile PEG segments.

$$\log \tau_{max} = \log \tau_0 + \frac{B}{T - T_0} \quad (2)$$

where B is the apparent activation energy and T_0 is the “ideal” glass temperature. For PBLG₁₄ these parameters are $\log \tau_0 = -10.5$, $B = 432$ K, $T_0 = 247$ K. However, the same process in the copolymers with volume fractions 0.25 to 0.53 displays distinctly different characteristics which are depicted in Figure 5 with the different T -dependence of the α -process relaxation times. At the same time, the normalized intensity (shown in Figure 6) is higher from the expected intensity of a PBLG homopolymer. Both the different $\tau(T)$ and the higher intensity of the α -process in the copolymers implies a different local friction due to mixing of PBLG segments with the much faster PEG segments ($T_g^{PEG} \sim 200$ K). Interestingly, for the triblock with $f_{rod}=0.25$, no mixing was found in the structure investigation, however, DS is a sensitive local probe of the local segmental dynamics. For the copolymers with a higher rod volume fraction (0.82, 0.89), this effect of the PBLG dynamics diminishes due to the small PEG volume fraction. In some cases ($f_{rod}=0.064$, $f_{rod}=0.67$) a mixed α -process was found (PBLG/PEG) relaxing at intermediate rates between the PBLG and PEG segmental dynamics.

The operationally defined T_g is plotted in Figure 7 as a function of the degree of polymerization for the different oligopeptides and the PBLG in the triblock copolymers. The α -process in the oligopeptides, was found to have a molecular weight dependence

suggesting the importance of chain-end effects. The molecular weight dependence is reminiscent to the dependence found in other amorphous polymers, i.e.

$$T_g(K) = 285.9 - \frac{83.7}{x} \quad (3)$$

In the triblock copolymers with $f_{\text{rod}}=0.25, 0.43$ and 0.53 , the lower PBLG T_g results from mixing with the faster moving species (PEG), in agreement with the $\tau(T)$ and $T\Delta\epsilon$ results.

In conclusion, the structure and the associated dynamics in a series of PBLG-PEG-PBLG triblock copolymers reveal interfacial mixing between the unlike segments with consequences on the type of the peptide secondary structures and the location of the local/segmental dynamics. The peptide α -helical structure is the only to survive mixing, however, an intact helical structure is only an idealization in PBLG peptides.

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References

1. Walton, A.G.; Blackwell, J. (1973) *Biopolymers*; Academic Press: New York.
2. Block, H. (1983) *Poly(γ -benzyl-L-glutamate) and other glutamic acid containing polymers*; Gordon and Breach Science Publishers: New York.
3. Papadopoulos, P., Floudas G. et al (2003) Self-assembly and dynamics of poly(γ -benzyl-L-glutamate) peptides, *Biomacromolecules* (submitted).
4. Floudas, G., Papadopoulos, P., Klok, H.-A. et al (2003) Hierarchical self-assembly of poly(γ -benzyl-L-glutamate)-Poly(ethylene glycol)-poly(γ -benzyl-L-glutamate) rod-coil-rod triblock copolymers, *Macromolecules* **36**, 3673-3683.
5. Watanabe, J., Kazumichi, I., Gehani, R, Uematsu, I. (1981) *J. Polym. Sci., Polym. Phys. Ed.* **19**, 653.
6. Wada, A. (1958) *J. Chem. Phys.*, **29**, 674; (1959) **30**, 328; (1959) **30**, 324.
7. Mori, Y., Ookubo, N., Hayakawa, R., Wada, Y. (1982) *J. Polym. Sci., Polym. Phys. Ed.* **20**, 211.
8. Moscicki, J.K., Williams, G. (1983) *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 197; (1983) **21**, 213.
9. Hartmann, L., Kratzmuller, T., Braun, H.-G., Kremer, F. (2000) *Macromol. Rapid. Commun.* **21**, 814.

NONLINEAR DIELECTRIC SPECTROSCOPY OF BIOLOGICAL SYSTEMS: PRINCIPLES AND APPLICATIONS

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Abstract. Biological cells can be seen, electrically, as consisting of conducting internal and external media separated by a more-or-less non-conducting cell membrane. The classical, linear, β -dielectric dispersion results from the charging up of this nominally 'static' membrane capacitance according to a Maxwell-Wagner type of mechanism, and typically occurs in the radiofrequency range. However, because practically all of the external macroscopic field is dropped across the 5 nm thick cell membrane, there is an effective and substantial *amplification* of the field across this membrane. This is predicted, and is found, to produce substantial nonlinearities when attempts are made to measure harmonics of the single-frequency exciting field. The nature (odd vs even) and magnitude of these harmonics changes substantially with cell status and environment, providing opportunities for using the cells themselves as sensing elements to describe their surroundings. Electrode polarisation effects producing nonlinear dielectricity can confound these measurements and must be bypassed or taken into account. Nonlinear dielectric spectroscopy (NLDS) provides a wholly non-invasive approach to cellular characterisation and diagnosis.

1. Introduction

The linear, passive audio- and radio-frequency electrical properties of biological systems have been studied since the end of the 19th century, and have been summarised in a number of reviews [1-9].

For cellular systems, it is conventional to recognise three major dielectric dispersions, in which the permittivity and conductivity change significantly with frequency. These are known as the α -, β - and γ -dispersions, and occur typically in the audio, radio- and microwave-frequency ranges, respectively [1].

The β -dispersion is the most significant for our initial purposes, as it defines the frequency range below which the cell membrane is charged up by the external exciting electrical field. A typical β -dispersion for microbes is shown in Fig 1. Here the permittivity changes between 'high' values at 'low' frequencies and 'low' values at 'high' frequencies. The frequency at which this is half-completed is known as the characteristic frequency f_c , and is often of the order of 1 MHz or so, although it increases with both internal and external conductivity, and decreases with the cell radius. Such measurements are of historical interest as they led to the recognition that the large membrane capacitance that could be calculated therefrom (approx. $1\mu\text{F}\cdot\text{cm}^{-2}$) meant that cell membranes must be of molecular thickness (say 5 nm). The dielectric increment depends on cell concentration, and we have therefore also exploited measurements of the β -dispersion to advantage for the on-line, real-time estimation of microbial biomass [10-15].

One consequence of these effects is that at audio frequencies the membrane of biological cell suspensions is effectively fully charged up by the exciting field and thus the cell membrane itself is seen as more or less entirely non-conducting under these circumstances. Specifically, if a cell is exposed to a low-frequency electric field the cell membrane will polarise, amplifying the electric field across the membrane by several orders of magnitude [4; 7; 8; 16; 17]. Consequently, the activity of polar and polarisable membranous enzymes can be modified significantly even by rather weak fields [18]. This strength of amplification means that the fields to which these enzymes are subject can produce nonlinear dielectric effects. In particular, enzymes whose conformational states display different dipole moments are affected kinetically by alternating fields during changes between states [18-24]; correspondingly, one should also expect *on theoretical grounds* [22; 23; 25] that these interactions would be observable via the harmonics produced by their nonlinear dielectric response to a sinusoidal field (Fig 2).

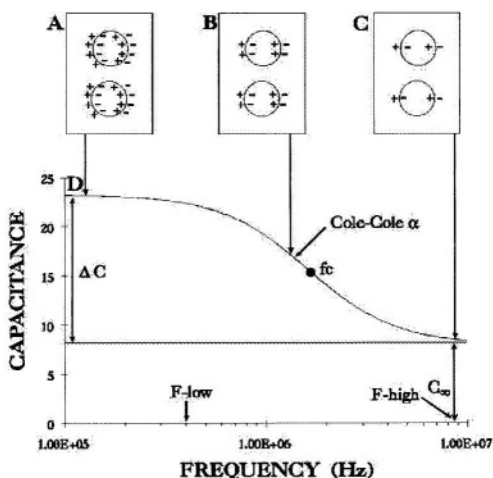


Figure 1. The β -dielectric dispersion of a typical biological tissue or cell suspension. At low frequencies, there is time for intra- and extra-cellular ions to migrate to the cell membrane and charge it up fully (A). This occurs less and less as the frequency is increased (B,C), giving a curve of capacitance against frequency of the form shown in (D). A non-zero value for the Cole-Cole α [26] of the β -dispersion, which characterises its breadth, is usually interpreted (but see [27]) in terms of a heterogeneity of relaxation times caused by heterogeneity in cell size, shape, membrane capacitance and internal conductivity.

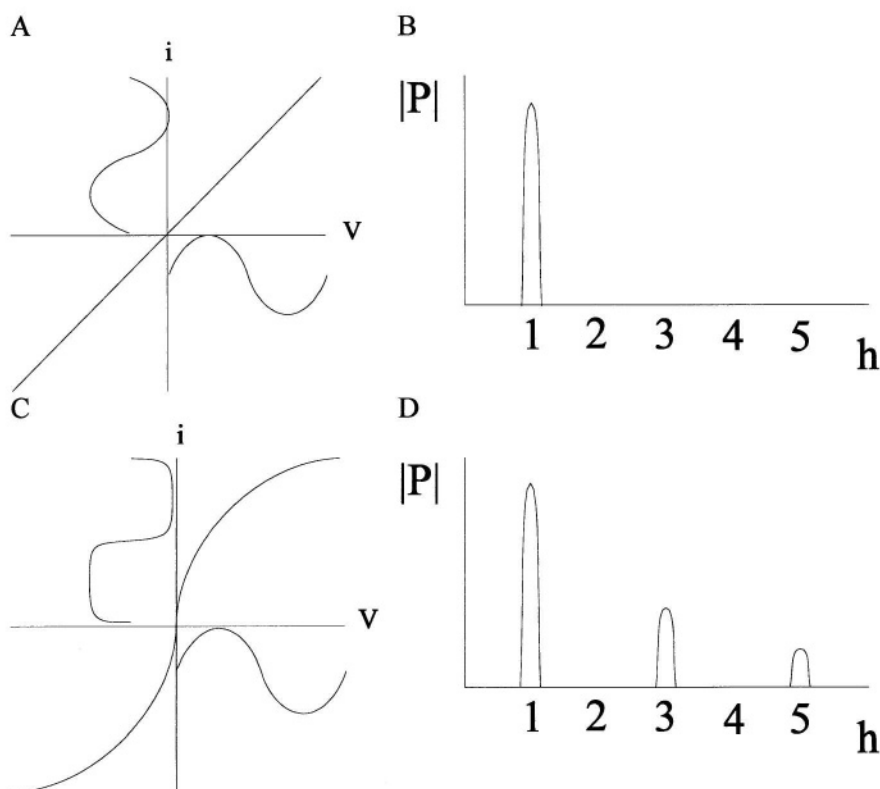


Figure 2. Linear and nonlinear dielectric responses. If the current-voltage characteristic of a system is linear (A) then the result is an output of electrical energy only at the frequency of the exciting voltage (B). Nonlinear systems display a nonlinear current-voltage characteristic and therefore produce harmonics.

Of course nonlinear effects have been at the heart of our understanding of neurotransmission for many years (e.g. [3]), but in those cases the measurements are done with transmembrane electrodes (i.e. at least one cell is intracellular). Our discussion here is confined to those cases in which all the electrodes are extracellular.

The generation of harmonics in response to a purely 'extracellular' sinusoidal electrical field is perhaps most easily understood in terms of the '4-state enzyme' model of a membranous carrier which has a higher affinity for extracellular than intracellular substrate (and conversely a reciprocal kinetic relationship for 'forward' and 'reverse' reactions so as to obey both the Second Law and the Haldane relationship [28]). In addition it has a mobile negative charge in functional linkage to the substrate binding

site. The enzyme can make serial transitions between the 4 states (charge inside/outside, substrate bound/free) and starts with state 4 being the most highly populated (Fig 3A), i.e. with the negative charge facing outwards and the external substrate bound.

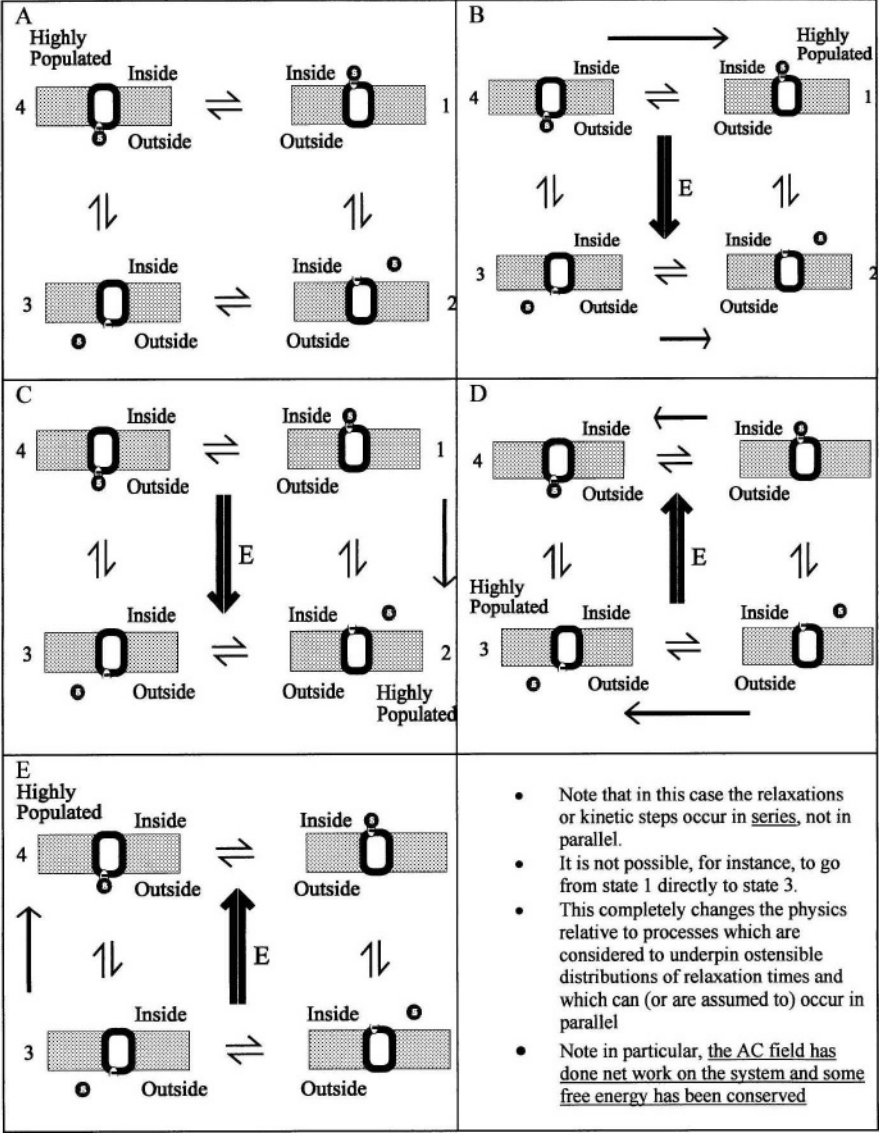


Figure 3. The 4-state enzyme model whose responses to a purely sinusoidal exciting field can be seen as underpinning the generation of nonlinear dielectricity,. For details see the text.

The imposition of the first (positive-going) phase of the sinusoidal electric field causes the negative charge to move across the membrane (Fig 3B) and the enzyme to adopt state 1. Since the affinity for the substrate when facing inwards is much lower, the enzyme relaxes in an electrically silent manner to state 2 (Fig 3C). Now the polarity of the sinusoidal field reverses, and the negative charge moves back to face outwards (state 3, Fig 3D), after which it again binds fresh substrate (state 4, Fig 3E). The result of this is that although the enzyme and the field are both back where they started, the field has caused the enzyme to do chemical work by moving a molecule of substrate across the membrane. Thus the field affects the enzyme [18-20] and some 15 years ago we pointed out that the enzyme must therefore affect the field, specifically by giving a nonlinear response in a dielectric measurement [22; 23; 25]. It was therefore predicted that Fourier analysis of the voltage induced across the inner electrodes in a conventional 4-terminal set-up of the type we and others had used in linear dielectrics [4; 8; 29-32] would demonstrate the transduction of single-frequency excitations into harmonics.

2. Results

Starting in the early 1990s, we showed that these predictions were indeed borne out [33-38]. The basic schematic of the apparatus is given below.

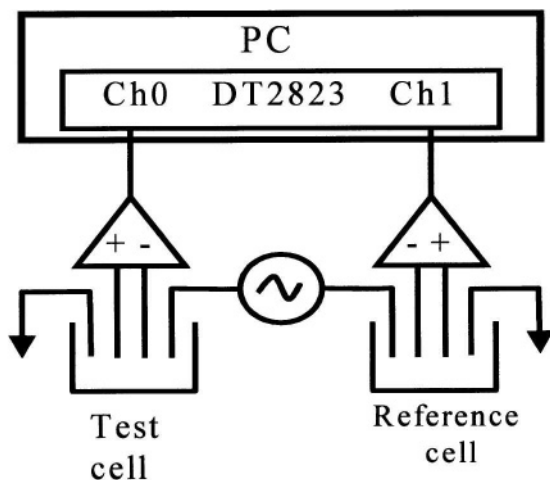


Figure4. A set-up for nonlinear dielectric spectroscopy (redrawn after [37]). AC (usually in the form of a pure sinusoid, but other waveforms are possible – e.g. [36]) is applied to the outer electrodes of a 4-terminal system and the resulting waveform captured across the inner electrodes using an analogue-to-digital converter connected to an input amplifier of high input impedance. Fourier transformation (following Blackman-Harris windowing) permits the determination of harmonic or other frequencies not present in the exciting waveform. To remove the contribution of electrode-derived nonlinearities the signal from the reference cell, containing only conductivity-matched supernatant, is removed from the signals obtained in the test cell. In the original work gold pin electrodes were used. A survey of other electrode materials is given in [39].

Using this apparatus, it was established that a variety of biological cell suspensions produced harmonics when excited by single-frequency electrical fields, odd-numbered harmonics were favoured when cells were resting, with the balance shifting towards even-numbered ones when they were metabolically active. These harmonics were not produced by boiled cells, could be found only in rather narrow voltage and frequency windows, the latter typically in the decade 10-100 Hz, and could be related to the kinetics of the 'target' enzymes. Inhibitor and mutant studies showed that identifiable membranous enzymes were the main source of the nonlinear dielectricity. In the eukaryotic baker's yeast (*Saccharomyces cerevisiae*) the enzyme was the membrane-located H^+ -ATPase [35; 37], while in the bacteria *Micrococcus luteus* [34] and *Rhodobacter capsulatus* [33] the membrane-located respiratory chains were involved. The optimal excitation frequency for observing these effects, which could also be elicited by excitation at 2 frequencies, neither of which alone could serve, was considered to equate to the turnover number of the main target enzyme [36]. Other nonlinear effects, believed to reflect other motions in membranes, could be observed at higher excitation frequencies [34]. The use of multivariate and machine learning methods, including statistical, neural and evolutionary computing [39; 40], allowed quantitative models to be formed which could relate (a) the pattern of harmonics generated in response to varying voltages and frequencies to (b) the concentration of molecules such as glucose. Of course the non-invasive measurement of glucose is of massive significance in the management and prognosis of diseases such as diabetes [41]. Some data from glucose biotransformations by *S. cerevisiae* are given in Fig 5.

