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Florian Scheck

Statistical Theory of Heat

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Preface

The theory of heat plays a peculiar and outstanding role in theoretical physics. Because of its general validity, it serves as a bridge between rather diverse fields such as the theory of condensed matter, elementary particle physics, astrophysics and cosmology. In its classical domain, it describes primarily averaged properties of matter, starting with systems containing a few particles, through aggregate states of ordinary matter around us, up to stellar objects, without direct recourse to the physics of their elementary constituents or building blocks. This facet of the theory carries far into the description of condensed matter in terms of classical physics. In its statistical interpretation, it encompasses the same topics and fields but reaches deeper and unifies classical statistical mechanics with quantum theory of many-body systems.

In the first chapter, I start with some basic notions of thermodynamics and introduce the empirical variables which are needed in the description of thermodynamic systems in equilibrium. Systems of this kind live on low-dimensional manifolds. The thermodynamic variables, which can be chosen in a variety of ways, are coordinates on these manifolds. Definitions of the important thermodynamical ensembles, which are guided by the boundary conditions, are illustrated by some simple examples.

The second chapter introduces various thermodynamic potentials and describes their interrelation via Legendre transformations. It deals with continuous changes of states and cyclic processes which illustrate the second and third laws of thermodynamics. It concludes with a discussion of entropy as a function of thermodynamic variables.

The third chapter is devoted to geometric aspects of thermodynamics of systems in equilibrium. In a geometric interpretation, the first and second laws of thermodynamics take a simple and transparent form. In particular, the notion of latent heat, when formulated in this framework, becomes easily understandable.

Chapter 4 collects the essential notions of the statistical theory of heat, among them *probability measures* and *states* in statistical mechanics. The latter are illustrated by the three kinds of statistics, the classical, the fermionic and the bosonic statistics. Here, the comparison between classical and quantum statistics is particularly instructive.

Chapter 5 starts off with phase mixtures and phase transitions, treated both in the framework of Gibbs' thermodynamics and with methods of statistical mechanics.

Finally, a last, long section of this chapter, as a novel feature in a textbook, discusses the problem of stability of matter. We give a heuristic discussion of an intricate analysis that was developed fairly late, about half a century after the discovery of quantum mechanics.

I am very grateful to the students whom I had the privilege to guide through their "years of apprenticeship", to my collaborators and to many colleagues for questions, comments and new ideas. Among the latter, I thank Rolf Schilling for advice. Also, I owe sincere thanks to Andrès Reyes Lega who read the whole manuscript and made numerous suggestions for improvement and enrichment of the book.

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Mainz, Germany Florian Scheck
August, 2016

Contents

Basic Notions of the Theory of Heat

1

1.1 Introduction

This chapter summarizes some basic notions of thermodynamics and defines the empirical variables which are needed for the description of thermodynamic systems in equilibrium. Empirical temperature and several scales used to measure temperature are defined. The so-called "zeroth law of thermodynamics" is formulated which says that systems which are in mutual equilibrium have the same temperature. Thermodynamic ensembles corresponding to different macroscopic boundary conditions are introduced and are illustrated by simple models such as the ideal gas. Also, entropy appears on the scene for a first time, both in its statistical and its thermodynamical interpretation. Gibb's fundamental form is introduced which describes different ways a given system exchanges energy with its environment.

1.2 First Definitions and Propositions

As a rule the theory of heat and statistical mechanics deal with *macroscopic* physical systems for which the number of degrees freedom is very large as compared to 1. A neutron star, a piece of condensed matter, a gas or a liquid, a heat reservoir in a thermodynamic cycle or a swarm of photons, contain very many elementary objects whose detailed dynamics is impossible to follow in any meaningful manner.