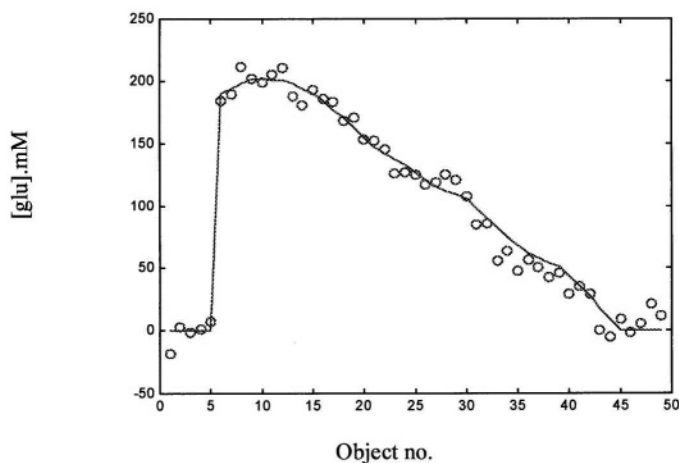


Figure 5. Predicted glucose in a fermentation run using a model produced using genetic programming (see e.g. [42-49]) from an entirely separate run [40]

A problem with all of these measurements, however, is that the nonlinear current-voltage relationships characteristic of the electrode-electrolyte interface [39; 50-52] also generate harmonics. These must be compensated in either hardware or software to

determine the 'purely' cellular responses, they can vary 'stochastically' in response to changes in electrode surface conditions, especially fouling by proteins, and seem to be largest when using electrodes (such as Pt) normally considered best for *linear* dielectric measurements in lossy media [39]. Although this is adequate for laboratory measurements, and some electrodes such as heavily chlorided Ag/AgCl may be essentially satisfactory [39] and can be greatly improved by chemical protection of the electrode surfaces [53], electrode polarisation interferences present the greatest impediment to the uptake of NLDS for the purposes of non-invasive sensing. Present work is aimed at eliminating them completely.

3. Conclusions and Prospects

Nonlinear dielectric spectroscopy of biological systems is an important (if recondite) technique with which one can interrogate cells directly so as to establish their responses to a variety of substances, which thereby become determinands. The essential basis of the effect is understood in qualitative terms, and there have been a number of successes in exploiting it for diagnostics. The elimination or bypassing of electrode polarisation interferences remains the most important obstacle to be overcome; this would open up the field completely. To date we have not measured the nonlinear phase angle, and this is an attractive possibility. Technical advances mean that higher frequencies are more easily accessible than they were before. We also need to improve our understanding of, and ability to attack, the 'inverse problem' of NLDS (and see [54] for metabolic systems), i.e. given the nonlinear dielectric responses, produce a parameterised nonlinear dynamic model which can explain them. Finally, the availability of systematic gene knockout [55; 56] and other strains, whose metabolic changes can be determined straightforwardly [57], provides an obvious avenue for the further and more detailed dissection of those gene products contributing to the generation of nonlinear dielectricity in biological systems.

4. References

1. Schwan, H. P. (1957). Electrical properties of tissues and cell suspensions. *Adv. Biol Med. Phys.* **5**, 147-209.
2. Grant, E. H., Sheppard, R. J. & South, G. P. (1978). *Dielectric behaviour of biological molecules in solution*. Clarendon Press, Oxford.
3. Schanne, O. F. & Ceretti, E. R. P. (1978). *Impedance measurements in biological cells*. John Wiley, New York.
4. Pethig, R. (1979). *Dielectric and electronic properties of biological materials*. Wiley, Chichester.
5. Kell, D. B. & Harris, C. M. (1985). Dielectric spectroscopy and membrane organisation. *Bioelectricity* **4**, 317-348.
6. Foster, K. R. & Schwan, H. P. (1986). Dielectric Properties of Tissues. In *CRC Handbook of Biological Effects of Electromagnetic Fields* (ed. C. Polk and E. Postow). CRC Press, Boca Raton, FL.
7. Kell, D. B. (1987). The principles and potential of electrical admittance spectroscopy: an introduction. In *Biosensors; fundamentals and applications* (ed. A. P. F. Turner, I. Karube and G. S. Wilson), pp. 427-468. Oxford University Press, Oxford.
8. Pethig, R. & Kell, D. B. (1987). The passive electrical properties of biological systems: their significance in physiology, biophysics and biotechnology. *Phys. Med. Biol.* **32**, 933-970.
9. Foster, K. R. & Schwan, H. P. (1989). Dielectric properties of cells and tissues: a critical review. *CRC Crit. Rev. Biomed. Eng.* **17**, 25-102.

10. Harris, C. M., Todd, R. W., Bungard, S. J., Lovitt, R. W., Morris, J. G. & Kell, D. B. (1987). The dielectric permittivity of microbial suspensions at radio frequencies: a novel method for the estimation of microbial biomass. *Enzyme Microbial Technol.* **9**, 181-186.
11. Kell, D. B., Samworth, C. M., Todd, R. W., Bungard, S. J. & Morris, J. G. (1987). Real-time estimation of microbial biomass during fermentations using a dielectric probe. *Studia Biophysica* **119**, 153-156.
12. Kell, D. B., Markx, G. H., Davey, C. L. & Todd, R. W. (1990). Real-time monitoring of cellular biomass: Methods and applications. *Trends Anal. Chem.* **9**, 190-194.
13. Kell, D. B. & Todd, R. W. (1998). Dielectric estimation of microbial biomass using the Aber instruments biomass monitor. *Trends Biotechnol.* **16**, 149-150.
14. Markx, G. H. & Davey, C. L. (1999). The dielectric properties of biological cells at radiofrequencies: Applications in biotechnology. *Enzyme and Microbial Technology* **25**, 161-171.
15. Yardley, J. E., Kell, D. B., Barrett, J. & Davey, C. L. (2000). On-line, real-time measurements of cellular biomass using dielectric spectroscopy. *Biotechnol. Genet. Eng. Rev.* **17**, 3-35.
16. Davey, C. L. & Kell, D. B. (1995). The Low-Frequency Dielectric Properties of Biological Cells. In *Bioelectrochemistry of Cells and Tissues. Bioelectrochemistry Principles and Practice* (ed. D. Walz, H. Berg and G. Milazzo), pp. 159-207. Birkäuser, Zürich.
17. Rigaud, B., Morucci, J. P. & Chauveau, N. (1996). Bioelectrical impedance techniques in medicine .1. Bioimpedance measurement - Second section: Impedance spectrometry. *Critical Reviews in Biomedical Engineering* **24**, 257-351.
18. Tsong, T. Y. & Astumian, R. D. (1988). Electroconformational Coupling - How Membrane-Bound ATPase Transduces Energy From Dynamic Electric Fields. *Annual Review of Physiology* **50**, 273-290.
19. Sepersu, E. H. & Tsong, T. Y. (1984). Activation of Electrogenic Rb⁺ Transport of (Na, K)-ATPase by an Electric Field. *J. Biol. Chem.* **259**, 7155-7162.
20. Westerhoff, H. V., Tsong, T. Y., Chock, P. B., Chen, Y. & Astumian, R. D. (1986). How Enzymes can Capture and Transmit Free Energy from an Oscillating Electric Field. *Proc. Natl. Acad. Sci. USA* **83**, 4734-4738.
21. Tsong, T. Y. & Astumian, R. D. (1987). Electroconformational Coupling and Membrane Function. *Progr. Biophys. Mol. Biol* **50**, 1-45.
22. Kell, D. B., Astumian, R. D. & Westerhoff, H. V. (1988). Mechanisms for the interaction between nonstationary electric fields and biological systems . 1. Linear dielectric theory and its limitations. *Ferroelectrics* **86**, 59-78.
23. Westerhoff, H. V., Astumian, R. D. & Kell, D. B. (1988). Mechanisms for the interaction between nonstationary electric fields and biological systems .2. Nonlinear dielectric theory and free-energy transduction. *Ferroelectrics* **86**, 79-101.
24. Xie, T. D., Chen, Y. D., Marszalek, P. & Tsong, T. Y. (1997). Fluctuation-driven directional flow in biochemical cycle: Further study of electric activation of Na,K pumps. *Biophysical Journal* **72**, 2496-2502.
25. Davey, C. L. & Kell, D. B. (1990). The dielectric properties of cells and tissues what can they tell us about the mechanisms of field/cell interactions. In *Emerging Electromagnetic Medicine* (ed. M. E. O'Connor, R. H. C. Bental and J. C. Monahan), pp. 19-43. Springer-Verlag, New York.
26. Cole, K. S. & Cole, R. H. (1941). Dispersion and Absorption in Dielectrics. 1. Alternating Current Characteristics. *J. Chem. Phys.* **9**, 341-351.
27. Markx, G. H., Davey, C. L. & Kell, D. B. (1991). To what extent is the Magnitude of the Cole-Cole α of the β -dielectric Dispersion of Cell Suspensions Explicable in terms of the Cell Size Distribution? *Biochemistry and Bioenergetics* **25**, 195-211.
28. Cornish-Bowden, A. (1995). Fundamentals of enzyme kinetics, 2nd ed. Portland Press, London.
29. Schwan, H. P. (1963). Determination of electrical impedances. In *Physical techniques in biological research Vol VIB* (ed. W. L. Nastuk), pp. 323-407. Academic Press, New York.
30. Symons, M., Korenstein, R., Harris, C. M. & Kell, D. B. (1986). Dielectric-Spectroscopy of Energy Coupling Membranes - Chloroplast Thylakoids. *Bioelectrochemistry and Bioenergetics* **16**, 45-54.
31. Harris, C. M. & Kell, D. B. (1985). On the Dielectrically Observable Consequences of the Diffusional Motions of Lipids and Proteins in Membranes .2. Experiments With Microbial Cells, Protoplasts and Membrane Vesicles. *European Biophysics Journal* **13**, 11-24.
32. Harris, C. M. & Kell, D. B. (1983). The radio-frequency dielectric properties of yeast cells measured with a rapid, automated, frequency-domain dielectric spectrometer. *Bioelectrochem. Bioenerg.* **11**, 15-28.
33. McShea, A., Woodward, A. M. & Kell, D. B. (1992). Nonlinear dielectric properties of *Rhodobacter capsulatus*. *Bioelectrochem. Bioenerg.* **29**, 205-214.

34. Woodward, A. M. & Kell, D. B. (1991). On the relationship between the nonlinear dielectric properties and respiratory activity of the obligately aerobic bacterium *Micrococcus luteus*. *Bioelectrochem. Bioenerg.* **26**, 423-439.
35. Woodward, A. M. & Kell, D. B. (1991). Confirmation by using mutant strains that the membrane-bound H^+ -ATPase is the major source of nonlinear dielectricity in *Saccharomyces cerevisiae*. *FEMS Microbiol. Lett.* **84**, 91-95.
36. Woodward, A. M. & Kell, D. B. (1991). Dual-frequency excitation- a novel method for probing the nonlinear dielectric properties of biological systems, and its application to suspensions of *Saccharomyces cerevisiae*. *Bioelectrochem. Bioenerg.* **25**, 395-413.
37. Woodward, A. M. & Kell, D. B. (1990). On the nonlinear dielectric properties of biological systems. *Saccharomyces cerevisiae. Bioelectrochem. Bioenerg.* **24**, 83-100.
38. Jones, A., Rowland, J. J., Woodward, A. M. & Kell, D. B. (1997). An instrument for the acquisition and analysis of the nonlinear dielectric spectra of biological samples. *Trans. Inst. Meas. Control* **19**, 223-230.
39. Woodward, A. M., Jones, A., Zhang, X., Rowland, J. & Kell, D. B. (1996). Rapid and non-invasive quantification of metabolic substrates in biological cell suspensions using nonlinear dielectric spectroscopy with multivariate calibration and artificial neural networks. Principles and applications. *Bioelectrochem. Bioenerg.* **40**, 99-132.
40. Woodward, A. M., Gilbert, R. J. & Kell, D. B. (1999). Genetic programming as an analytical tool for non-linear dielectric spectroscopy. *Bioelectrochem. Bioenerg.* **48**, 389-396.
41. Tamada, J. A., Garg, S., Jovanovic, L., Pitzer, K. R., Fermi, S. & Potts, R. O. (1999). Noninvasive glucose monitoring - Comprehensive clinical results. *J. Amer. Med. Assoc.* **282**, 1839-1844.
42. Koza, J. R. (1992). *Genetic programming: on the programming of computers by means of natural selection*. MIT Press, Cambridge, Mass.
43. Banzhaf, W., Nordin, P., Keller, R. E. & Francone, F. D. (1998). *Genetic programming: an introduction*. Morgan Kaufmann, San Francisco.
44. Langdon, W. B. & Poli, R. (2002). *Foundations of genetic programming*. Springer-Verlag, Berlin.
45. Langdon, W. B. (1998). *Genetic programming and data structures: genetic programming + data structures = automatic programming!* Kluwer, Boston.
46. Kell, D. B. (2002). Defence against the flood: a solution to the data mining and predictive modelling challenges of today. *Bioinformatics World (part of Scientific Computing News)* **Issue 1**, 16-18
http://www.aberge.com/biwppl6-18_as_publ.pdf.
47. Kell, D. B. (2002). Genotype:phenotype mapping: genes as computer programs. *Trends Genet.* **18**, 555-559.
48. Kell, D. B. (2002). Metabolomics and machine learning: explanatory analysis of complex metabolome data using genetic programming to produce simple, robust rules. *Mol Biol Rep* **29**, 237-41.
49. Kell, D. B., Darby, R. M. & Draper, J. (2001). Genomic computing: explanatory analysis of plant expression profiling data using machine learning. *Plant Physiol* **126**, 943-951.
50. Bockris, J. O. M. & Reddy, A. K. N. (1970). *Modern Electrochemistry, Vols 1 and 2*. Plenum Press, New York.
51. McAdams, E. T. & Jossinet, J. (2000). Nonlinear transient response of electrode - electrolyte interfaces. *Med. Biol. Eng. Comput.* **38**, 427-432.
52. McAdams, E. T., Lacknermeier, A., McLaughlin, J. A., Macken, D. & Jossinet, J. (1995). The linear and nonlinear electrical properties of the electrode-electrolyte interface. *Biosensors & Bioelectronics* **10**, 67-74.
53. Woodward, A. M., Davies, E. A., Denyer, S., Olliff, C. & Kell, D. B. (1999). Non-linear dielectric spectroscopy: antifouling and stabilisation of electrodes by a polymer coating. *Bioelectrochemistry* **15**, 13-20.
54. Mendes, P. & Kell, D. B. (1998). Non-linear optimization of biochemical pathways: applications to metabolic engineering and parameter estimation. *Bioinformatics* **14**, 869-883.
55. Oliver, S. G. (1999). Redundancy reveals drugs in action. *Nature Genet.* **21**, 245-246.
56. Winzler, E. A., Shoemaker, D. D., Astromoff, A., Liang, H., Anderson, K., Andre, B., Bangham, R., Benito, R., Boeke, J. D., Bussey, H., Chu, A. M., Connelly, C., Davis, K., Dietrich, F., Dow, S. W., El Bakkoury, M., Foury, F., Friend, S. H., Gentelen, E., Giaever, G., Hegemann, J. H., Jones, T., Laub, M., Liao, H., Liebundguth, N., Lockhart, D. J., Lucau-Danila, A., Lussier, M., M'Rabet, N., Menard, P., Mittmann, M., Pai, C., Rebischung, C., Revuelta, J. L., Riles, L., Roberts, C. J., Ross-MacDonald, P., Scherens, B., Snyder, M., Sookhai-Mahadeo, S., Storms, R. K., Veronneau, S., Voet, M., Volckaert, G., Ward, T. R., Wysocki, R., Yen, G. S., Yu, K. X., Zimmermann, P., Philippsen, P., Johnston, M. & Davis, R. W. (1999). Functional characterization of the *S. cerevisiae* genome by gene deletion and parallel analysis. *Science* **285**, 901-906.

57. Allen, J. K., Davey, H. M., Broadhurst, D., Heald, J. K., Rowland, J. J., Oliver, S. G. & Kell, D. B. (2003). High-throughput characterisation of yeast mutants for functional genomics using metabolic footprinting. *Nature Biotechnol.* **21**, 692-696.

MEASUREMENT METHOD OF ELECTRIC BIREFRINGENCE SPECTRUM IN FREQUENCY DOMAIN

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1 Introduction

Birefringence externally induced by orientation or deformation of molecules has been used frequently for investigation of the microscopic molecular-level properties closely related to molecular conformation and polarization. When the electric field is adopted out of a wide variety of external fields, the observed phenomenon is called electric birefringence or Kerr effect [1]. Because of molecular symmetry, electric birefringence is intrinsically a function of the square of the electric field, that is, a second-order nonlinear effect. In addition, a time-dependent electric field yields electric birefringence relaxation, which gives us information on the dynamic behavior of molecules such as molecular rotation, molecular deformation and internal motion of carriers. Thus the electric birefringence relaxation is a powerful method to investigate microscopic properties of electro-active molecules and have been applied to various systems [1].

Measurement methods for electric birefringence relaxation have two categories on the applied electric field: time domain electric birefringence (TEB) and frequency domain electric birefringence (FEB). In TEB, a rectangular pulse field is applied and transient raise and decay response is analyzed, while in FEB, an oscillating field with an angular frequency ω is applied and dc and 2ω components of the birefringence response are detected as functions of ω . Also, as is treated by Déjardin et al. [2], another FEB method is available, in which an offset sinusoidal field is applied and then ω and 2ω components of birefringence response are observed. Both categories should seek the same electro-optic properties of molecules. Although the responses in both time and frequency domains are theoretically calculated by Déjardin et al. [2] and Wegener [3] in the case of orientation of molecules with optical anisotropy, it is still lacking what type of experimental measurement can connect both categories. Unlike the Fourier transform in linear response [4], the nonlinearity prevents easy transform between the time and frequency domain responses. Although second-order nonlinear after-effect function requires two time variables to describe the whole dynamics of the nonlinear phenomenon, each category couples the variables in its own way to give us a single variable function of time or frequency and thereby loses the key for mutual interpretation.

To clear up the situation, we need to describe the nonlinear response in terms of the nonlinear after-effect function as is treated phenomenologically in the Volterra [5] and Nakada's [6] formula. Once the after-effect function of the nonlinear phenomenon is obtained, mutual interpretation between both categories can be easily achieved using a multidimensional Fourier transform. Furthermore, the nonlinear after-effect function yields the nonlinear response to applied external field of arbitrary form. We can select the type of applied field appropriate to the specimen similar to linear responses, avoiding deficiencies that conventional nonlinear measurement methods might give. Further, we aim to establish a measurement method for the nonlinear response function obtained by Fourier transform of the nonlinear after-effect function [7]. This response function is derived from a general time-evolution equation and compared with the previous form proposed phenomenologically by Volterra [5] and Nakada [6]. Subsequently, as a specific model for the theory, we considered rod-like molecules with permanent and induced dipole moments and then calculated the electric birefringence relaxation function in a two-dimensional frequency domain, that is, the nonlinear response function. To verify the theoretical calculations, we developed a measurement system for two-dimensional spectroscopy of the electric birefringence relaxation and measured two-dimensional electric birefringence spectra of sodium poly-styrenesulfonate (NaPSS) in aqueous solution as a typical specimen showing large electric birefringence. Finally, in order to show the advantage of the frequency domain measurement, we measured the FEB spectrum of conducting polymer solution as an example of the electric birefringence induced by molecular orientation.