While at atomic and subatomic scales it seems obvious that a system like the hydrogen atom can be studied without regard to the state of the "rest of the universe", a theory of heat must be based on some postulates that must be tested by experience. In the physics at macroscopic scales boundary conditions should be experimentally realizable which define a physical system without including its environment in nature. For this reason we start with the following definitions:

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Definition 1.1 (Thermodynamic Systems)

i) A separable part of the physical universe which is defined by a set of macroscopic boundary conditions is called a *system*. It is said to be *simple* if it is *homogeneous, isotropic* and *electrically neutral*, and if boundary effects are negligible.

ii) For *closed* systems one distinguishes

   - *Materially closed systems.* These are systems in which there is no exchange of matter particles with the environment;
   - *Mechanically closed systems* are systems without exchange of work;
   - *Adiabatically closed systems* are systems which are enclosed in thermally isolating walls.

iii) A thermodynamic system is said to be *closed,* for short, if there is neither exchange of matter particles nor exchange of work with the environment, and if it is adiabatically closed.

iv) If none of these conditions is fulfilled the system is said to be an *open system.*

Up to exceptions thermodynamic systems have macroscopic dimensions and, accordingly, most observables are defined macroscopically. For example, it is impossible to determine the some 6×10^{23} or more coordinates $q_i(t)$ and momenta $p_j(t)$ of the molecules in a gas. It makes more sense, instead, to characterize the state of the gas as a whole by means of general *state variables* which are amenable to measurements in the laboratory. Variables of this kind are *pressure,* the *volume* taken by the system, *particle number* N, *energy* E, *entropy* S and many more that will be defined later in this chapter.

This book deals with *equilibrium states.* These are states which, for given stationary boundary conditions, do not change or change only adiabatically. Practical experience tells us that such states can be described by a finite number of state variables. Indeed, it will be shown that simple thermodynamic systems in equilibrium can be characterized by only three state variables. In view of the very large number of (internal) degrees of freedom of the system this may seem a surprising observation.

A thermodynamic system will generally be denoted by Σ. The set of its states is denoted by M_Σ where M stands for "manifold." Indeed, the set M_Σ is a differential manifold whose dimension is finite and which is at least of type C^1. Its dimension $f = \dim M_\Sigma$ is the number of variables, that is, the number of coordinates that are needed to describe equilibrium states of the system. The state variables, in general, are piecewise continuous, often even differentiable, real functions on M_Σ,

$$F \,:\, M_\Sigma \longrightarrow \mathbb{R}\,. \tag{1.1}$$

As an example, consider a manifold of states in equilibrium where $f = \dim M_\Sigma = 3$ and which is described by the "coordinates" E (energy), N (particle number) and V (volume). The pressure p and the temperature T of a given state on M_Σ are state variables and, hence, functions $p(E,N,V)$ and $T(E,N,V)$ on M_Σ, respectively. If, in addition, the number of particles is held fixed the manifold becomes two-dimensional, E and V are the coordinates which serve to describe M_Σ.

Of course, the reader knows that *temperature* is a global state variable which averages over irregular motions in the small and which is caused by microscopic motion of the constituents of the system. Temperature is an empirical quantity whose definition should fulfill the following expectations:

Definition 1.2 (Temperature)

i) It is possible to compare two systems and to determine whether they have the same temperature;
ii) There exists a scale for temperature which allows to compare disjoint systems;
iii) Temperature is a linear quantity;
iv) There exists an absolute temperature which refers to an origin defined by physics. This origin is reached when all motions of the constituents (classically) have ceased and are frozen. Or, according to quantum physics, when the system is reduced to a ground state of minimal motion which is just compatible with the uncertainty relation.

Remarks

i) Consider two systems Σ_1 and Σ_2, placed side by side, both of which are in states of equilibrium. Replace then the wall separating them by a diathermal baffle as sketched schematically in Fig. 1.1. After a while, by thermal balancing which is now possible, a new state of equilibrium Σ_{12} of the combined system is reached. The corresponding manifold has a dimension which is smaller than the sum of the individual systems, $\dim \Sigma_{12} < \dim \Sigma_1 + \dim \Sigma_2$. In the example there will be some exchange of energy until their sum reaches a final value $E = E_1 + E_2$. From then on the system stays on the hypersurface defined by $E = E_1 + E_2 = \text{const.}$ and depends on one degree of freedom less than before. From these considerations one concludes

Systems in equilibrium with each other have the same temperature.

ii) This assertion is often referred to as the *zeroth law of thermodynamics.*
iii) Obviously, thermal equilibrium is a transitive property: If Σ_1 and Σ_2 are in equilibrium and if the same statement applies to Σ_2 and Σ_3, then also Σ_1 and Σ_3 are in equilibrium. Symbolically this may be described as follows,

$$\Sigma_1 \sim \Sigma_2 \quad \text{and} \quad \Sigma_2 \sim \Sigma_3 \Longrightarrow \Sigma_1 \sim \Sigma_3 \; .$$

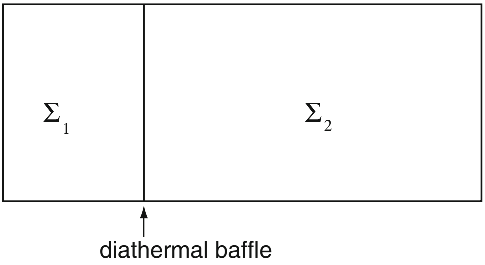

Fig. 1.1 Two initially independent systems now in thermal contact through a diathermal baffle

iv) Imagine three or more systems in equilibrium are given, $\Sigma_1, \Sigma_2, \dots, \Sigma_n$, each of which is in thermal contact with every other. After some time every pair will be in thermal equilibrium, $\Sigma_i \sim \Sigma_j$. Mathematically speaking this defines an equivalence relation $[\Sigma_i]$ of n systems, all of which can be assigned the same temperature.

Let Σ_0 be a given reference system and $z_0 \in M_{\Sigma_0}$ a state of this system. The states $z_i \in M_{\Sigma_i}$ of some other system Σ_i will be compared to the state of reference z_0. To have a concrete idea of such states one may assume, for example, z_0 and z_i to stand for the triples $z_0 = (E^{(0)}, N^{(0)}, V^{(0)})$ and $z_i = (E^{(i)}, N^{(i)}, V^{(i)})$, respectively, of energy, particle number and volume. The states $z_i \in M_{\Sigma_i}$ of a system different from Σ_0 which are in equilibrium with z_0 are points on a hypersurface in M_{Σ_i}, i.e. on a submanifold of M_{Σ_i} with codimension 1.[1] These are called *isothermals*. If one varies the choice of z_0, one obtains a set of isothermals of the kind shown in Fig. 1.2. From a mathematical point of view this yields a foliation of the manifold Σ_i.

Clearly, this comparison does not depend on the selected state z_0 of Σ_0. Furthermore, by the zeroth law of thermodynamics, the foliation of M_{Σ_i} into curves of equal temperature does not depend on the choice of reference system Σ_0.

As a first result of these simple arguments one notes that, empirically, temperature T is a state function which, by definition, takes a constant value on every isothermal but which takes different values on two distinct fibres.

Remark So far, nothing is known about the relative ordering of the values of temperature on isothermals such as those of the example Fig. 1.2. We will see that it is the first law of thermodynamics which imposes an ordering of the values of T, $T_1 < T_2 < \cdots$. Also, the scale of possible temperatures does not continue arbitrarily but is limited from below by an absolute zero. This will be seen to be a consequence of the second law of thermodynamics.

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[1] The codimension is the difference of the dimensions of the manifold and the submanifold. So if N is a submanifold of M, $N \subset M$, with dimensions $n = \dim N$ and $m = \dim M$, respectively, the codimension of N in M is $m - n$.