2. Theoretical Treatment of Nonlinear After-effect Function

Here, we consider the nonlinear after-effect function according to Morita's procedure [8,9]. At first, let us consider distribution function ρ satisfying the following general evolution equation:

$$\frac{\partial \rho}{\partial t}(x, t) = [\hat{D}_0(x) + \lambda p(t) \hat{D}_1(x)] \rho(x, t), \quad (1)$$

where x represents a set of all independent variables except time t , $\hat{D}_0(x)$ and $\hat{D}_1(x)$ an unperturbed and perturbed operator, respectively, λ a small parameter, and $p(t)$ a motivation function of time. Expanding ρ in power series of λ , we can get the n th-order perturbed term using eigenfunctions $g_i(x)$ and eigenvalues λ_i of: $\hat{D}_0(x)$:

$$\rho(x, t) = \rho_0(x) + \lambda \rho_1(x, t) + \lambda^2 \rho_2(x, t) + \dots, \quad (2)$$

$$\begin{aligned} \rho_n(x, t) &= \int dt' \int dx' g(x, x', t - t') \hat{D}_1(x') p(t') \rho_{n-1}(x', t) \\ &= \int_{t \geq t_1 \geq t_2 \geq \dots \geq t_n \geq 0} dt_1 dt_2 \dots dt_n \int dx_1 dx_2 \dots dx_n \\ &\quad g(x, x_1, t - t_1) \hat{D}_1(x_1) g(x_1, x_2, t_1 - t_2) \hat{D}_1(x_2) \dots \\ &\quad g(x_{n-1}, x_n, t_{n-1} - t_n) \hat{D}_1(x_n) \rho_0(x_n) p(t_1) p(t_2) \dots p(t_n) \quad (n \geq 2), \end{aligned} \quad (3)$$

$$g(x, x', t - t') = g(x, x', t) = \sum_i e^{-\lambda_i(t-t')} g_i(x) g_i^*(x'). \quad (4)$$

Then the ensemble average of a physical quantity $A(x)$ is written as

$$\begin{aligned}\langle A(x) \rangle_n &= \int dx A(x) \rho_n(x, t) \\ &= \int dt_1 dt_2 \cdots \mathcal{E}(t - t_1, t_1 - t_2, \cdots, t_{n-1} - t_n) p(t_1) p(t_2) \cdots p(t_n),\end{aligned}\quad (5)$$

where $\mathcal{E}$ is n th-order nonlinear after-effect function defined by

$$\begin{aligned}\mathcal{E}(t - t_1, t_1 - t_2, \cdots, t_{n-1} - t_n) \\ = \int dx A(x) \mathbf{g}(x) \cdot \mathbf{D}_1(t - t_1) \cdot \mathbf{D}_1(t_1 - t_2) \cdots \mathbf{D}_1(t_{n-2} - t_{n-1}) \cdot \tilde{\rho}(t_{n-1} - t_n),\end{aligned}\quad (6)$$

$$\begin{aligned}[\mathbf{g}(x)]_i &= g_i(x), \quad [\mathbf{D}_1(t)]_{ij} = u(t) e^{-\lambda_i t} \int dx g_i^*(x) \hat{D}_1(x) g_j(x), \\ [\tilde{\rho}(t)]_i &= u(t) e^{-\lambda_i t} \int dx g_i^*(x) \hat{D}_1(x) \rho_0(x).\end{aligned}\quad (7)$$

Although Eq. (6) resembles Volterra and Nakada's formula [5,6], our formula is given by the product of the exponential terms with decay rates λ_i , which is not constant, different from Nakada's formula of $\mathcal{E}(t - t_1, t_1 - t_2, \cdots, t_{n-1} - t_n) = e^{-t_1/\tau} e^{-t_2/\tau} \cdots e^{-t_n/\tau}$ with a single relaxation time τ .

Eq. (5) and (6) describe the dynamic behavior of the nonlinear phenomenon in time domain. Comparatively, the Fourier transform of Eq. (6) yields the dynamic behavior in frequency domain:

$$\begin{aligned}\mathcal{E}(\omega_1, \omega_2, \cdots, \omega_n) \\ = \int dx A(x) \mathbf{g}(x) \cdot \tilde{\mathbf{D}}(\omega_1 + \omega_2 + \cdots + \omega_n) \cdot \tilde{\mathbf{D}}(\omega_1 + \omega_2 + \cdots + \omega_{n-1}) \cdots \tilde{\mathbf{D}}(\omega_1 + \omega_2) \tilde{\rho}(\omega_1),\end{aligned}\quad (8)$$

with the matrices $\tilde{\mathbf{D}}(\omega)$ and $\tilde{\rho}(\omega)$ defined by

$$[\tilde{\mathbf{D}}(\omega)]_{ij} = \frac{1}{\lambda_i + i\omega} \int dx g_i^*(x) \hat{D}_1(x) g_j(x), \quad (9)$$

$$[\tilde{\rho}(\omega)]_i = \frac{1}{\lambda_i + i\omega} \int dx g_i^*(x) \hat{D}_1(x) \rho_0(x). \quad (10)$$

Let us consider the dc component as the response function with the sum of all the frequencies confined to zero. The dc component of the response function is written as

$$\begin{aligned}\mathcal{E}(\omega_1, \omega_2, \cdots, \omega_n)_{\omega_1 + \omega_2 + \cdots + \omega_n = 0} \\ = \int dx A(x) \mathbf{g}(x) \cdot \tilde{\mathbf{D}}(0) \cdot \tilde{\mathbf{D}}(\omega_1 + \omega_2 + \cdots + \omega_{n-1}) \cdots \tilde{\mathbf{D}}(\omega_1 + \omega_2) \tilde{\rho}(\omega_1).\end{aligned}\quad (11)$$

If non-zero components of $\tilde{\mathbf{D}}(\omega_1 + \omega_2 + \cdots + \omega_{n-1}) \cdots \tilde{\mathbf{D}}(\omega_1 + \omega_2) \tilde{\rho}(\omega_1)$ do not vanish through the succeeding operation, the measurement of the dc component of the nonlinear response function capture the information on the lower-order nonlinear response directly, because $\tilde{\mathbf{D}}(0)$ does not produce a new relaxation time. Especially, the dc component of a second-order nonlinear response function is possible to correspond to a linear response function. This simple relation is derived only in the frequency domain, which indicates an advantage of frequency domain measurement for nonlinear responses.

As a specific nonlinear effect, let consider the birefringence due to orientation of molecules with optical anisotropy. Then, $A(x)$ is given by

$$A(x) = \frac{c}{2n} \left\{ \left(\alpha_3^o - \frac{\alpha_1^o + \alpha_2^o}{2} \right) P_2(\cos \theta) + \frac{\alpha_1^o - \alpha_2^o}{4} P_2^2(\cos \theta) \cos 2\psi \right\}, \quad (12)$$

where c is molecular density, n the unperturbed mean refractive index, α_j^o optical polarizability along the j axis, and θ and ψ Eulerian angles between the external field and the molecule. Here, we adopt a general ellipsoidal model with permanent and induced dipole moments, of which dynamics is governed by the following diffusion equation [10]:

$$\frac{\partial \rho}{\partial t} = \hat{D}_R \rho + \sum_{j,k>0} \hat{D}_{jk} \rho \quad (13)$$

where $\hat{D}_R$ is the Perrin's operator for rotational diffusion [10] and $\hat{D}_{jk}$ describes the internal motion which interact with an external field:

$$\hat{D}_{jk} \rho = \frac{k_B T}{\xi_{jk}} \frac{\partial}{\partial \mu_{jk}} \left(\frac{\partial \rho}{\partial \mu_{jk}} + \frac{\rho}{k_B T} \frac{\partial U}{\partial \mu_{jk}} \right), \quad (14)$$

$$U = U_0 - \sum_{j>0} \mu_j E_j, \quad \mu_j = \mu_{j0} + \sum_{k>0} \mu_{jk}, \quad E_j = E(t) \gamma_j, \quad U_0 = \sum_{j,k>0} a_{jk} \mu_{jk}^2 / 2, \quad (15)$$

where μ_{jk} is the k th mode of induced dipole moment, μ_{j0} the permanent dipole moment along the j axis. According to the procedure mentioned above, the second-order nonlinear after-effect function of the electric birefringence can be written as

$$\mathcal{E}(t-t_1, t_1-t_2) = \frac{\pi c}{5n} \sum_{i=1}^3 (\alpha_{i-1}^o - \alpha_{i+1}^o) \varepsilon_i(t-t_1, t_1-t_2), \quad (16)$$

where

$$\begin{aligned} \varepsilon_i(t-t_1, t_1-t_2) = & \frac{\alpha_{i-1}(t_1-t_2) - \alpha_{i+1}(t_1-t_2)}{2k_B T} \left\{ \left(e^{-\lambda_{i-}(t-t_1)} + e^{-\lambda_{i-}(t-t_1)} \right) D_i \right. \\ & \left. + \frac{2(D_i^2 - D_{i-1}D_{i+1})}{\Delta} \left(e^{-\lambda_{i+}(t-t_1)} - e^{-\lambda_{i-}(t-t_1)} \right) \right\}, \quad (17) \end{aligned}$$

$$\lambda_{\pm} = 2(D_1 + D_2 + D_3) \pm \Delta, \quad \Delta = \sqrt{2} \sqrt{(D_1 - D_2)^2 + (D_2 - D_3)^2 + (D_3 - D_1)^2}, \quad (18)$$

$$\alpha_j(t) = \sum_{k=0} \frac{\alpha_{jk}^0}{\tau'_{jk}} e^{-t/\tau'_{jk}}, \quad (19)$$

$$\tau_{j0}^{-1} = \tau'_{j0}^{-1} = D_1 + D_2 + D_3 - D_j, \quad \tau_{jk} = \xi_{jk} / a_{jk}, \quad \tau_{jk}^{-1} = \tau_{j0}^{-1} + \tau_{jk}^{-1}, \quad (20)$$

$$\alpha_{j0}^0 = \mu_{j0}^2 / k_B T, \quad \alpha_{jk}^0 = 1 / a_{jk}. \quad (21)$$

Then, the second-order nonlinear response function of the electric birefringence is given by

$$\varepsilon(\omega_1, \omega_2) = \frac{\pi c}{5n} \sum_{i=1}^3 (\alpha_{i-1}^o - \alpha_{i+1}^o) \frac{\alpha_{i-1}(\omega_1) - \alpha_{i+1}(\omega_1)}{2k_B T} \left\{ \left(\frac{1}{\lambda_+ + i(\omega_1 + \omega_2)} + \frac{1}{\lambda_- + i(\omega_1 + \omega_2)} \right) D_i + \frac{2(D_i^2 - D_{i-1}D_{i+1})}{\Delta} \left(\frac{1}{\lambda_+ + i(\omega_1 + \omega_2)} - \frac{1}{\lambda_- + i(\omega_1 + \omega_2)} \right) \right\}, \quad (22)$$

where $\alpha_j(\omega)$ is the Fourier transform of $\alpha_j(t)$. For the simplicity, we assume one axis of rotational symmetry on the model, i.e., $D_1 = D_2 = D_r \ll D_3$ as a rod-like molecule. Then the after-effect and response function is given by

$$\varepsilon(t - t_1, t_1 - t_2) = \frac{2\pi c D_r (\alpha_3^o - \alpha_1^o)}{5n k_B T} \sum_{k=0} \left(\frac{\alpha_{3k}^0}{\tau'_{3k}} e^{-(t_1 - t_2)/\tau'_{3k}} - \frac{\alpha_{1k}^0}{\tau'_{1k}} e^{-(t_1 - t_2)/\tau'_{1k}} \right) e^{-6D_r(t - t_1)}, \quad (23)$$

$$\varepsilon(\omega_1, \omega_2) = \frac{2\pi c D_r (\alpha_3^o - \alpha_1^o)}{5n k_B T} \sum_{k=0} \left(\frac{\alpha_{3k}^0}{1 + i\omega_1 \tau'_{3k}} - \frac{\alpha_{1k}^0}{1 + i\omega_1 \tau'_{1k}} \right) \frac{1}{6D_r + i(\omega_1 + \omega_2)}. \quad (24)$$

At this stage, the after-effect function $\varepsilon(t - t_1, t_1 - t_2)$ in the time domain is equivalent to the response function $\varepsilon(\omega_1, \omega_2)$ in the frequency domain through two-dimensional Fourier transform, similar to the linear response theory. To measure the whole feature of these functions, we need to apply the following double-impulse field in the time or frequency domain:

$$E(t) = E_1 \delta(t - t_1) + E_2 \delta(t - t_2), \quad (25)$$

$$E(\omega) = E_1 \delta(\omega - \omega_1) + E_2 \delta(\omega - \omega_2). \quad (26)$$

3. Measurement of Nonlinear Response Function

Figure 1 schematically shows block diagram of two-dimensional electric birefringence relaxation spectroscopy, which gives us $\varepsilon(\omega_1, \omega_2)$ in Eq. (24) [7].

As an optical probe, we employ light from a semiconductor laser with the wavelength λ of 830 nm. The light passes through a linear polarizer, Kerr cell with thermally controlled, quarter-wavelength plate, and analyzer with small offset angle θ from its extinction position. After the analyzer, the light reaches photodiode to be detected. Light intensity I after the analyzer can be rewritten for $\delta \ll \theta \ll 1$ as

$$I = \xi P (\theta^2 + \theta \delta), \quad (27)$$

where ξ is the quantum efficiency of photo detection, P the light intensity on the specimen. We should note the second term is proportional to Δn as $\delta = 2\pi \Delta n / \lambda$ where l is the light path length of the Kerr cell.

Electric fields applied to the specimen consist of two frequency components.

Because the phase component of the response function is to be measured, the electric fields need to have the same initial phase on every averaging process. To achieve this, we synchronized two wave generators (HP 33120A), which burst out two sinusoidal electric fields with two different frequencies. These electric fields were mixed up as $E(t) = \text{Re}[E_1 e^{i\omega_1 t} + E_2 e^{i\omega_2 t}]$ and applied to the specimen. Each amplitude E_i was 2.5 V/cm and each frequency $f_i = \omega_i/2\pi$ ranged from 30 Hz to 90 kHz. The applied electric field yields the birefringence signal Δn consisting of five components with different frequencies of 0(dc), $2\omega_1$, $2\omega_2$, $\omega_1 + \omega_2$, and $\omega_1 - \omega_2$. Of these five frequency components, we paid attention to the $\omega_1 \pm \omega_2$ components.

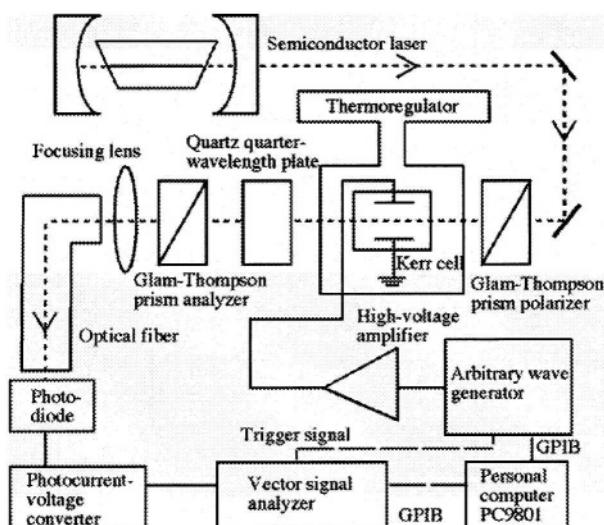


Figure 1. Block diagram of the two-dimensional FEB apparatus.

The birefringence signal passes through a photodiode as photocurrent and then through current-voltage converter as voltage signal. The voltage signal was detected by the digital lock-in demodulation method: A two-phase demodulator (vector signal analyzer HP 89410A) demodulated the signal with reference waves of $\cos(\omega_1 \pm \omega_2)t$ and $\sin(\omega_1 \pm \omega_2)t$, then real and imaginary parts of the $\omega_1 \pm \omega_2$ components of the signal were detected. If either one of the angular frequencies ω_i equals zero, the applied field, an offset sinusoidal field, allows direct current in the specimen and measurement is difficult to carry out because of the electrode polarization. Therefore we avoided zero-frequency and interpolated data points to obtain two-dimensional spectra.

The sample was the sodium poly(styrenesulfonate) (NaPSS). The NaPSS was purchased from Pressure Chemical Co. The sample with molecular weight of 3.6×10^5 and a nominal M_w/M_n ratio of 1.10 was dissolved in pure water (distilled and de-ionized water). Then the solution was dialyzed against pure water, passed through a mixed-bed ion exchange resin (IR-120 and IR-45) column, neutralized by the addition of

a freshly prepared NaOH solution, and used after dilution with pure water. In these procedures, the sample solution was handled under atmospheric nitrogen gas. The polymer concentration, measured by titration with NaOH, was 4.5×10^{-3} M.

Figure 2 shows the nonlinear response function of NaPSS solution with no added salt as a function of $\log(\omega_1 \pm \omega_2)/2$. The real part of the spectra exhibits a plateau when variables of $(\omega_1 + \omega_2)/2$ and $(\omega_1 - \omega_2)/2$ are small, and decreases as both variables increase. Meanwhile, the imaginary part of the spectra shows an extremum at $(\omega_1 + \omega_2)/2 \sim 1$ kHz, which decays toward the $(\omega_1 - \omega_2)/2$ axis.

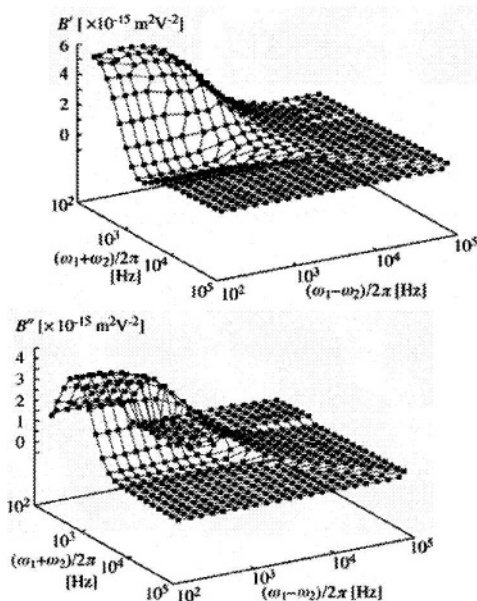


Figure 2. Real and imaginary part of nonlinear response function of NaPSS solution.

Further, we can easily create the conventional FEB spectra from the response function. The edged curves of the spectra where $\omega_1 \pm \omega_2 = 0$ give the dc and 2ω component of the conventional FEB spectra as is shown in Fig. 3. The positive relaxation in the 2ω component is due to the rotation of the polymer chain, and that the positive relaxation and the negative one in the dc component are ascribed to the induced dipole moments with slow and fast relaxation times. It is well known that the dielectric relaxation spectra of linear polyelectrolyte solution, such as NaPSS one, show two kinds of relaxation modes: the low frequency mode in the kHz range and high frequency modes in the MHz range [11]. This coincides with the experimental results. Table 1 shows the hydrodynamic diameter L_h calculated from rotational relaxation time and relaxation time of low τ_l and high frequency relaxation τ_h , and it is found that our result agrees with those of previous study [12]. Since this is a salt-free system, polymer has a considerably extended

conformation. As mentioned before, the information from the dc component of the FEB spectra concerns the internal motion of carriers and is equivalent to that from the linear response of the dielectric relaxation. The present experimental results confirm the validity of the theoretical prediction.

TABLE 1. Relaxation times and hydrodynamic diameter of NaPSS obtained by the dynamic electric birefringence, where L_c is contour length of polymer chain.

$1/2D_r$ (ms)	L_h/L_c	τ_1 (ms)	τ_2 (ms)
0.68	0.75	4.0	0.14

By the two-dimensional Fourier transform of Fig. 3, it is possible to obtain the after-effect function of the electric birefringence, which can create nonlinear response in time domain to applied electric field of any form. Figure 4 shows the TEB response of the polyelectrolyte solution created from the after-effect function using reversing- pulse field. However, this response does not indicate the existence of three kinds of relaxation, the rotational relaxation, low and high frequency relaxation of induced dipole moment directly. From this result, you can find the advantage of the FEB method.

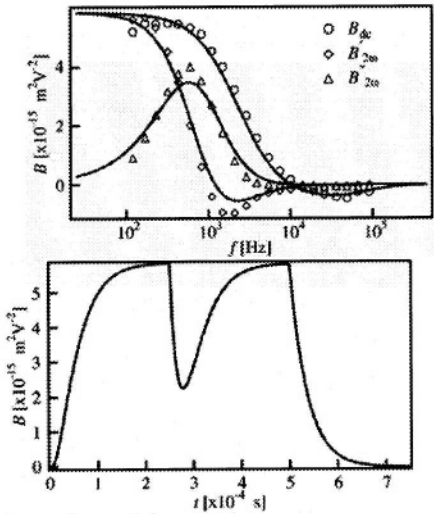


Figure3. The curves extracted from Fig. 2 where $\omega_1 \pm \omega_2 = 0$. They agree with the conventional FEB spectra of NaPSS solution.