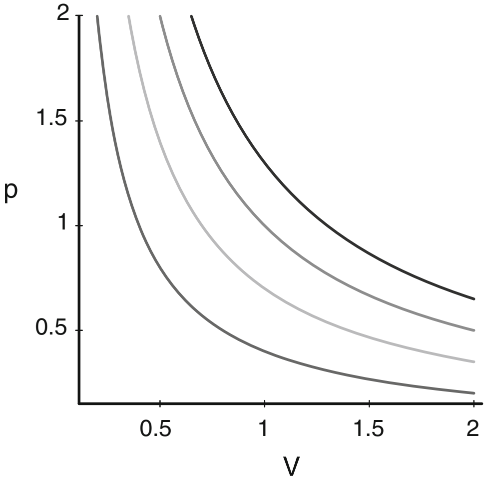

Fig. 1.2 Curves of constant temperature in a pressure and volume diagram. Here for the example of the ideal gas, see (1.31)

In the theory of heat it is particularly important to carefully distinguish *extensive* quantities from *intensive* quantities:

Definition 1.3 (Extensive and Intensive Variables) *Extensive state variables* are those which increase (decrease) additively if the size of the system is increased (decreased). *Intensive state variables* are those which remain unchanged when the system is scaled up or down in size.

Examples from mechanics are well known: The mass of an extended body as well as the inertia tensor of a rigid body are extensive quantities. If one joins two bodies of mass m_1 and m_2, respectively, the combined object has mass $m_{12} = m_1 + m_2$. The inertia tensor of a rigid body which was obtained by soldering two rigid bodies, is equal to the sum of the individual inertia tensors (see Mechanics, Sect. 3.5). Similarly, the mechanical momentum p is an extensive variable.

In contrast, the density ϱ, or the velocity field v of a swarm of particles are examples of intensive quantities. If one chooses the system bigger (or smaller) the density does not change nor does a velocity field.

In the theory of heat the volume V, the energy E, the particle number N and the entropy S are extensive variables. Upon enlarging the system they increase additively. The pressure p, the density ϱ and the temperature T, in turn, are intensive variables.

As will be seen below it is useful to group thermodynamic state variables in *energy-conjugate pairs* such as, for example,

$$(T, S)\ , \qquad (p, V)\ , \qquad (\mu_C, N)\ , \tag{1.2}$$

(with μ_C the chemical potential). They are called energy-conjugate because their product has the physical dimension (energy). The first in each pair is an *intensive* variable, while the second is an *extensive* variable.

Remark Also here there are analogues in mechanics: The pairs (v, p) and (F, x) where $F = -\nabla U$ is a conservative force field, are energy-conjugate pairs. This follows from the equation describing the change of energy when changing the momentum and shifting the position,

$$\mathrm{d}E = v \cdot \mathrm{d}p - F \cdot \mathrm{d}x \ .$$

The first quantity in each pair, v or F, respectively, is an intensive quantity while the second is an extensive quantity. Anticipating later results, note that there are also important differences: As by assumption the force is a potential force, the two terms of the mechanical example are total differentials,

$$v \cdot \mathrm{d}p = \mathrm{d}E_{\text{kin}} \quad \text{and} \quad -F \cdot \mathrm{d}x = \mathrm{d}E_{\text{pot}} \ ,$$

so that one can integrate to obtain the total energy $E = E_{\text{kin}} + E_{\text{pot}} + \text{const.}$ of the mechanical system. In thermodynamics expressions of the kind of $T\,\mathrm{d}S$ or $p\,\mathrm{d}V$ are not total differentials.

Typically, macroscopic systems of the laboratory contain some moles of a substance, i.e. some 10^{23} elementary particles. Even though the number of particles N in the system is very large and, in fact, is not known exactly, it is reasonable to assume that number to be held fixed. One distinguishes *macrostates* of the system from its *microstates,* the former being characterized by a few global variables while the latter may be thought to refer to the present states of motion of the constituent particles. Intuitively one expects a given macroscopic state to be realizable by very many, physically admissible microscopic configurations. Although it is practically impossible to observe or to measure them, for the analysis of the given macrostate it is important to be able to count the microstates, at least in principle, which are hidden in the macroscopic state. This is a task for theory, not for the art of doing experiments. As long as quantum effects are not relevant yet one can apply classical canonical mechanics. A microstate is then a point $x \in \mathbb{P}^{6N}$ in the $6N$-dimensional phase space,

$$\begin{aligned} x \equiv (q, p) &= \left(q^{(1)}, \ldots, q^{(N)}; p^{(1)}, \ldots, p^{(N)}\right) \\ &\equiv (q_1, \ldots, q_{3N}; p_1, \ldots, p_{3N}) \ . \end{aligned} \tag{1.3}$$

The number of possible microstates which yield the same macrostate is given by a *partition function* or *probability density* $\varrho(q, p)$ whose properties are described by the following definition.

Definition 1.4 (Probability Density) The probability density $\varrho(q, p)$ describes the differential probability

$$\mathrm{d}w(q, p) = \varrho(q, p)\ \mathrm{d}^{3N}q\ \mathrm{d}^{3N}p \ , \tag{1.4}$$

to find the N-particle system at time $t = t_0$ in the volume element $\mathrm{d}^{3N}q\, \mathrm{d}^{3N}p$ around the point (q, p) in phase space. It has the following properties:

i) It is normalized to unity,

$$\int \mathrm{d}^{3N}q \int \mathrm{d}^{3N}p\ \varrho(q,p) = 1\ ; \tag{1.5a}$$

ii) The statistical mean of an observable $O(q, p)$ at time $t = t_0$ is given by

$$\langle O \rangle = \int \mathrm{d}^{3N}q \int \mathrm{d}^{3N}p\ O(q,p)\varrho(q,p)\ ; \tag{1.5b}$$

iii) The time dependence of the probability density is determined by Liouville's equation,

$$\frac{\partial \varrho}{\partial t} + \{H, \varrho\} = 0\ , \quad \text{(Liouville)} \tag{1.5c}$$

with H the Hamiltonian function.

Remarks

i) Equation (1.5c) contains the Poisson bracket as defined in [Mechanics]. Thus, with $f, g : \mathbb{P} \to \mathbb{R}$ two differentiable functions one has

$$\{f, g\} = \sum_{i=1}^{3N} \left(\frac{\partial f}{\partial p_i} \frac{\partial g}{\partial q^i} - \frac{\partial f}{\partial q^i} \frac{\partial g}{\partial p_i} \right)\ . \tag{1.6}$$

ii) Liouville's equation (1.5c) states that the *orbital derivative* of the density ϱ vanishes. Remember that the orbital derivative is the derivative along solutions of the equations of motion. An easy way to see this is by introducing the compact notation

$$x = \left(q^1, \dots, q^{3N}; p_1, \dots, p_{3N}\right)^T\ , \qquad x \in \mathbb{P}\ ,$$

for points in phase space: Making use of the canonical equations $\dot{q} = \partial H/\partial p$ and $\dot{p} = -\partial H/\partial q$, or in compact notation $\dot{x} = \boldsymbol{J} H_{,x}$, where

$$\boldsymbol{J} = \begin{pmatrix} \mathbf{0} & \mathbb{1} \\ -\mathbb{1} & \mathbf{0} \end{pmatrix} \quad \text{and} \quad H_{,x} = \left(\frac{\partial H}{\partial q}, \frac{\partial H}{\partial p} \right)^T\ ,$$

the Poisson bracket of the Hamiltonian function and the density is equal to

$$\{H, \varrho\} = \sum_{i=1}^{3N} \left(\dot{q}^i \frac{\partial \varrho}{\partial q^i} + \dot{p}_i \frac{\partial \varrho}{\partial p_i} \right) \equiv \dot{x} \cdot \nabla_x \varrho(x)\ .$$

On the other hand one would calculate the orbital derivative of the density as follows

$$\frac{\mathrm{d}\varrho}{\mathrm{d}t} = \frac{\partial\varrho}{\partial t} + \dot{x} \cdot \nabla_x \varrho(x)$$

By Liouville's equation (1.5c) this derivative is equal to zero. This means that an observer co-moving with the flux in phase space sees a constant density, $\varrho(x(t), t) = \varrho(x(t_0), t_0)$.