Figure4. The TEB response of NaPSS solution using reversing- pulse field created from the Fig. 2.

4. Measurement of Electric Birefringence Spectrum in Frequency Domain

As an example to show the advantage of the frequency domain measurement, we measured the FEB spectrum of conducting polymer solution [13,14]. In the solid state

(bulk or films) of the conducting polymers, three types of transport mechanisms of carriers, that is, the intra-molecular, inter-molecular and inter-fibrillar hoppings, can contribute to the electric conductivity. Thus, it is difficult to distinguish each contribution by the experimental results of the conductivity in the solid state. On the other hand, in the dilute solution of the conducting polymers, the motion of carriers is restricted within a single chain, since polymer chains are isolated from each other in the solvent, which acts as an insulator. Then, we can exclusively obtain the information on the intrinsic one-dimensional intra-molecular conduction by investigating the motion of carriers in the dilute solution of the conducting polymers. So, we applied the FEB method to this conducting polymer solution.

The poly(3-hexylthiophene) (P3HT) sample used in this study was lightly doped with FeCl_2 anions of which number ratio to the monomer units of P3HT was ca. 1.5%. The weight-average molecular weight M_w of the sample was 2.5×10^5 and M_w/M_n was 5.5. As a solvent we used methylene chloride, in which P3HT had a rod-like conformation at room temperature. The concentration of P3HT in solutions was fixed at 4.0×10^{-3} w%.

Figure 5 shows the FEB spectra of P3HT at room temperature. The rotational relaxation can be observed in $B_{2,00}$ and from this relaxation frequency we can obtain the hydrodynamic radius of polymer chain. With increasing temperature, relaxation frequency shifts to high frequency and relaxation strength decreases. Calculated effective polymer length decreases with increasing temperature. While this transition has been investigated mainly by optical absorption spectroscopy so far [15], it is noted that the FEB method enables us to detect the rod-coil transition directly. It has been suggested that the competition between π -electron conjugation and conformational entropy causes this rod-coil transition of conducting polymer [16].

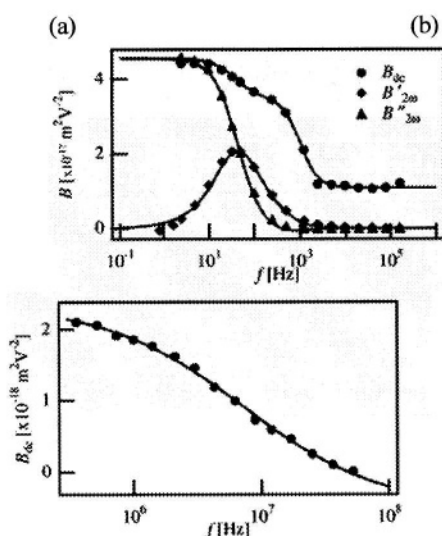


Figure 5. (a) The FEB spectrum of conducting polymer solution at room temperature and (b) the dc component in high frequency region.

From B_{dc} , we can see the low frequency (LF) relaxation with a relaxation frequency of ca. 1 kHz, and the high frequency (HF) one with a relaxation frequency of ca. 10 MHz. Incidentally, the relaxation with a relaxation frequency of ca. 40 Hz can be ascribed to the rotational relaxation owing to the permanent or quasi-permanent dipole moment. In addition, HF relaxation can be observed by dielectric relaxation as predicted by the theoretical treatment. These relaxations can be ascribable to the intra-chain carrier transport. Since the relaxation time of LF relaxation was strongly dependent on the polymer length, it is found that the LF mode is ascribed to the carrier diffusion within the longer range up to the contour length and diffusion constant can be estimated to be $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. While since the relaxation time of HF relaxation was independent of the polymer length, it is found that the HF mode arises from the diffusion within the more local range between the defects, which cut off the π -electrons conjugation system on the polymer chain and the diffusion constant can be estimated to be $2 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. This is consistent with that of polaron measured by NMR and ESR previously [17,18]. The experimental result that the diffusion constant of the LF relaxation is much smaller than that of the HF one indicates that these defects hinder the long-range hopping of carriers along the polymer chain.

5. Conclusion

In terms of power series expansion, we calculated the nonlinear after-effect and response function from the general time-evolution equation. From the result, we theoretically elucidated the connection between TEB and FEB. Also we clarified that the dc component of the electric birefringence relaxation yielded the information similar to that from the dielectric relaxation. We confirmed that our theoretical treatment agreed with the experimental results of NaPSS by two-dimensional electric birefringence relaxation spectroscopy. Further, we measured the FEB spectrum of conducting polymer solution. As a result, we detected the rod-coil transition directly by the FEB method. In addition, we clarified the two kinds of intra-molecular carrier transport mechanisms, that is, the carrier diffusion within the contour length and the diffusion within the more local range between the defects.

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7. References

1. For a review, see O'Konski, C.T. (1976) *Molecular Electro-optics*, Marcel Dekker, New York.

2. For a review, see Déjardin, J.-L. (1995) *Dynamic Kerr Effect*, World Scientific, Singapore.
3. Wegener, W.A. (1986) Transient electric birefringence of dilute rigid-body suspensions at low field strengths, *J. Chem. Phys.* **84**, 5989-6004; Sinusoidal electric birefringence of dilute rigid-body suspensions at low field strengths, *J. Chem. Phys.* **84**, 6005-6012.
4. Kubo, R., Toda, M., and Hashitsume, N. (1991) *Statistical Physics II. Nonequilibrium Statistical Mechanics*, Springer-Verlag, New York.
5. Schetzen, M. (1980) *The Volterra and Wiener Theories of Nonlinear Systems*, Wiley, New York.
6. Nakada, O. (1960) Theory of non-linear response, *J. Phys. Soc. Jpn.* **15**, 2280-2288.
7. Hosokawa, K., Shimomura, T., Frusawa, H., Kimura, Y., Ito, K., and Hayakawa, R. (1999) Two-dimensional spectroscopy of electric birefringence relaxation in frequency domain: Measurement method for second-order nonlinear after-effect function, *J. Chem. Phys.* **110**, 4101-4108.
8. Morita, A. (1986) Theory of nonlinear response, *Phys. Rev. A* **34**, 1499-1504.
9. Morita, A. and Watanabe, H. (1987) Nonlinear response and its behavior in transient and stationary processes, *Phys. Rev. A* **35**, 2690-2696.
10. Perrin, P. F. (1934) Mouvement brownien d'un ellipsoïde: Dispersion diélectrique pour des molécules ellipsoïdales, *J. Phys. Radium*, **5**, 497-511.
11. Mandel, M. and Odijk, T. (1984) Dielectric-properties of poly-electrolyte solutions, *Annu. Rev. Phys. Chem.* **35**, 75-108.
12. Ookubo, N., Hirai, Y., Ito, K., and Hayakawa, R. (1989) Anisotropic counterion polarizations and their dynamics in aqueous poly-electrolytes as studied by frequency-domain electric birefringence relaxation spectroscopy, *Macromolecules* **22**, 1359-1366.
13. Shimomura, T., Sato, H., Furusawa, H., Kimura, Y., Okumoto, H., Ito, K., Hayakawa, R., and Hotta, S. (1994) Intrachain conduction and main-chain conformation of conducting polymer as studied by frequency-domain electric birefringence spectroscopy, *Phys. Rev. Lett.* **72**, 2073-2076.
14. Shimomura, T., Kimura, Y., Ito, K., and Hayakawa, R. (1999) Relation between intra-chain conduction and main-chain conformation of conducting polymers in solutions as studied by electric birefringence spectroscopy, *Colloids and Surfaces A: Physicochem. Eng. Aspects* **148**, 155-162.
15. Rughooputh, S.D.D.V., Hotta, S., Heeger, A.J., and Wudl, F. (1987) Chromism of soluble polythienylenes, *J. Polym. Sci., Polym. Phys.* **25**, 1071-1078.
16. Schweizer, K.S. (1986) Order-disorder transitions of pi-conjugated polymers in condensed phases: I. General-theory, *J. Chem. Phys.* **85**, 1156-1175; II. Model-calculations, *J. Chem. Phys.* **85**, 1176-1183.
17. Nechtschein, M., Devreux, F., Genoud, F., Guglielmi, M., and Holczer, K. (1983) Magnetic-resonance studies in undoped trans-polyacetylene (CH)_x II, *Phys. Rev. B* **27**, 61-78.
18. Mizoguchi, K., Kume, K., and Shirakawa, H. (1984) Frequency-dependence of electron spin-lattice relaxation rate at 5-450 MHz in pristine trans-polyacetylene :New evidence of one dimensional diffusive motion of electron-spin (neutral soliton), *Solid State Commun.* **50**, 213-218.

MELTING/FREEZING IN NARROW PORES; DIELECTRIC AND EPR STUDIES

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Abstract. We report results of a study of the phenomena associated with melting of nano-phases confined within narrow pores. The study was performed by differential scanning calorimetry, dielectric spectroscopy, nonlinear dielectric effect measurements and electron paramagnetic resonance. Results of theoretical calculations concerning the phenomena are also presented. It has been proved, by experimental and theoretical methods, that the phenomena of melting in nano-phases are accompanied by the appearance of new phases (contact layer phases, hexatic phase), the nature of which depends on the structure of the walls and the pore size. The melting temperatures also depend strongly on these factors.

1. Introduction

The aim of this paper is to present phenomena associated with freezing and melting of nano-phases confined within narrow pores, using calorimetric, dielectric and spectroscopic (EPR) methods. Questions of interest in this field include the following: Is there a first order phase transition? What is the effect of confinement on the freezing temperature and how does this vary with the pore size, pore shape, the nature of the material and confined substance? What new phases, if any, occur that are not observed in bulk systems? What is the effect on the enthalpy change on transition? These questions are of fundamental scientific interest. In addition, an understanding of freezing in confined systems is of practical importance in lubrication, adhesion, and nanotribology. Freezing in narrow pores is important in understanding frost heaving and the distribution of pollutants in soils. Freezing in porous media has also been widely employed in the characterization of porous materials using the method of thermoporometry [1]. In this method the change in the freezing temperature is related to the pore size through the Gibbs-Thomson equation.

Prior to our work, relatively few experimental studies had been carried out, primarily for freezing of fluids in silica-based materials with pores of roughly cylindrical geometry. These experiments showed a lowering of the freezing temperature relative to the bulk value, $\Delta T_f = (T_{f,pore} - T_{f,bulk}) < 0$. For a porous medium with sufficiently large pores, the Gibbs-Thomson equation (the freezing analogue of the Kelvin equation for condensation), relates the shift in the freezing temperature to the surface tensions (γ) involved and pore width (H) by the equation:

$$\frac{\Delta T_f}{T_{f,bulk}} = -2 \frac{(\gamma_{ws} - \gamma_{wl})v}{H\lambda_{f,bulk}} \quad (1)$$

where subscripts w , s and l indicate wall, (confined) solid and (confined) liquid, respectively, and v and λ_f are the molar volume and latent heat of fusion for the bulk liquid. This equation, which predicts a linear relation between the shift in freezing temperature and H^{-1} , is based on classical thermodynamic arguments, and neglects effects due to the inhomogeneity of the confined phase and to intermolecular interactions with the wall. It will break down for small pores.

2. Experimental Studies

The experimental methods used were: differential scanning calorimetry (DSC), dielectric relaxation spectroscopy (DRS), nonlinear dielectric effect (NDE) measurements and electron paramagnetic resonance (EPR). In DSC phase transitions appear as sharp peaks at the transition temperature, and the area under the peak gives the enthalpy release (or adsorption) for the transition. DSC is a relatively simple and quick measurement to perform. However, it does not give information about the nature of the phases involved beyond the latent heat of transition, and subtle transitions, such as contact layer phases are difficult to detect. In DRS the complex relative permittivity of the system, $\kappa^* = \kappa' - i\kappa''$, is measured by applying an alternating electrical potential to the system, whose frequency can be varied over a wide range. Here κ' is the dielectric constant, and the imaginary part κ'' measures energy dissipation in the system, including that due to viscous damping of the rotational motion of the molecules in the alternating field. Measurements of κ' were used to locate the phase transition in the confined phase, since it exhibits large and sharp changes on freezing. Measurements of κ'' yield the dielectric relaxation time, τ . This characteristic time is very sensitive to the nature and structure of the phase. For example, $\tau \sim 10^{-9}$ s for liquids, 10^{-3} s for crystalline phases. Intermediate between these two phases are glassy phases ($\tau \sim 10^{-7}$ s) and hexatic phases ($\tau \sim 10^{-5}$ s). Thus the dielectric relaxation time is a sensitive measure of the nature of the phase, changing by orders of magnitude and giving important information about the nature of the phases observed. Evidence for the character of the phase transitions observed has been obtained using NDE measurements [10].

The NDE is defined as a change in the electric susceptibility induced by a strong electric field E :

$$\Delta\kappa' / E^2 = \kappa'^E - \kappa'^0 / E^2 \quad (2)$$

where κ'^E and κ'^0 are the electric susceptibility under an additional strong electric field E , and in its absence, respectively. The sign and magnitude of NDE of a liquid depends on the kind of inter- and intramolecular interactions and their energies [15]. The NDE vs. T divergence is typical of continuous phase transitions and its finite value is characteristic of NDE in confined systems [23,24]. The temperature dependence of the NDE near a phase transition temperature is described by a scaling law, and the value of the associated critical exponent can give information about the character of the phase transition that is observed.

For characterization of the nature of the liquid-walls interaction and also estimation of the pore size of ACF, we applied the electron paramagnetic resonance (EPR) method. EPR is a phenomenon in which particles with a non-zero magnetic moment (paramagnetic centres, i.e. unpaired electrons) are subjected to a constant and high-frequency alternate magnetic field adjusted to cause resonance absorption of energy. The transitions between the neighbouring energy levels of a particle [in a given energy state and in a given surroundings] are the sources of EPR signals. The resonance condition is:

$$h\nu = g\beta H \quad (3)$$

where ν is the frequency of the alternating field, (most often microwave), g is the spectroscopic splitting factor, β the Bohr magneton, and H is the intensity of the external magnetic field used to tune the system to resonance conditions. The surroundings of a paramagnetic centre can be the source of an additional local field, which permits characterisation of the energy state of the particle and its environment. We determine the spectroscopic splitting factor g (for a free electron equal to 2.0023). For a given substance it takes different values, and is a proportionality factor between the spin energy state and the magnetic field value. It can be treated as a parameter characterising the close environment of the particle studied. Additional information on the interaction of the paramagnetic centres and their interactions with the environment can be inferred from the fine or hyperfine structure of the spectrum.

The nano-porous materials that have been studied include controlled pore glasses (CPG) and Vycor, MCM-41 (a templated mesoporous material), and activated carbon fibers (ACF). The first three materials are silica-based, with pores that are roughly cylindrical. Vycor has pores of about 4.5 nm diameter, while CPG can have pore widths ranging from 7.5 nm to hundreds of nanometers. MCM-41 can have pore widths ranging from about 1.5 to 10 nm. The activated carbon fibers used were pitch based and had pore widths from 1.0 to about 1.6 nm. In the ACF the pores were roughly slit-shaped. All of these materials are relatively regular in their pore structure, and the pores are uniform in size, with little spread in pore width about the mean value. Comparison of results from these various materials provides information on the effects of pore shape (slit versus cylinder), size and nature of the surface. The ACF's have strongly adsorbing surfaces due to the close packing of the carbon atoms on the surface, while the silica-based materials have much more weakly attracting surfaces.

3. Molecular Simulation Studies

The conventional thermodynamic integration methods used to study freezing in bulk liquids fail for phases confined within pores, due to the presence of contact layer and other phases that arise due to the walls. To overcome the failure of the integration method, Radhakrishnan and Gubbins [14] used a method based on calculation of the Landau free energy, $\Lambda(\Phi)$, as a function of an effective bond order parameter, Φ . The Landau free energy is given by [15]:

$$\Lambda[\Phi] = -kT \ln(P[\Phi]) + C \quad (4)$$

where C is a constant, k is Boltzmann's constant and $P[\Phi]$ is the probability density of observing the system with an order parameter value between Φ and $\Phi+d\Phi$. The probability distribution function $P[\Phi]$ is calculated in a Grand Canonical Monte Carlo (GCMC) simulation using a histogram with umbrella sampling [17]. In-plane pair spatial and orientational correlation functions help identify the nature of the phases that correspond to the minima in the Landau free energy. The grand free energy, Ω , is calculated from the Landau free energy by:

$$\exp(-\Omega/kT) = \int d\Phi \exp(-\Lambda[\Phi]/kT) \quad (5)$$

This approach is not affected by phase changes in the contact layer, and can be used for repulsive, weakly attractive and strongly attractive walls.

Further Landau free energy studies, together with application of the Law of Corresponding States, show that for small adsorbate molecules the freezing behavior is largely controlled by a parameter $\alpha = c\epsilon_{fw}/\epsilon_{ff}$, which measures the ratio of the strength of the fluid-wall attraction to the fluid-fluid attraction [3,11]. Here ϵ_{fw} and ϵ_{ff} are the intermolecular potential well-depths for the fluid-wall and fluid-fluid interactions, and c is a parameter that accounts for the density and arrangement of the wall atoms. This enables global freezing phase diagrams to be constructed, showing the reduced freezing temperature vs. α , with regions corresponding to the various phases present (fluid, hexatic, contact layer, crystal, etc.). Comparisons with experimental data show good agreement in general. For small α , typically $\alpha < 0.8$ to 1.0, T_f is lower in the pore than in the bulk material, while for $\alpha > 0.8$ to 1.0 T_f is higher in the pore than in the bulk phase. For larger pores, where the number of adsorbed layers is greater than 2, contact layers also occur [11].

In two-dimensional systems, according to the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory [18,19], melting involves two separate transitions; the first is a transition from a 2-d crystal (with positional and orientational order) to a hexatic phase (long-range orientational order, but positional disorder); the second occurs at a higher temperature and is from the hexatic to the liquid phase (positional and orientational disorder). The hexatic phase has been observed experimentally in thin films of liquid

crystals, using electron diffraction [20-22]; the diffuse electron intensity pattern displays a six-fold symmetry for hexatic phases. Hexatic phases have been clearly observed in our simulation studies of LJ fluids in carbons having narrow slit pores [10, 11, 14]. In these systems the strong adsorbate-wall attraction gives rise to pronounced layering of the adsorbate molecules. Each of these layers comprises a quasi-two-dimensional system. The crystal-hexatic and hexatic-liquid transitions are located by the Landau free energy method, and the hexatic phase shows the diffuse six fold symmetry in the structure factor, and other features characteristic of this phase. Recent DSC measurements on CCl_4 and aniline in activated carbon fibers show transitions that appear to correspond to crystal-hexatic and hexatic-liquid transitions; moreover, the transition temperatures agree within 5°C with those predicted in the simulations

4. Results and Discussion

4.1 DSC, DRS and NDE

Experimental studies have been carried out for carbon tetrachloride using DSC and for nitrobenzene using DSC and DRS in CPG, Vycor, MCM-41 and ACF [2-8]. In addition, aniline [8,10], benzene [8], water and methanol [9] have been studied in ACF. The studies in CPG, Vycor and MCM-41, all of which have roughly cylindrical, silica-based, pores, all showed a decrease in the freezing temperature, as predicted in the simulations. For the larger pores, of widths 7nm and greater, the depression of the freezing temperature was inversely proportional to the pore width, as predicted by the Gibbs-Thomson equation. For smaller pores, however, significant nonlinearity was observed indicating the breakdown of the Gibbs-Thomson equation. In addition to the freezing transition, evidence of a contact layer phase was obtained from the DRS experiments in many cases. The simulations predict such a phase, in which the adsorbed layer next to the pore wall has a structure (fluid or solid) different from that of the inner layers (solid or fluid). In these cases the experiments showed two relaxation times, one intermediate in magnitude between those of solids and liquids. For large cylindrical pores, $H > 20\sigma$, where σ is the diameter of the adsorbed fluid molecules, the adsorbate appeared to freeze to a crystalline structure, but for somewhat smaller pores only partial freezing occurred yielding a frustrated microcrystal structure together with amorphous regions. For pore diameters below 15σ only amorphous structures were observed.

In the case of activated carbon fibers, which possess strongly attractive walls, we observed a substantial increase (by as much as 60K.) in the freezing temperature for both benzene and carbon tetrachloride. Such an increase had been previously observed by Kaneko et al. [12], and had been predicted in the simulations [8,10-13]. In the ACF the adsorbate phase is strongly layered, due to the small pore width (about 1.0-1.5 nm) and strong attractive forces from the carbon walls. We observe evidence of a stable hexatic phase that occurs between the crystal and liquid phases in these adsorbed layers. Such a hexatic phase had been predicted in the simulations for carbons with slit-shaped pores [10,11,14].

Recent NDE measurements on CCl_4 and aniline in activated carbon fibers show transitions that appear to correspond to crystal-hexatic and hexatic-liquid transitions; moreover, the transition temperatures agree within 5°C with those predicted in the

simulations. The pretransitional NDE anomalies have been described in terms of the phenomenological model of Landau – de Gennes [25,], used for the description of transitions from the liquid crystal phase to the isotropic phase, in which the presence of small liquid crystal regions of size $\xi(T)$ and uncorrelated orientations is assumed, and the size of the ordered regions are small when compared to the light wavelength. Then the intensity of the scattered radiation is $I \sim \xi^2$. Assuming the correlation range is in agreement with the scaling theory of KTHNY, the temperature dependence of NDE in the vicinity of the phase transitions in a quasi-two-dimensional system can be described as:

$$E^2/\Delta\kappa \sim \exp(-A / \{T - T_c\}^\gamma) \quad (6)$$

where $\gamma = 0.50$ for the transition liquid-hexatic phase, $\gamma = 0.37$ for the transition hexatic phase-crystal, and A is the amplitude. Fig. 1 presents the temperature dependence of NDE recorded for CCl_4 confined in ACF, in the vicinity of the two phase transitions noted. The solid lines in Fig. 1 correspond to the relation (9) for the appropriate values of the exponent γ . This result provides experimental verification of the presence of a stable hexatic phase in quasi-two-dimensional systems of small molecules.

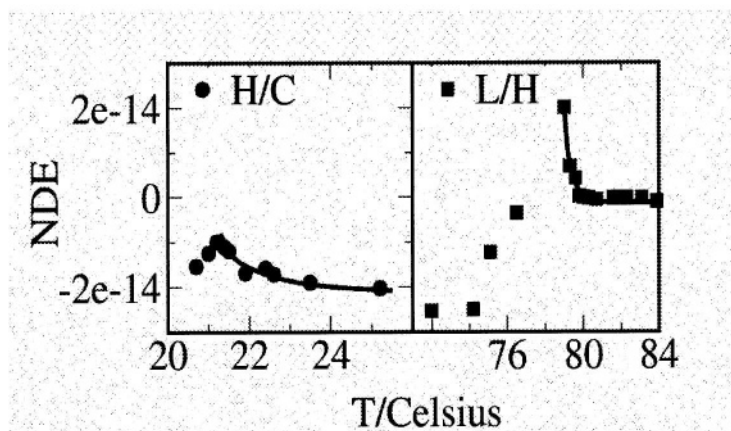


Figure 1. Temperature dependence of NDE for CCl_4 in ACF showing phase transitions: liquid to hexatic phase (L/H) and hexatic phase to crystal (H/C) [10].

4.2 EPR

In order to explain the nature of interactions of molecules with the pore walls we have undertaken a study by electron paramagnetic resonance. We wanted to determine whether the interactions are those typical of physical adsorption (van der Waals forces) and whether there are regions of specific interactions related to local irregularities of the pore walls or charge exchange in the interface for different pore materials. This paper presents results of the study on substances confined in graphite ACF pores.

EPR measurements of ACF (host) filled with various liquids: CCl_4 , C_6H_6 and $\text{C}_6\text{H}_5\text{NO}_2$ (guests), were performed in order to get information about the host $\leftrightarrow$ guest interaction. When guest molecules are adsorbed in ACF voids a broader component of EPR signal appears for all studied systems. There is no EPR signal from guest molecules: no charge transfer from ACF to guest molecules – no hyperfine splitting arising from interaction with nuclear spins of H or N was observed. The strongest modification of the EPR spectrum of ACF was observed for ACF with $\text{C}_6\text{H}_5\text{NO}_2$. The EPR signal of ACF with $\text{C}_6\text{H}_5\text{NO}_2$ consists of three lines [26]. The narrow line – line width $\Delta B_{1s} \approx 0.3$ mT (line (1)) – is characteristic for pristine ACF. Its g-value is equal to $g_{\perp}$ of graphite ($= 2.0031$) [27]. Its line width and g-factor are temperature-independent. Two broader components of the signal are also connected with the graphite structure of ACF. These are: line (2) with $\Delta B_{1s} \approx 1.7$ mT and $g = 2.0029$ (both temperature independent), and line (3) with strong ΔB_{1s} and g-factor temperature dependency: $\Delta B_{1s}(120\text{K}) \approx 13.2$ mT; $\Delta B_{1s}(4.2\text{K}) \approx 4.3$ mT; $g_{120\text{K}} = 2.0029$ and $g_{4.2\text{K}} = 1.9970$ (Fig.2). The line (2) originates from graphite particles (host) surrounded by guest molecules captured in nanopores. Similarly to component (1), the line width and g-factor are temperature independent. Broadening of the line (2), compared to (1), is caused by the shorter relaxation time of the more dense system. The line width and g-factor of the component (3) of the observed EPR spectrum strongly depends on temperature. Such behavior can be explained as a surface effect in ACF.

Stronger instabilities of paramagnetic centers at the surface of ACF or in its larger pores appear as a temperature effect. When temperature is lowered below 20 K, both line width and g-factor reach values characteristic for graphite nanoparticles surrounded by guest molecules captured in pores. No Dysonian shape of the EPR line is observed for each component. This shows that the ACF crystallite size is lower than $3.2 \mu\text{m}$ – the penetration depth of the microwave field in graphite. Each of the three lines obeys the Curie law. No hyperfine splitting from interaction with H or N nuclei, together with the Curie law for all three components, confirm the localization of paramagnetic centers within crystallites of ACF. According to the model of ACF proposed in [28] and the theory of EPR of small particles [29] these two effects make it possible to treat ACF as

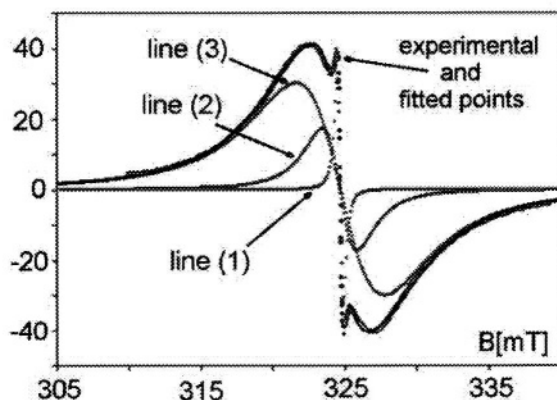


Figure 2. EPR spectrum for ACF filled with nitrobenzene; fit is a sum of lines (1),(2) and (3)

a system of nanographite particles in which quantum size effects can appear. Estimation based on the theory of EPR of small particles gives an average ACF nanocrystallite radius of 1.34 nm [26]. This value is in good agreement with the model of ACF proposed in [30] where graphite plates 1–3 layers thick and 2.5 nm in diameter are separated with nanopores of size 1–2 nm. The EPR results enable us to conclude that only weak $\text{host} \leftrightarrow \text{guest}$ interactions occur in these systems; these lead to a modified EPR spectrum of pristine ACF, where van der Waals forces are significant.

5. Conclusions

As follows from the results of a dielectric study of the melting/ freezing phenomena of liquids confined in nanopores of different size and wall structure, and from the theoretical calculations, the qualitative behavior of these phenomena depends on a competition between the fluid-wall and fluid-fluid interactions, described by α parameter. When α is large, melting temperature increases on confinement. It has also been shown that even for simple fluids, several new phases appear: a few kinds of contact layer phases and hexatic phases. In cylindrical pores confinement effects are greater, but for pore diameters below $20\sigma_{\text{ff}}$ we do not observe crystallization, but either partial crystallization or glassy phases.

Taking into regard the significance of the type of interactions between the pore walls and the substance inside them, the strength of the interactions has been estimated for a few substances confined in the ACF pores by the EPR method. Results of this study have indicated the occurrence of van der Waals forces and the absence of strong local charge-transfer interactions between ACF pores and the substances within them.

6. Acknowledgments.

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7. References

1. Eyraud, C., Quinson, J.F., and Brun, M. (1988), in K. Unger, J. Rouquerol, K.S.W. Sing, and H.Kral (eds.), *Characterization of Porous Solids*, Elsevier, Amsterdam, pp. 307-315.
2. Śliwińska-Bartkowiak, M., Gras, J., Sikorski, R., Radhakrishnan, R., Gelb, L.D., and Gubbins, K.E. (1999) Phase Transitions in Pores: Experimental and Simulation Studies of Melting and Freezing, *Langmuir* **15**, 6060-6069.
3. Radhakrishnan, R., Gubbins, K.E. and Śliwińska-Bartkowiak, M. (2000) Effect of the Fluid-Wall Interaction on Freezing of Confined Fluids: Towards the Development of a Global Phase Diagram, *Journal of Chemical Physics* **112**, 11048-11057.
4. Śliwińska-Bartkowiak, M., Dudziak, G., Sikorski, R., Gras, R., Radhakrishnan, R. and Gubbins, K.E. (2001) Melting/Freezing Behavior of a Fluid Confined in Porous Glasses and MCM-41: Dielectric Spectroscopy and Molecular Simulation, *Journal of Chemical Physics* **114**, 950-962.
5. Śliwińska-Bartkowiak, M., Gras, J., Sikorski, R., Dudziak, G., Radhakrishnan, R. and Gubbins, K.E. (2000) Experimental and Simulation Studies of Melting and Freezing in Porous Glasses, Unger, in K.K., Kreysa, G. and Baselt, J.P. (eds.), *Characterization of Porous Solids V*, Elsevier, Amsterdam, pp. 141-150.
6. Radhakrishnan, R., Gubbins, K.E., Śliwińska-Bartkowiak, M. and Kaneko, K. (2000) Understanding Freezing Behavior in Pores, in Do, D.D. (ed.), *Adsorption Science and Technology*, World Scientific, Singapore, pp. 234-238.
7. M. Sliwinski-Bartkowiak, G. Dudziak, R. Gras, R. Sikorski, R. Radhakrishnan, and K.E. Gubbins, "Freezing Behavior in Porous Glasses and MCM-41", *Colloids & Surfaces A*, **187-188**, 523-529 (2001).
8. Śliwińska-Bartkowiak, M., Dudziak, G., Sikorski, R., Gras, R., Gubbins, K.E., Radhakrishnan, R. and Kaneko, K. (2001) Freezing Behavior in Porous Materials: Theory and Experiment, *Polish Journal of Physical Chemistry*, **75**, 547-555 (2001).
9. Śliwińska-Bartkowiak, M., Dudziak, G., Sikorski, R., Gras, R., Gubbins, K.E. and Radhakrishnan, R. (2001) Dielectric Studies of Freezing Behavior in Porous Materials: Water and Methanol in Activated Carbon Fibers (2001) *Phys. Chem. Chem. Phys.* **3**, 3, 1179-1184.
10. Radhakrishnan, R., Gubbins, K. E. and Śliwińska-Bartkowiak, M. (2002) Existence of Hexatic Phase in Porous Media, *Physical Review Letters* **89**, 076101-1-4.
11. Radhakrishnan, R., Gubbins, K.E. and Śliwińska-Bartkowiak, M. (2001) Global Phase Diagrams for Freezing in Porous Media, *Journal of Chemical Physics*, **116**, 1147-1155 (2002).
12. Kaneko, K., Watanabe, A., Iiyama, T., Radhakrishnan, R. and Gubbins, K.E. (1999) A Remarkable Elevation of Freezing Temperature of CCl₄ in Graphitic Micropores, *Journal of Physical Chemistry B* **103**, 7061-7063.
13. Radhakrishnan, R., Gubbins, K.E., Watanabe, A. and Kaneko, K. (1999) Freezing of Simple Fluids in Microporous Activated Carbon Fibers: Comparison of Simulation and Experiment, *Journal of Chemical Physics* **111**, 9058-9067.
14. Radhakrishnan, R. and Gubbins, K.E. (1999) Free Energy Studies of Freezing in Slit Pores: An Order-Parameter Approach using Monte Carlo Simulation, *Molecular Physics* **96**, 1249-1267.
15. Chełkowski A. (1993) *Physics of Dielectric*, 3rd edition, PWN, Warsaw
16. Landau, L.D. and Lifshitz, E.M. (1980) *Statistical Physics* 3rd edition, Pergamon Press, London.
17. Torrie, G.M. and Valleau, J.P. (1974) Monte Carlo Free Energy Estimates Using Non-Boltzmann Sample: Application to the Sub-Critical Lennard-Jones Fluid, *Chemical Physics Letters* **28**, 578-585.
18. Kosterlitz, J.M. and Thouless, D.J. (1972), *Journal of Physics C* **5**, L124.; *ibid.* **6**, 1181 (1973).
19. Halperin, B.I. and Nelson, D.R. (1978) Theory of Two - Dimensional Melting, *Physical Review Letters* **41**, 121-131; Nelson, D.R. and Halperin, B.I. (1979) Dislocation-Mediated Melting in Two Dimensions, *Physical Review B* **19**, 2457-2484; Young, A.P. (1979) Melting and the Vector Coulomb Gas in Two Dimensions, *Physical Review B* **19**, 1855-1866.
20. Brock, J.D., Birgenau, R.J., Lister, J.D. and Aharony, A. (1989) Liquids and Crystals and Liquid Crystal, *Physics Today* Volume, 52-59.
21. Chao, C.Y., Chou, C.F., Ho, J.T., Hui, S.W., Jin, A. and Huang, C.C. (1996) Nature of Layer-by Layer Freezing in Free-Standing 40.8 Films, *Physical Review Letters* **77**, 2750-2757.

22. Chou, C.F., Jin, A.J., Huang, S.W. and Ho, J.T. (1998) Multiple-Step Melting in Two Dimensional Hexatic Liquid-Crystal Film, *Science* **280**, 1424-1426.
23. Gelb, L.D., Gubbins, K.E., Radhakrishnan, R. and Śliwińska-Bartkowiak, M. (1999) Phase Separation in Confined Systems, *Reports on Progress in Physics* **62**, 1573-1659.
24. Śliwińska-Bartkowiak M., Sowers S.L., Gubbins K.E. (1997) Liquid-Liquid Phase Equilibria on Porous Materials, *Langmuir* **13**, 1182-1188
25. deGennes P.G. (1974) *The Physics of Liquid Crystals*, Clarendon Press, Oxford
26. Kempański, M., Śliwińska-Bartkowiak, M. and Kempański, W., Host↔guest interaction in ACF: EPR study, *this issue*
- Stankowski, J., Piekara-Sady, L., Kempański, W., Huminiecki, O. and Szczaniecki, P. B. (1997) EPR of graphite and fullerenes, *Fullerenes Science and Technology* **5**(6), 1203-1217
27. Fung, A.W. P., Wang, Z. H., Dresselhaus, M. S., Dresselhaus, G., Pekala, R. W. and Endo, M. (1994) Coulomb-gap magnetotransport in granular and porous carbon structures, *Physical Review* **B49**, 17325-17335
28. Buttet, J., Car, R. and Myles, Ch.W. (1982) Size dependence of the conduction-electron-spin-resonance g shift in a small sodium particle: Orthogonalized standing-wave calculations, *Physical Review* **B26**, 2414-2431.; Myles, Ch. W. (1982) Shape dependence of the conduction-electron spin-resonance g shift in a small sodium particle, *Physical Review* **B26**, 2648-2651.]

ELECTRODILATOMETRY OF LIQUIDS, BINARY LIQUIDS, AND SURFACTANTS

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Abstract. When a liquid is subjected to high electric field, its volume change (ΔV) can be increased or decreased depending upon the liquid under investigation. A *new* technique has been developed from our laboratory to measure the relative volume change per E^2 and is known as “*Electrodilatometry (ED)*” which may be expressed as:

$$R = \frac{V - V_0}{V_0} \frac{1}{E^2} = \frac{\Delta V}{V_0} \frac{1}{E^2}, \text{ where } R \text{ is known as “Electrodilatometric Effect (EDE)”}, V \text{ and } V_0 \text{ are the}$$

volume of liquid with and without the field, respectively. ED is one of the nonlinear effects such as electro-optic Kerr effect, the electrostriction, dielectrophoresis, nonlinear dielectric effect (NDE). ED is found to be very sensitive to hydrogen-bonded liquids. It has been applied to study pure liquids, binary mixtures, alcohols, and non-ionic surfactants such as Triton X-100. The signs of EDE (R), Kerr constant (B) and NDE ($\Delta\epsilon/E^2$) are compared and contrasted. A few models have been used to calculate R with limited success. Not only can ED be used with smaller molecules but it should also be a potential tool to study polymer solutions and supramolecular assemblies.

1. Introduction

The change in pressure following the impact of high electric field on a liquid is known in the literature as electrostriction and is the topic of many investigations [1,2]. This method suffers from one drawback i.e. the choice of the reference pressure varies from one laboratory to another [3]. This makes it difficult to compare experimental results. In order to avoid this, we are investigating the impact of high electric field on the change in the volume of a liquid. While there were a couple of reports in the old literature that electric fields were used to study some liquids as cited in ref.[4], these investigations did not look at the volume change as we proposed hereunder. To the best of our knowledge, the electric field-induced volume change is a new technique and it is proposed that this new technique, originated from our laboratory, be called “*Electrodilatometry*” (ED). The change in volume was found to vary directly as the square of the externally applied electric field strength (E^2). Thus, ED is one of the nonlinear methods and is similar to the Kerr effect [5], nonlinear dielectric effect (NDE) [6,7], electrostriction, dielectrophoresis (non-uniform field) [8] and other nonlinear methods [9]. These

methods share one common feature with ED in that application of high electric fields is required. They differ only which physical parameter is used to monitor the change. For example, for ED it is the volume change; for Kerr effect, the difference between refractive indices (Δn); for NDE, the change in relative permittivity ($\Delta \epsilon$); etc. Thus for a given sample of liquid subjected to an applied field, ED can yield unique information on ΔV which may be integrated with information provided by Kerr effect and NDE. The presentation is organized in the following manner: the theories related to ED are presented in section 2, the experimental procedure (section 3), results (section 4), discussion (section 5), and the conclusions are drawn in section 6.

2. Theories

The volume of a liquid is changed when it is subjected to high static electric field. Such a volume change has been derived. In the case of fluid flow into a region from the source of constant chemical potential, the volume change is given [10], i.e.

$$(1) \quad \left(\frac{\partial V}{\partial E} \right)_{T,P} = - \left(\frac{V_0 E}{4\pi} \right) \left(\frac{\partial \epsilon}{\partial P} \right)_{T,E}$$

Where V, P, T are the volume, pressure and temperature, respectively; V_0 is the liquid volume without the field, and E is the applied electric field. Integration of equation (1) yields:

$$(2) \quad R = \left(\frac{V - V_0}{V_0 E^2} \right) = - \left(\frac{1}{8\pi} \right) \left(\frac{\partial \epsilon}{\partial P} \right)_T$$

Where ϵ is the relative permittivity of liquid. Left hand side of equation (2) may be written as $R = \frac{\Delta V}{V_0 E^2}$, where $\Delta V = V - V_0$ and V is the volume of liquid

under the applied field. R represents the relative volume change per E^2 and it is henceforward called the “*Electrodilatometric Effect*” (EDE). In another derivation, attempts are made to include some geometry of a dielectric [1] as shown in equation (3):

$$(3) \quad \frac{V - V_0}{V} = \frac{E^2}{8\pi} \left[\frac{\epsilon - 1}{n\epsilon + 1 - nK} \frac{1}{K} - \frac{1}{(n\epsilon + 1 - n)^2} \left(\frac{\partial \epsilon}{\partial P} \right)_T \right]$$

Here, $1/K$ is the compressibility of the liquid, and n is the parameter depending on the geometry of the dielectric. A model which allows for change in molecular volume when a dielectric ellipsoid is placed under electric field, has been advanced [11] as shown:

$$(4) \quad R_a = \frac{1}{2} \varepsilon_0 \left[\frac{\varepsilon + 2\varepsilon_0}{3\varepsilon_0} \right]^2 \frac{\varepsilon_i - \varepsilon_0}{(\varepsilon_i - \varepsilon_0)L_a + \varepsilon_0} \frac{1}{K_i} \left[1 - \frac{\varepsilon_i + 2\varepsilon_0}{3\{(\varepsilon_i - \varepsilon_0)L_a + \varepsilon_0\}} \right]$$

Where R_a is R evaluated with maximum semi-principal axis (a) parallel to the field, and L_a is the depolarizing factor of the ellipsoid. K_i is the internal bulk modulus of the molecule, ε_i is the internal permittivity and ε_0 is the permittivity of vacuum.

In fact, the observed volume change ($\Delta V_{\text{observed}}$) for some liquids may be due to other contributions, in addition to the classical electrostriction ($\Delta V_{\text{electro}}$), as in equation (5):

$$(5) \quad \Delta V_{\text{observed}} = \Delta V_{\text{electro}} + \Delta V_{\text{interac}} + \Delta V_{\text{struct}}$$

Where $\Delta V_{\text{interac}}$ is the volume change due to interactions; and ΔV_{struct} is the volume change due to structural interactions. $\Delta V_{\text{electro}}$ is the volume change due to the deformation of the dielectric without changing its shape [1], or electrically-induced distortional strain [8]. $\Delta V_{\text{electro}}$ is calculated from (2) and the net contribution of this term will be small and negative [4]. $\Delta V_{\text{interac}}$ is the volume change due to, e.g. the induced dipole-induced dipole, dipole-induced dipole interactions. It has been shown that for the case of ionic interactions involving central metal ion and the surrounding solvent molecules, this term is large and negative [12]. ΔV_{struct} is the volume change due to structural interactions. It is caused by molecules with permanent dipole moments, which respond to an external electric field by realignment so as to reduce their potential energy, and sometimes known as orientational polarization [8]. This process may lead to several volume changes as a consequence, e.g. *inter-* and *intra-* steric interactions, forming and breaking of H-bonds, changes in molecular conformation, etc. For a hydrogen-bonded system, ΔV_{struct} is likely to be large and positive due to the net change in the number of hydrogen bonds as the molecules are forced to realign with the field.

3. Experiment

The detailed construction of ED cell and its assembly was provided earlier [13] and is briefly described. Two stainless steel cylindrical electrodes, inner one was solid and the outer one hollow. They were assembled concentrically leaving an electrode gap of 0.105 cm. They were sufficiently large in order to sink any Joule heat generated during a measurement. Two electrically insulating plates were used to cap securely both ends of the electrodes. Liquid sample was introduced through an inlet port located at the bottom of the cell and it moved up the electrode gap and out through the outlet port at the top of the cell into a connecting line. The latter was connected to a glass capillary. The liquid sample partially filled the capillary. Water jackets were used for the cell and the capillary so that the temperature was kept constant and controlled to $\pm 0.02\text{K}$ by a circulating bath.

The apparatus was assembled as shown schematically in Figure 1. Laser light (Spectra Physics) at 632.8 nm, passed through a cylindrical lens and was converted

to a vertical line and focused on to the sample liquid level in the capillary. The image of the level was captured by a linear charge-coupled device, CCD (Texas Instruments, TC-104).

The output from the board was fed into an A/D board of a PC. Regulated high DC voltages were generated from a power supply (Bertan, 205A-20R). Typical field strength

used was in the range $(0.15 - 4.0) \times 10^6$ V/m, depending upon the sample used. The

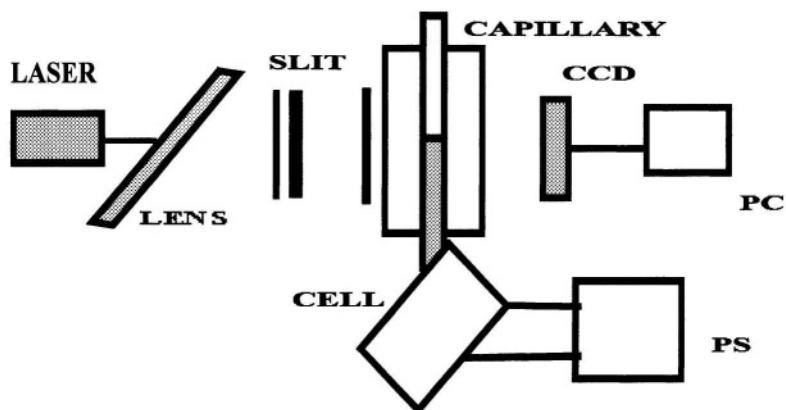


Figure 1. A diagram of ED apparatus (See text for details).

change in pixel number was converted to physical height by calibration. The net change in height was used to calculate the ΔV . The system is sensitive to change in 10^{-9} dm^3 .

Pure liquids used were of spectroscopic grade and were dried by molecular sieves (heptane and cyclohexane by sodium wire) and filtered. Triton X-100 [TX-100]

(t-octylphenoxy polyethoxy ethanol) (Aldrich) $[\text{C}(\text{CH}_3)_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_n\text{OH}]$, with $n \approx 10$ and the water content was $\approx 0.3\%$ by weight. The reduced form of TX-100 was obtained from the same source whose structure is similar to the regular TX-100, except the phenyl ring was hydrogenated to cyclohexyl.

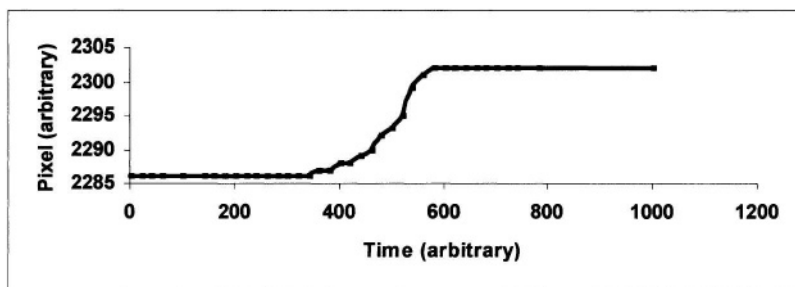


Figure 2. Sample output of cyclohexanol, field off (lower) and on (upper).

4. Results

Figure 2. shows a typical output of a signal in a measurement in which the pixel number is plotted against the time (arbitrary unit). Figure 3. shows a sample plot of the difference in pixel number against the square of the applied voltage, E^2 . Table 1. is a collection of R values for various liquids at 298 K, unless stated otherwise. For some hydrogen-bonded liquids, e.g. some pentanols, the binary mixtures with n-heptane are also shown because of the availability of the Kerr constants. In addition, the values of calculated R from equation (2) are shown for some liquids where the data for $\left(\frac{\partial \epsilon}{\partial P}\right)_T$ are available in the literature. Some data for the Kerr constants (B) and the nonlinear dielectric effect

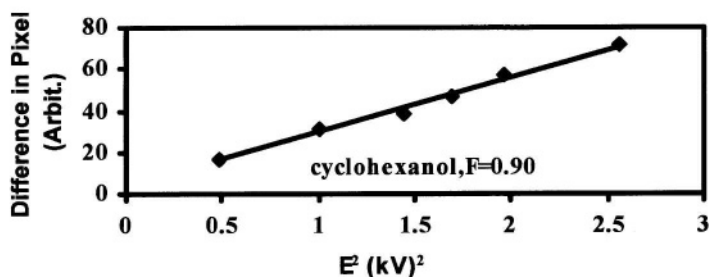


Figure 3. Plot of difference in pixel number (arbit.) vs. $E^2(\text{kV})^2$

$(\Delta \epsilon/E^2)$ are also collected in the same Table for comparison. Table 2. shows the various R values at 293 K for each isomer of pentanols mixed with n-heptane at various mole fraction (F). Table 3. is a collection of R at 298 K values for a series of cyclohexanol mixed with n-heptane. The values of R for TX-100 in cyclohexane at various concentrations (mole/kg) and at 298 K are collected in Table 4.

5. Discussion

The discussion is divided into 5 sections: 5.1 General aspects, 5.2 Pure and hydrogen-bonded liquids, 5.3 Pentanols and cyclohexanol, and 5.4 Triton-X 100 solutions.

5.1 General aspects

It may be seen from Figure 3. that the plot of the change in height (hence, the volume) is directly proportional to E^2 . This shows that Electrodilatometry (ED) is one of the nonlinear techniques similar to Kerr effect and nonlinear dielectric effect.

5.2 Pure and hydrogen –bonded liquids

From Table 1., if the signs are neglected and only the magnitude of R is inspected by normalizing against the carbon disulfide, the normalized magnitude is comparable to when the Kerr constant (B) is normalized against its carbon disulfide, for most liquids. However, there are two liquids on the list which do not follow such a trend, i.e. nitrobenzene and 2-pentanol in n-heptane at F=0.601. While nitrobenzene has very large B value, the 2-pentanol mixture has very large R value. It shows that for some hydrogen-bonded systems, ED is a very sensitive technique.

If the attention is now paid to the signs of R (excluding the t-pentanol), it may be seen that the sign of experimental R value is opposite to the sign of B and the sign of $\Delta\epsilon/E^2$, for those liquids (and mixtures) where these values are available. While the exact reasons are not known, only plausible suggestions to this are hereby given.

At this time, only the signs of R and B are discussed first, and the signs of $\Delta\epsilon/E^2$ are to be discussed later. Take the case of a non-hydrogen-bonded liquid, the negative value

of R suggests that the volume decreases in the presence of the applied field. The existence of the high electric field gives rise to high pressure. The latter forces the molecules to be closer, hence the observed volume decrease. This is accompanied by the B value being positive, which suggests that the refractive indices $n_{||} > n_{\perp}$. On the other hand, for a hydrogen-bonded liquid, the volume is increased under the field (R is positive). To account for this, it is plausible that the electric field forces the molecules to reorientate and in so doing, the system experiences the net loss of the number of hydrogen bonds. This lessened intermolecular forces, could translate into the observed expansion of the volume under the field. This is similar to the term “structure breaking effect” which was used in the magneto-optical investigations of associated liquids [19]. This positive R is accompanied by $n_{||} < n_{\perp}$ (B being negative).

The sign of NDE ($\Delta\epsilon/E^2$) is the same as the sign of B, for all the liquids where these values are available. While some forms of explanations may be offered to account for the sign of R and B, it is, however, more subtle to pin down the origin of the sign of NDE. This is because the sign of NDE depends upon an intricate balance of several

TABLE 1. Experimental and calculated electrodilatometric effect (R)*, electro-optic Kerr constants (B), nonlinear dielectric effect ($\Delta\epsilon/E^2$) values for various liquids at 298 K (unless stated otherwise).

Liquids Ref.	$R(m^2/V^2)$		B	Ref.	$\Delta\epsilon/E^2$	
	expt.(10^{-19})	calc.(10^{-21})	($10^{-15}m/V^2$)		($10^{-19}m^2/V^2$)	
<i>Non-dipolar</i>						
Carbon disulfide	-55.4 ^b	-5.9	35.1	[14]	1.25 ± 0.1	[7]
Cyclohexane	-7.7 ^b		0.6	[5]	1.5 ± 0.2	[15]

Benzene	-12.5 ^b	-4.4	3.9	[16]	0.035±0.02	[7]
Mesitylene	-6.7 ^b		6.3	[16]		
<i>Dipolar</i>						
Toluene	-9.4 ^b	-6.6	7.9	[16]	0.17 ±0.03	[7]
Nitrobenzene	-381.0 ^b		4400.0	[5]	3229 ^e	[17]
Chlorobenzene	-121.0 ^b	-9.8	136.0	[16]		
<i>Hydrogen-bonded</i>						
Chloroform	35.5 ^b	-13.4	-30.5	[16]	-16.0	[18]
1-Pentanol	447.2		-274 ^d		-2152 ^e	[17]
1-Pentanol,F=0.601	31.6 ^c				-68.0 ^c	
2-Pentanol,F=0.800	5305.0 ^c				-9.8 ^c	
3-Pentanol,F=0.601	28.7 ^c				-10.2 ^c	
t-Pentanol	61.9 ^c				29.2 ^c	

^aError in R is $\approx \pm 9\%$; ^bFrom ref.[4]; ^cMeasured at 293 K., ^dAt 212 K ^eEstimated from graph of ref.[17]

competing factors [18] which are briefly summarized. (a) At large field ($>10^6$ V/m), the contribution from the higher terms of the Langevin function must be taken into account. This leads to the “normal saturation” and its contribution to $\Delta\epsilon/E^2$ is negative. (b) In an equilibrium, the field shifts the equilibrium in favour of the more polar species. This is called the “anomalous saturation” and makes a positive contribution to the $\Delta\epsilon/E^2$. (c) For species with anisotropic polarizability, the axis of highest polarizability is forced to align in the direction of the field (which is related to the Kerr effect). Its contribution to the $\Delta\epsilon/E^2$ is positive. (d) Contributions from the first (β) and second (γ) hyperpolarizabilities should also be considered and their contributions to $\Delta\epsilon/E^2$ can be either negative or positive depending on the parameters β and γ . Some of these factors were used to explain the anomalous behaviour of NDE for solutions of 1-pentanol [20].

For the t-pentanol, R is positive (like other hydrogen bonded liquids) and is the same sign as B (contrary to other hydrogen-bonded liquids on the list.). This unique situation may be due to the unique ability of t-pentanol to form a cyclic trimers (not excluding higher cyclic multimers). These trimers can also form stacking structure in which one ring stacks on top of another and many rings may be involved. Each ring is staggered from the lower one by about 60°. This facilitates two things; firstly, the formation of inter-ring hydrogen bonds by the bifurcated hydrogen bonds of O and H atoms; secondly, the bulky t-pentyl groups are displaced further away from each other. This structure is consistent with the results of our studies from other techniques: i.e. Kerr effect [21], viscometry [22], NMR [23], and photochromic reaction probe [24].

The calculated R [from equation (2)] for some liquids and their values are approximately 2 orders of magnitude lower than the experimental ones. For all the liquids calculated, all of them gives *negative* sign. This is the same as the experimental ones, except for chloroform for which the sign is *positive*. The latter is

explained in the next section. While the signs of experimental and calculated R [based on equation (4)] are in agreement, the discrepancy in their magnitude has yet to be resolved. The discrepancy in magnitude may be partly due to the contribution to volume change from other factors as shown in equation (5), i.e. $\Delta V_{\text{interac}}$ and ΔV_{struct} in addition to $\Delta V_{\text{electro}}$.

TABLE 2. Collection of R values ($10^{-19} \text{ m}^2/\text{V}^2$) for various pentanols in n-heptane at various concentrations (mole fraction, F) for 293 K.

Mole Fraction	1-Pentanol	2-Pentanol	3-Pentanol	t-pentanol
0.301	5.406			
0.400	9.778	11.18		
0.499	19.64	49.25	2.902	
0.601	31.57	182.3	28.69	
0.700	99.59	951.7	289.7	
0.800	769.6	5305	488.6	
0.900	739.0		1533	16.00
1.00	447.2		2340	61.92

Estimated error in R is $\pm 9\%$.

5.3 Pentanol and cyclohexanol

For pentanols in n-heptane as shown in Table 2., all R values are positive, i.e. the volume is increased under the applied fields. Some of the concentrations could not be measured due to difficulties in obtaining concordance readings, and for t-pentanol, the changes at low concentrations are too small for the measurements. At low concentrations the changes in R values are small and tend to increase with increasing concentration. This suggests that for 1-, 2- and 3- pentanol, the linear multimers tend to dominate. However, for 2-pentanol at $F=0.800$, $R= 5305$ ($10^{-19} \text{ m}^2/\text{V}^2$) which is the greatest among the measured values. To account for this, it is necessary to use the linear model of multimers where O of one molecule is connected to H of another by H-bond. This situation is repeated to form a chain whose "pendant" groups are the various alkyl groups of the alcohols, i.e. n-pentyl, $\text{CH}_3(\text{CH})\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2(\text{CH})\text{CH}_2\text{CH}_3$, for 1-,2-and 3-pentanol, respectively. It is likely that the unsymmetrical alkyl groups attached to the C with -OH group, interact with each other by way of the intra- and inter- chain interactions as the molecules are forced to realign by the field. Such interactions make positive contribution to the terms ΔV_{struct} . A similar contribution for 1- and 2- pentanol is expected to be smaller. For the case of t-pentanol, only measurements at high concentrations are obtained and their values are small. This information together with results from other techniques as mentioned earlier, indicates that the cyclic multimers are dominant. One of the possibilities is the cyclic trimers. However, it does not exclude other higher cyclic multimers. For the cyclic trimers, a model may be visualized by taking the chair form of a cyclohexane and replace all the six C atoms with alternating O and H atoms. Each of the three t-pentyl groups is attached to each O atom. These rings can form stacking structure as mentioned in section 5.2. To account for such a low magnitude of R, it is plausible that each stacking structure responds to the applied field as a unit with minimum disruption of the bifurcated H-

bonds. Consequently, the $\Delta V_{\text{struct.}}$ is small and the volume increase is found to be the smallest among the pentanols at the same concentrations.

TABLE 3. R values for cyclohexanol in n-heptane at 298 K

Mole Fraction (F)	R (10^{-18}) (m^2/V^2)
0.39	0.71
0.49	0.72
0.60	0.66
0.70	2.8
0.80	4.0
0.90	9.2
1.0	21

For cyclohexanol, R is positive and small and remains unchanged until $F=0.60$. This suggests that probably a similar stacking associates may be formed similar to the case of t-pentanol, except that the t-pentyl group is replaced by a bulky cyclohexyl one. At higher concentrations, R increases with increasing concentration until $F=1.0$. Such a rapid increase in R implies that a different type of associates may be formed.

5.4 Triton X-100

ED has been extended to hydrogen-bonded surfactants: Triton X-100 (regular) and Triton X-100 (reduced) [25]. Due to limited space, only the regular form of Triton X-100 (TX-100) is hereby given. From Table 4, R values may be divided into 3 groups.

TABLE 4. R values for Triton X-100 in cyclohexane at 298 K

concentration (molal)	R (10^{-18} m^2/V^2)
0.21	15
0.30	30
0.42	40
0.69	120
0.91	128
1.2	105
1.6	150
3.3	451
9.2	570
12	530

(a) From $m=0.2-0.42$, here R increases with increasing concentration. It is plausible that reverse micelles are formed in this region. When more surfactant is added, more micelles formed and led to the increase in R . This view is in agreement with QELS [26] and dye probe [27]. (b) In the region $m=0.69-1.6$, R values are greater than region (a) but their values are hardly changed. If the associates were to be of the reverse micellar type as in (a), we should have observed the increase in R with increasing concentration. It is likely that the associates change to a new type with a rod-like structure. This may be formed from a cyclic multimers, which may be stacked together similar to the t-pentanol case. As more surfactant is added, the rods are extended in a one-dimensional growth. In the presence of a field, only the $\Delta V_{\text{electro}}$ and $\Delta V_{\text{interac}}$ are the major contributions to R . So only small change in R with increasing concentration is observed, (c) From $m=3.3-12$, here R values increase from region (b) but stay more or less the same with increasing concentration. It is likely that the associates change to an inverted bilayers shape. One possibility would be the association of the $-OH$ groups in one plane with their tails perpendicular to it. The $-OH$ groups of such a plane can be realigned with $-OH$ groups of another plane. The growth can be extended in two directions (two-dimensional growth). When the field is applied the dipolar groups such as $-OH$ and $-OCH_2CH_2-$ are forced to realign and this should make a positive contribution to the ΔV_{struct} in addition to $\Delta V_{\text{electro}}$ and $\Delta V_{\text{interac}}$.

6. Conclusions

It has been shown that the new technique of ED can provide unique and valuable information on liquids. The information can be used to integrate with other nonlinear techniques such as Kerr effect and NDE in order to enhance our understanding of liquids at the molecular level. ED is particularly sensitive to H-bonded systems. It has been used to investigate simple liquids, binary mixtures and surfactants. It should also be very useful to study supramolecular assemblies [28] and polymer solutions.

7. References

1. Landau, L.D., Lifshitz, E.M. and Pitaevskii, L.P. (1984) *Electrodynamics of Continuous Media* 2nd Ed., Butterworth-Heinemann, Oxford, pp. 51-54.
2. Corson, D.R. and Lorrain, P. (1962) *Introduction to Electromagnetic fields and Waves*, Freeman San Francisco, p.117.
3. Guggenheim, E.A. (1967) *Thermodynamics*, 5th Ed., North Holland, Amsterdam, p.335.
4. Rappon, M. (1985) Electro dilatometry of simple liquids, *Chem. Phys. Lett.* **118**, 340-344.
5. Buckingham, A.D. (1976) Electric birefringence in gases and liquids, in O'Konski, C.T. (ed.), Pt I. *Molecular Electro-Optics*, Dekker, New York, pp. 27-62.
6. Kielich, S. (1972) in Dielectric and related molecular processes, Davies M.(ed.), Vol.1, The Chemical Society, London, p. 192.
7. Hellemans, L. and DeMaeyer, M. (1982) High electric field effects and permittivity changes in non-dipolar liquids, *J. Chem. Soc. Faraday Trans. II* **78**, 401-416.
8. Pohl, H.A. (1978) *Dielectrophoresis*, Cambridge University Press, Cambridge.
9. Bloembergen, N. (1982) Nonlinear optics and spectroscopy, *Rev. Mod. Phys.* **54**, 685-695.
10. Buckingham, A.D. (1964) *The Laws and Applications of Thermodynamics*, Pergamon Press, London, p.168.
11. Brevik, I. and Høy, J.S. (1988) Note on the electro-dilatometric effect, *Physica* **149A**, 206-214.

12. Borsarelli, C.D., Corti, H., Goldfarb, D. and Braslavsky, S.E. (1997) Structural volume change in photoinduced electron transfer reactions, *J. Phys. Chem. A* **101**, 7718-7724.
13. Rappon, M. and Johns, R.M. (1999) Molecular association of pentanols in n-heptane V: electrodilatometric effect, *J. Mol. Liquids* **80**, 65-76.
14. Crossley, J., Morgan, B.K. and M. Rujimethabhas (Rappon) (1979) New Kerr cell for low-temperature measurements, *Rev. Sci. Instrum.* **50**, 1400-1402.
15. Krupkowski, T., Jones, G.P. and Davies, M. (1974) Permittivity increments in non-dipolar solvents due to high electric fields, *J. Chem. Soc. Faraday Trans. II* **70**, 1348-1355.
16. Rujimethabhas (Rappon), M. and Crossley, J. (1980) Temperature dependence of electro-optic Kerr effect for liquids at 632.8 nm, *Can. J. Phys.* **58**, 1319-1325.
17. Piekara, A. (1962) Dielectric saturation and hydrogen bonding, *J. Chem. Phys.* **36**, 2145-2150.
18. Böttcher, C.J.F. (1973) *Theory of Electric Polarization*, Vol.1, Elsevier, Amsterdam, pp. 289-326.
19. Dawber, J.G., (1984) Magneto-optical rotation studies of liquid mixtures, *J. Chem. Soc. Faraday Trans. I* **80**, 2133-2144.
20. Malecki, J. (1962) Dielectric saturation in aliphatic alcohols, *J. Chem. Phys.* **36**, 2144-2145.
21. Rappon, M. and Greer, J. M. (1987) Molecular association of pentanols in n-heptane I: Temperature dependence of Kerr effect, *J. Mol. Liquids* **33**, 227-244.
22. Rappon, M. and Kaukinen, J.A. (1988) Molecular association of pentanols in n-heptane II: Viscosities as a function of temperature covering the low temperature range, *J. Mol. Liquids* **38**, 107-133.
23. Rappon, M. and Johns, R.M. (1989) Molecular association of pentanols in n-heptane III: Temperature and concentration dependence of proton NMR chemical shift of hydroxyl group, *J. Mol. Liquids* **40**, 155-179.
24. Rappon, M., Syvitski, R.T. and Ghazalli, K.M. (1994) Molecular association of pentanols in n-heptane IV: A photochromic reaction probe, *J. Mol. Liquids* **67**, 159-179.
25. Rappon, M. Electrode dilometry of Triton X-100 (reduced form), to be submitted for publication.
26. Zhu, D.-M. Feng, K.-I. and Schelly, Z.A. (1992) Reverse micelles of Triton X-100 in cyclohexane, *J. Phys. Chem.* **96**, 2382-2385.
27. Zhu, D.-M. and Schelly, Z.A. (1992) Investigation of the microenvironment in Triton X-100 reverse micelles in cyclohexane, using methyl orange as a probe, *Langmuir* **8**, 48-50.
28. Lehn, J.M. (1995) *Supramolecular Chemistry*, VCH, Weinheim

INFLUENCE OF STRONG ELECTRIC FIELD ON DIELECTRIC PERMITTIVITY OF POLYCRYSTALLINE ICE DOPED BY SMALL AMOUNTS OF NaOH

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Electric permittivity of polycrystalline ice measured at 5 MHz was found to decrease proportionally to the square of the electric field intensity. In this paper it is demonstrated that implementation of NaOH molecules in ice structure considerably increases the amplitude of the NDE increment (the difference between permittivity measured at strong and weak electric field). The obtained result confirms the Bjerrum-type model proposed previously for explanation of the observed effect.

1. Introduction

So far, many experimental and theoretical studies concerning the properties of polycrystalline and mono-crystalline ice were published [1-11]. In dielectric measurements, very pronounced dispersion of low frequency permittivity and conductivity ($f < 1$ kHz) was observed [7,12-14]. The dispersion was found to be of the Debye type and the temperature dependence of the relaxation time follows the Arrhenius formula. Explanation of the observed properties is based on the assumption of the existence of defects in the ideal ice structure. The structure and ordering of protons in crystal lattice follows the Bernal – Fowler rule [15]. Violation of this rule leads to the lattice defects: orientational (so called Bjerrum defects) and ionic defects. The Bjerrum defects are formed by rotation of water molecules, what gives one doubly “H” occupied bond ($\text{O} - \text{H} \cdots \text{H} - \text{O}$ called as “D defect”) and the vacant bond ($\text{O} \cdots \text{O}$ “L defect”). Ionic defects result from a shift of the proton between two water molecules and formation of two ions ($\text{HO} - \text{H} \cdots \text{OH}_2 \rightarrow \text{HO}^+ \cdots \text{H} - \text{OH}_2^-$). In pure ice, Bjerrum defects are much more frequent than the ionic ones, and they are supposed to be responsible for dielectric properties. However, the estimated amount of defects (10^{-7} per mole of ice [16]) cannot explain very large value of static electric permittivity of ice ($\epsilon_0 = 80$ at -10°C). It is supposed that the defects (both Bjerrum and ionic ones) can migrate over the lattice and facilitate polarization of ice samples [17]. Doping of ice produces larger number of ionic defects and enhances conductivity and permittivity [17-19] proportionally to the concentration of a dopant. The mentioned proportionality is observed for the low concentrations only. For higher concentrations ($C \geq 10^{-3}\text{N}$ in the case of ice doped by NH_3 [20]) conductivity of ice increases only slightly. It was supposed that Bjerrum and ionic defects mutually interact and form trapped ions,

which do not participate in the global current [20].

Dielectric investigations gave evidences that dielectric relaxation time in doped ice is shortened compared to that in pure ice [18,21,22]. This effect was found both in ice doped by acids (e.g. HCl, HF, HNO₃, H₂SO₄ [12,18,19]) and hydroxides (NaOH, KOH, Ca(OH)₂, LiOH [12,18,21-23]. The self – diffusion coefficient seems to be unaffected by doping and is almost this same as in pure ice [24,25].

In our previous paper [26] we presented results of measurements of non-linear dielectric effect (NDE) in polycrystalline ice. Non-linear dielectric effect (NDE) consists in measurements of the difference between electric permittivity obtained in strong (ϵ^E) and weak (ϵ^0) electric fields. In NDE experiments a sample is polarised by rectangular HV pulses of amplitudes up to 10^6 V/m and dielectric permittivity is measured by low amplitude, high frequency field ($E \cong 10^3$ V/m, $f \cong 1$ -10 MHz). The non-linear dielectric increment is defined as $\Delta\epsilon_{\text{NDE}} = \epsilon^E - \epsilon^0$. In measurements performed in polycrystalline ice we found that electric permittivity decreases when strong DC field is applied (the NDE increment is negative). The mentioned change was observed in megahertz frequencies, where most of processes responsible for the low-frequency permittivity dispersion of ice are inactive [27]. Following the same arguments as those in the model explaining dielectric dispersion, we proposed that the defects in ice structure are responsible for the negative NDE increment. Taking into account the above it seems that implementation in ice structure of molecules capable to create of defects, should increase the amplitude of the NDE increment. In this paper we demonstrate the influence of small amounts of NaOH, treated as a “dopant”, on the NDE increment in ice.

2. Experimental

The influence of a strong electric field on an electric permittivity was measured using the method described in details previously [26]. Strong electric field was applied as rectangular pulses of 2 ms duration time and amplitude up to 2 kV (electric field strength up to $4 \cdot 10^6$ V/m). Electric permittivity was measured at 6 MHz. The change of permittivity, being a result of the applied strong field pulses, was measured with the resolution of $\Delta\epsilon/\epsilon = 10^{-7}$. The scheme of capacitor used in NDE experiments is presented in *Figure 1*.

The polycrystalline ice sample, with small amounts of NaOH, was obtained by freezing the dilute solutions of NaOH. Water was doubly distilled and degassed. NaOH (pure for analysis) was used without additional purification. To obtain homogenous ice film of good quality between electrodes, the solution has to be slowly frozen and the temperature of electrodes should be a bit lower than that of surrounding solution. We found that this procedure of preparation of the ice samples gives the best repeatability of the investigated properties. However, the content of NaOH in the first part of the frozen ice could be different from the mean concentration of NaOH in solution. To obtain the correct concentration of NaOH in the investigated sample, after NDE measurements the ice film placed between electrodes was melted and the concentration of NaOH was determined on the basis of the specific conductivity.

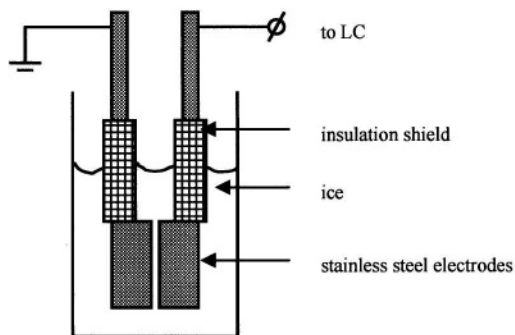


Figure 1. Scheme of the capacitor.

We found that for the largest concentrations, the contents of NaOH in the investigated ice film were approx. three times smaller than the mean concentration of the frozen solutions. Mole fractions of NaOH in the polycrystalline ice was $1.69 \cdot 10^{-6}$ to $2.04 \cdot 10^{-5}$. Stabilisation of temperature was better then 0.1K.

3. Results

Figure 2a presents an example of the dependence of electric permittivity increment versus time when rectangular HV pulses were applied. The data were obtained in an ice sample doped by $5.87 \cdot 10^{-6}$ mole fraction of NaOH. The $\Delta\epsilon_{\text{NDE}}$ increment is negative what means that permittivity of doped ice decreases when strong electric field pulses are applied. This is similar to that observed previously in pure polycrystalline ice, however, the amplitude of the effect in doped ice is much larger. We found that for small concentrations of NaOH the response is almost rectangular (as in Figure 2a) and follows the applied HV pulse. The peak appearing just after switching on the HV pulse is probably caused by the transient effects in the electronic circuit, often observed in NDE experiments when the rise of HV pulse is sufficiently fast. For high concentrations of NaOH the observed time dependence of NDE increment is different and as in example shown in Figure 1b. The NDE increment increases with time of HV pulse and permittivity of the sample after switching off the HV pulse is larger than before switching on. This difference could be a result of a polarization related to migration of Na^+ and/or OH^- ions towards electrodes. However, the purpose of the observed effect is not clear. In order to obtain the “corrected” NDE increment we used an extrapolation procedure as that presented in Figure 2b.

In measurements performed previously in pure polycrystalline ice for $T < 250$ K, a considerable delay of $\Delta\epsilon_{\text{NDE}}$ after switching on and off the HV pulse was observed [26].

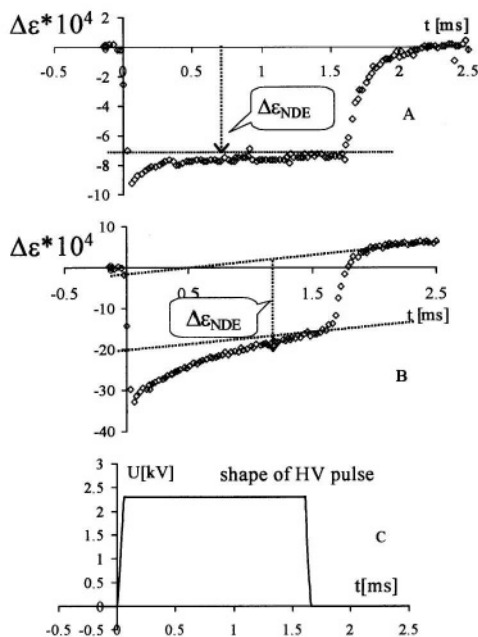


Figure 2. The NDE increment at 263K and field strength $2.6 \cdot 10^6$ V/m,
Figure 2a $x_{\text{NaOH}} = 5,87 \cdot 10^{-6}$, Figure 2b $x_{\text{NaOH}} = 1,47 \cdot 10^{-5}$

This effect was explained in terms of low-frequency relaxation already observed in ice [12]. Similar effect should be found in a doped ice, too. However, the present experiments were performed in temperatures 250 - 265 K and the delay was observed only as a short tail in the NDE answer.

According to the Debye-Langevin theory [16] NDE increment should be proportional to the square of electric field strength. This dependence is fulfilled in dipolar liquids, as well as in some solids [28,29]. In previously published data for polycrystalline ice we found that the predicted dependence is fulfilled in pure, polycrystalline ice, too. The dependence of the NDE increment versus square of electric field strength in a polycrystalline ice sample doped by $7.70 \cdot 10^{-6}$ mole fraction of NaOH is given in Figure 3. The obtained $\Delta\epsilon_{\text{NDE}}(E^2)$ is linear, confirming the expected dependence.

In the sample containing $1.47 \cdot 10^{-5}$ mole fraction of NaOH the measurements were performed in function of temperature in the range 250-265K (Figure 4). The NDE increment increases when temperature increases. Similar trend was observed in pure polycrystalline ice [26].

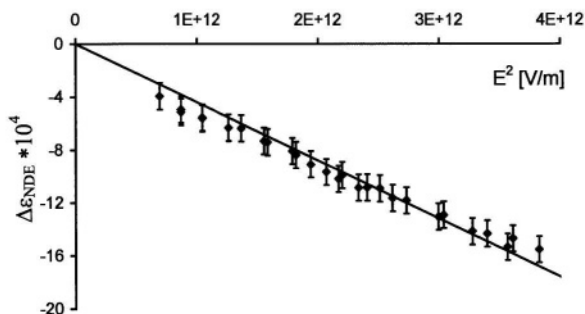


Figure 3. NDE increment versus E^2 of the ice doped by $7.70 \cdot 10^{-6}$ mole fraction of NaOH

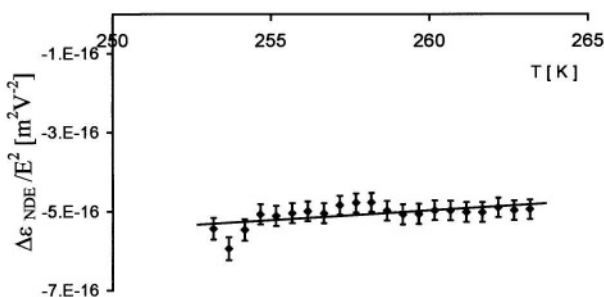


Figure 4. Temperature dependence of $\Delta\epsilon_{\text{NDE}}^\circ/E^2$ obtained in ice sample doped by $1.47 \cdot 10^{-5}$ mole fraction of NaOH.

Figure 5 presents the dependence of $\Delta\epsilon_{\text{NDE}}$ increment versus concentration of NaOH ($x_{\text{NaOH}} = 1.67 \cdot 10^{-6} \div 2.04 \cdot 10^{-5}$). When concentration of NaOH is small, $\Delta\epsilon_{\text{NDE}}$ is proportional to the mole fraction of NaOH, and the value extrapolated to the pure ice coincides with that obtained previously [26]. However, with the increase of concentration of NaOH, the $\Delta\epsilon_{\text{NDE}} = f(x_{\text{NaOH}})$ dependence seems to reach a constant value.

4. Discussion

Water molecules located close to defects in non-ideal ice structure can follow the external field much easier than those four-bounded in the ideal one. However, number of defects is rather small and is not sufficient to explain very large static electric

permittivity of ice. In Bjerrum model it is supposed that defects can migrate, what results in a stepwise polarization of crystal. Because the proposed mechanism is controlled by the diffusion of defects, it needs time, and consequently large electric permittivity is observed in low frequencies only. In high frequencies, as that used in our experiments ($f \approx 6$ MHz), only the molecules located close to defects can “answer” the external electric field perturbation.

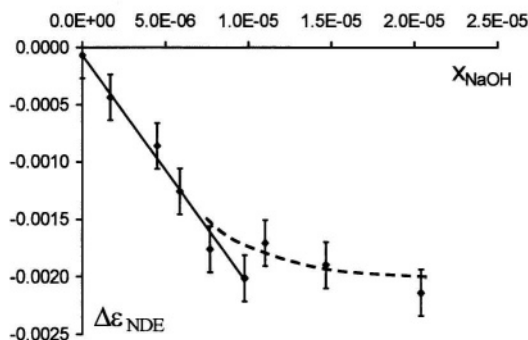


Figure 5. The NDE increment obtained at 263 K and $E = 2 \cdot 10^6$ V/m versus concentration of NaOH.

Application of strong DC field results in a stepwise polarization of the crystal. When the crystal is polarised both by DC field and by a high frequency low amplitude one, the latter influences polarisation much less than in the absence of the strong DC field. This model was used to explain the negative NDE increment in pure polycrystalline ice. It is obvious that Na^+ and OH^- ions in ice structure generate additional defects what, according to the discussed model, should increase permittivity of ice measured in the MHz region, and also it should increase the absolute value of the NDE increment. Polycrystalline ice samples were doped by small amounts of NaOH, and the number of defects is roughly proportional to the mole fraction of NaOH. The linear dependence of $\Delta\epsilon_{\text{NDE}}$ versus mole fraction of NaOH observed in lower concentrations confirms the proposed mechanism of the existence of negative NDE increment in polycrystalline ice. However, in larger concentrations the NDE increment does not decrease so fast as for low ones. When the concentration of a dopant is large, one could expect the recombination of ionic and Bjerrum defects. Consequently, the increase of NaOH concentration does not produce new centres capable to take part in polarisation at MHz frequencies.

5. Acknowledgements

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6. References

1. Cohan, N.V., Cotti, M., Iribarne, J.V., Weissmann, M. (1962) Electrostatic energies in ice and the formation of defects, *Trans. Faraday Soc.* **58**, 490-498.
2. Tsironis, G.P., Panevmatikos, S. (1989) Proton conductivity in quasi-one-dimensional hydrogen-bonded systems: Nonlinear approach, *Phys. Rev. B* **39**, 7161-7173.
3. Panevmatikos, S. (1988) Soliton dynamics of hydrogen-bonded networks: A mechanism for proton conductivity, *Phys. Rev. Lett.* **60**, 1534-1537.
4. Gränicher, H. (1958) Lattice disorder and physical properties connected with the hydrogen arrangement in ice crystals, *Proc. Roy. Soc. A* **247**, 453-461.
5. Dougherty, T.J. (1965) Electrical properties of ice. I. Dielectric relaxation in pure ice, *J. Chem. Phys.* **43**, 3247-3252.
6. Chan, R.K., Davidson, D.W., Whalley, E. (1965) Effect of pressure on the dielectric properties of ice I, *J. Chem. Phys.* **43**, 2376-2383.
7. Worz, O., Cole, R.H. (1969) Dielectric properties of ice I, *J. Chem. Phys.* **51**, 1546-1551.
8. von Hippel, A. (1971) Transfer of Protons through "pure" ice I_h Single Crystals. II. Molecular models for polarization and conduction, *J. Chem. Phys.* **54**, 145-149.
9. von Hippel, A., Knoll, D.B., Westphal, W.B. (1971) Transfer of Protons through "pure" ice I_h single crystals. I. Polarization Spectra of ice I_h , *J. Chem. Phys.* **54**, 134-144.
10. Johari, G.P. (1976) The dielectric properties of H_2O and D_2O ice I_h at MHz frequencies, *J. Chem. Phys.* **64**, 3998-4003.
11. Matsuoka, T., Fujita, S., Morishima, S., Mae, S. (1997) Precise measurement of dielectric anisotropy in ice I_h at 39 GHz, *J. Appl. Phys.* **81**, 2344-2348.
12. Auty, R.P., Cole, R.H. (1952) Dielectric properties of ice and solid D_2O , *J. Chem. Phys.* **20**, 1309-1314.
13. Evans, S. (1965) Dielectric properties of ice and snow, *J. Glaciology*, **5**, 773-792.
14. Takei, I., Maeno, N. (1997) Dielectric low-frequency dispersion and crossover phenomena of HCl-doped ice, *J. Phys. Chem. B* **101**, 6234-6236.
15. Seidensticker, R.G., Longini, R.L. (1969) Impurity effects in ice, *J. Chem. Phys.* **50**, 204-213.
16. edited by Franks, F. (1973) *Water – a Comprehensive Treatise* Vol. 2, Plenum Press New York – London.
17. Kelly, D.J., Salomon, R.E. (1969) Dielectric behavior of NaOH-doped ice, *J. Chem. Phys.* **50**, 75-79.
18. Kawada, S., Jin, R.G., Abo, M. (1997) Dielectric properties and 110K anomalies in KOH- and HCl-doped ice single crystals, *J. Phys. Chem. B* **101**, 6223-6225.
19. Matsuoka, T., Fujita, S., Mae, S. (1997) Dielectric properties of ice containing ionic impurities at microwave frequencies, *J. Phys. Chem. B* **101**, 6219-6222.
20. Arias, D., Levi, L., Lubart, L. (1966) Electrical properties of ice doped with NH_3 , *Trans. Faraday Soc.* **62**, 1955-1962.
21. Kawada, S., Dohata, H. (1985) Dielectric properties on 72K phase transition of potassium hydroxide – doped ice, *J. Phys. Soc. Jap.* **54**, 477-479.
22. Kawada, S., Shimura, K. (1986) Dielectric studies of rubidium hydroxide – doped ice and its phase transition, *J. Phys. Soc. Jap.* **55**, 4485-4491.
23. Sasaki, H., Kodera, E. (1996) Dielectric properties of $Ca(OH)_2$ -doped ice, *J. Phys. Soc. Jap.* **65**, 2343-2344.
24. Livingston, F.E., George, S.M. (2001) Diffusion kinetics of HCl hydrates in ice measured using infrared laser resonant desorption depth-profiling, *J. Phys. Chem. A* **105**, 5155-5164.
25. Camplin, G.C., Glen, J.W., Paren, J.G. (1978) Theoretical models for interpreting the dielectric behaviour of HF-doped ice, *J. Glaciology*, **21**, 123-141.
26. Szala, A., Orzechowski, K. (2001) Influence of strong electric field on dielectric permittivity of polycrystalline ice at MHz frequencies, *Chem. Phys. Lett.* **342**, 519-523.
27. Lamb, J., Turney, A. (1949) Dielectric properties of ice at 1.25 cm. wave length, *Proc. Phys. Soc. B* **62**, 272-273.
28. Orzechowski, K., Bator, G., Jakubas, R. (1992) Preliminary studies of the influence of an electric field on permittivity close to the ferroelectric-paraelectric phase transition in $(CH_3NH_3)_5Bi_2Br_{11}$ crystal, *Chem. Phys. Lett.* **199**, 325-328.
29. Orzechowski, K., Bator, G., Jakubas, R. (1995) Comparison studies of the influence of an electric field on permittivity close to ferroelectric – paraelectric phase transition in TGS, DMAC and DMABA crystals, *Ferroelectrics* **166**, 139-148.

HOST↔GUEST INTERACTION IN ACF: EPR STUDY

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Abstract. EPR measurements of ACF (host) filled with different liquids (guest) were performed in order to get information about the host↔guest interaction. Pristine ACF is characterized by single Lorentzian line recorded at $g = 2.0031$ – value which is characteristic of carbon materials. Only very weak host↔guest interaction which lead to modified EPR spectrum of pristine ACF was found. Estimation based on the theory of EPR of small particles, gives the ACF nanocrystallites size of 1.34 nm.

1. Introduction

Activated carbon fibres (ACF) are built of nanocrystallites made up of graphene sheets (approximately three). The nanocrystallites tend to align along fibers forming slit-shaped voids [1]. Spontaneous ordering of the molecules adsorbed in the voids makes the adsorbed phase a quasi-two-dimensional system. For such a system it is possible to investigate melting-freezing processes with crystal-hexatic and hexatic-liquid transitions for near-spherical molecules adsorbed in slit-shaped pores of ACF [2]. In the two-dimensional hexatic phase every particle has on average six neighbors. The occasional five-neighbored molecule is always adjacent to one with seven close contacts.

Nonlinear dielectric effect measurements for CCl_4 and aniline in ACF (pore width 1.4 nm) show divergence at the transition confirming the hexatic phase [2]. The two parameters: the ratio of fluid-pore walls interaction/fluid-fluid interactions as well as the pore sizes are mainly responsible for existence of these transitions [3]. Electron paramagnetic resonance (EPR) of ACF filled with different fluids was measured in order to find host↔guest interaction. The experiment has been thought out as a test for spontaneous ordering of the molecules captured in the nanopores system in ACF.

2. Experimental

The experiments were carried out on pristine and liquid-filled (CCl_4 , C_6H_6 and $\text{C}_6\text{H}_5\text{NO}_2$) porous ACF samples, with pores 1.4 nm wide. ACF was degassed at 10^{-5} Tr vacuum pump, and then filled with appropriate liquid.

EPR spectra were obtained using a Radiopan ES/X spectrometer equipped with Oxford Instruments gas flow helium cryostat within the temperature between $4.2 \div 300$ K. Microwave frequency was measured by microwave frequency counter with an accuracy of 5 kHz. The magnetic field was calibrated by tracking NMR magnetometer with an accuracy of 0.005 mT.

3. Results and Discussion

3.1 EPR of ACF

In order to get information about the host $\leftrightarrow$ guest interaction, EPR measurements of ACF (host) and CCl_4 , C_6H_6 and $\text{C}_6\text{H}_5\text{NO}_2$ (guests) were performed. Pristine ACF is characterized by single

Lorentzian line recorded at $g = 2.0031$ – g value which is characteristic of carbon materials (graphite $g_1 = 2.0031$ [4], nano-diamond $g = 2.0029$ [5], C_{60} fullerene $g = 2.0026$ [6]). Figure 1 shows EPR spectra for pristine ACF and ACF with adsorbed liquids. When guest molecules are adsorbed in ACF voids EPR spectrum of ACF is modified – a broader component of EPR signal appears for all studied systems. There is no EPR signal from guest molecules; no charge transfer from ACF to guest molecules – no hyperfine splitting arising from interaction with nuclear spins of H or N was observed. The strongest modification of EPR spectrum of ACF was observed for ACF with $\text{C}_6\text{H}_5\text{NO}_2$ and this system will be discussed in detail.

3.2 ACF + $\text{C}_6\text{H}_5\text{NO}_2$

EPR signal of ACF with $\text{C}_6\text{H}_5\text{NO}_2$ consists of three lines (Fig. 2 and 3). The narrow line (1) is characteristic for pristine ACF. Its g -value is equal to g_1 of graphite [4]. Its line width and g -factor are temperature independent (Fig. 3 a,b). Two broader components of the signal – lines (2) and (3) – are also connected with the nanographite structure of ACF. The line (2) originates from nanographite particles (host) surrounded by guest molecules captured in nanopores. Similarly to component (1), line width and g -factor are temperature independent. Broadening of the line (2), compared to (1), is caused by the shorter relaxation time of the more dense system. No Dysonian shape of EPR line is observed for each component. It means, that ACF crystallites size

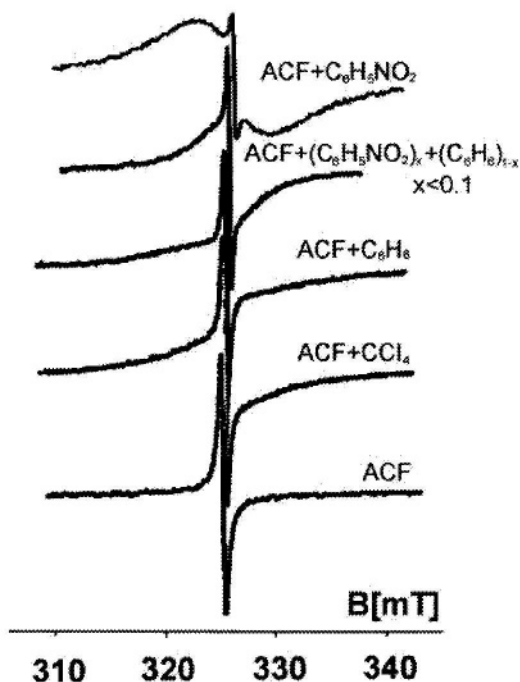


Figure 1. EPR of pristine ACF and ACF filled with different liquids.

is lower than $3.2\ \mu\text{m}$ – penetration depth of microwave field. Each of the three lines holds the Curie law (Fig.2 b, c, d). No hyperfine splitting from interaction with H or N nuclei together with the Curie law for all three components confirm the localization of paramagnetic centers within nanocrystallites of ACF.

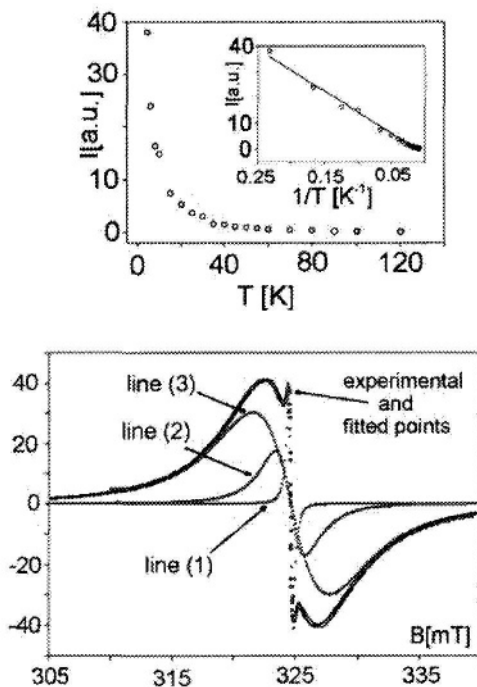


Figure 2. EPR spectrum for ACF: a) filled with nitrobenzene – fit is a sum of lines (1), (2) and (3); b) Curie law for line (1); c) Curie law for line (2); d) Curie law for line (3)

Line width and g -factor of the component (3) of observed EPR spectrum strongly depends on temperature (Fig. 3 a, b). Such a behavior one can explain as a surface effect in ACF. Stronger instabilities of paramagnetic centers at the surface of ACF or in its larger pores appear as a temperature effect. When temperature is lowered below 20 K, both, line width and g -factor reach values characteristic for graphite nanoparticles surrounded by guest molecules captured in pores.

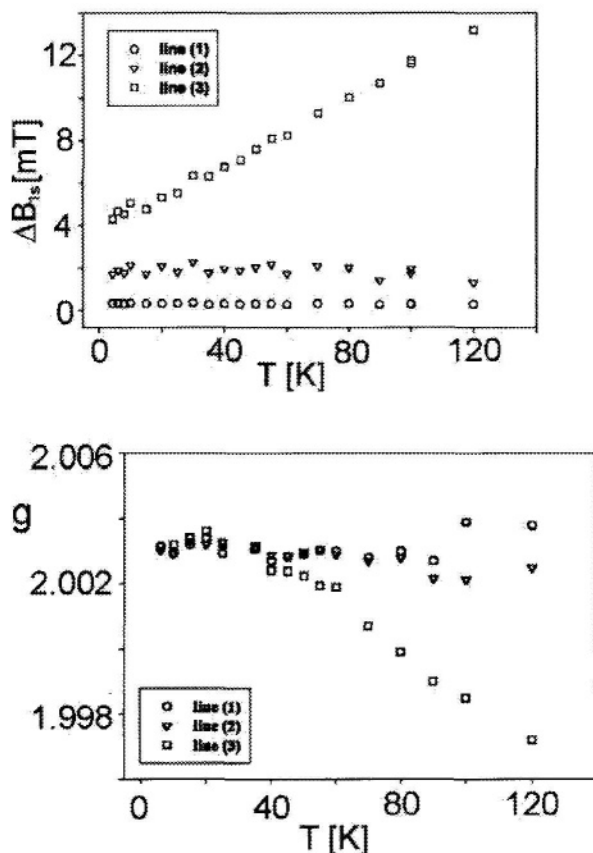


Figure 3. Temperature dependencies of: a) line width and b) g-factor.

3.3 EPR of small carbon particles

No hyperfine splitting arising from interaction of observed paramagnetic centers with nuclear spins of H or N and Curie law observed for all components of registered EPR spectrum make possible to treat ACF as a system of nanographite particles. Such approach were proposed for fullerenes [7] and UDD (ultra dispersed diamond) [5]. There are two effects modifying the electronic properties of small particles (nanoparticles) – surface effects and quantum size effects [8]. It is due to the fact that nanoparticles have discrete structure of energy levels [8,9]. There is a strong influence of the size of a nanoparticle on the g-factor value. General conclusion from the papers [8,9] is that the absolute value of the g-shift (Δg) should decrease with decreasing size of nanoparticle. The shift is described by following equation:

$$\Delta g(L) = \left[1 - \alpha \frac{a}{L} \right] \Delta g(\infty) \quad (1)$$

$\Delta g = g - g_e$

$g_e = 2.0023$ (value for free electron)

$\Delta g(L)$ – g-shift of nanoparticle

α – parameter of the order of unity

a – lattice constant 0.335 nm

L – radius of a spherical particle

$\Delta g(\infty)$ – g-shift of a bulk material

EPR measurements of paramagnetic centers localized on ACF nanocrystallites in the nitrobenzene-filled ACF show g-factor shift to lower values:

$$g_{\text{bulk}} = 2.0031$$

$$g_{\text{nanoparticle}} = 2.0029 = \overline{g_{(2)}}$$

where $\overline{g_{\text{nanoparticle}}} = \overline{g_{(2)}}$ is the mean value of g-factor of the line (2) (see Fig. 3 b).

Because of a strong temperature dependence of the width of the line (3) (Fig.3 a), which suggests that the line originates from the instabilities that may occur in large pores or the fibres' surface, only the g values of the lines (1) and (2) have been taken into account. Substituting these values to equation (1) it is possible to get the size of the cubic or spherical particles on which the paramagnetic centres are localised. This size is approximately 1.34 nm – ACF nanographite size [1].

4. Conclusions

Our EPR results suggest that the lines observed describe paramagnetic centers localized at nanocrystallites of ACF. There is no EPR signal from liquid molecules as has been observed. No hyperfine splitting arising from interaction of the EPR centers with nuclear spins of H or N and stronger modification for polar molecules of $C_6H_5NO_2$ leads to a conclusion that only very weak host-guest interaction can appear in the studied systems, and van der Waals forces are significant. This result confirms our molecular simulation results [3].

The size of nanoparticles obtained in our experiment based on the theory of EPR for small particles – 1.34 nm is in good agreement with the model for structure of ACF proposed in [1].

5. References

1. Fung, A.W. P., Wang, Z. H., Dresselhaus, M. S., Dresselhaus, G., Pekala, R. W. and Endo, M. (1994) Coulomb-gap magnetotransport in granular and porous carbon structures, *Physical Review* **B49**, 17325-17335.
2. Radhakrishnan, R., Gubbins, K. E. and Śliwińska-Bartkowiak, M. (2002) Existence of Hexatic Phase in Porous Media, *Physical Review Letters* **89**, 076101-1-4.
3. Śliwińska-Bartkowiak, M., Dudziak, G., Sikorski, R., Gras, R., Radhakrishnan, R. and Gubbins, K. E. (2001) Melting/freezing behavior of a fluid confined in porous glasses and MCM-41: Dielectric spectroscopy and molecular simulation, *Journal of Chemical Physics* **114**(2), 950-962.
4. Stankowski, J., Piekara-Sady, L., Kempański, W., Huminiecki, O. and Szczaniecki, P. B. (1997) EPR of graphite and fullerenes, *Fullerenes Science and Technology* **5**(6), 1203-1217.

5. Shames, A. I., Panich, A. M., **Kempiński, W.**, Alexenskii, A. E., Baidakova, M. V., Dideikin, A. T., Osipov, V. Y., Siklitski, V. I., Osawa, E. and Ozawa, M. (2002) Defects and impurities in nanodiamonds: EPR, NMR and TEM study, *Journal of Physics and Chemistry of Solids* **63(11)**, 1993-2001.
6. **Kempiński, W.**, Scharff, P., Stankowski, J., Piekara-Sady, L. and Trybula, Z. (1997) EPR of fullerene ions and superconductivity in K-fullerides at low doping levels, *Physica C* **274**, 232-236.
7. Stankowski, J., Piekara-Sady, L. and **Kempiński, W.** (2000) EPR of fullerene molecule-derived paramagnetic center as mesoscopic conducting object, *Applied Magnetic Resonance* **19**, 539-546.
8. Buttet, J., Car, R. and Myles, Ch.W. (1982) Size dependence of the conduction-electron-spin-resonance g shift in a small sodium particle: Orthogonalized standing-wave calculations, *Physical Review* **B26**, 2414-2431.
9. Myles, Ch. W. (1982) Shape dependence of the conduction-electron spin-resonance g shift in a small sodium particle, *Physical Review* **B26**, 2648-2651.