iii) If the Hamiltonian function does not depend on time, then

$$\nabla_x \varrho = \frac{\partial\varrho}{\partial H} \nabla_x H \quad \text{and} \quad \dot{x} \cdot \nabla_x H =$$

$$(\dot{q}_1, \ldots, \dot{q}_{3N}; \dot{p}_1, \ldots \dot{p}_{3N})^T \, (-\dot{p}_1, \ldots, -\dot{p}_{3N}; \dot{q}_1, \ldots, \dot{q}_{3N}) = 0 \, ,$$

and hence

$$\dot{x} \cdot \nabla_x \varrho = 0 \quad \text{and} \quad \frac{\partial\varrho}{\partial t} = 0 \, .$$

In this case the distribution function is stationary.

iv) A closed system at rest has vanishing total momentum $P = 0$ and also vanishing total angular momentum $L = 0$. Furthermore, the energy E is a constant of the motion. By general principles of mechanics these are the only constants of the motion. Therefore, the probability density is a functional of the (autonomous) Hamiltonian function,

$$\varrho(q, p) = f\,(H(q, p)) \ .$$

On a hypersurface in phase space which is defined by a constant value of the energy E, it seems plausible that all elementary configurations have equal a priori probabilities.

v) The system is called *ergodic*[2] if in states with fixed energy the temporal mean is equal to the microcanonical mean. An orbit with fixed energy E, in the course of time, comes arbitrarily close to every point of the submanifold $E =$ const. .

The definition above refers to the notion of microcanonical ensemble. Its definition is as follows:

Definition 1.5 (Microcanonical Ensemble) Let a macroscopic state be defined by a choice of the three variables (E, N, V). The set of all microscopic states which describe this state is called a *microcanonical ensemble.*

A *microcanonical* ensemble describes an isolated system with a fixed value of the energy E.

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[2] The name is derived from $\varepsilon\rho\gamma o\nu$, work or energy, and from $o\delta o\varsigma$, the path.

As we will discuss in more detail below, a *canonical ensemble* is a system which is in thermal contact with a *heat bath* of temperature T.

Finally, a *grand canonical ensemble* is one which can exchange both temperature with a heat bath and particles with a reservoir of particles.

1.3 Microcanonical Ensemble and Ideal Gas

We noted in remark (iv) above that on every energy surface

$$\{q,p|\, H(q,p) = E\} \tag{1.7}$$

the distribution function $\varrho(q,p)$ has a constant value. As the energy E is constant, all microstates which are compatible with the macrostate characterized by that value E, have the same probability.

Let $\widetilde{\Omega}_\Delta$ be the volume in phase space which contains all states whose energy lies between $E - \Delta$ and E, with Δ denoting a small interval. In that interval $E - \Delta \le H(q,p) \le E$ one has

$$\varrho(q,p) = \begin{cases} \varrho_0 & \text{for } E - \Delta \le H \le E \\ 0 & \text{otherwise} \end{cases} ,$$

with $\varrho_0 = 1/\widetilde{\Omega}_\Delta$.

As an instructive example for a microcanonical ensemble we study the (classical) *ideal gas.* For that purpose we need a formula for the volume of the sphere, more precisely the ball, with radius R in n-dimensional space:

Volume of the ball in dimension n:
Using polar coordinates in dimension n the volume element reads

$$\mathrm{d}^n x = r^{n-1}\, \mathrm{d}r\, \mathrm{d}\phi \prod_{k=1}^{n-2} \sin^k \theta_k\, \mathrm{d}\theta_k \ . \tag{1.8a}$$

The volume of the ball D^n_R with radius R is given by

$$V_R = \frac{\pi^{n/2}}{\Gamma\left(1 + \frac{n}{2}\right)} R^n \ . \tag{1.8b}$$

The angle ϕ runs through the interval $[0, 2\pi]$, all angles θ_k are in the interval $[0, \pi]$. The formula (1.8a) which is well-known for dimensions $n = 2$ and $n = 3$, is proven by induction, see Exercise 1.1. Integrating over the interior of the ball D^n_R, one has

$$I_1 := \int_0^R \mathrm{d}r\, R^{n-1} = \frac{1}{n} R^n ,$$

while the integral over all angles

$$I_2 := \int_0^{2\pi} \mathrm{d}\phi \prod_{k=1}^{n-2} \int_0^{\pi} \mathrm{d}\theta_k (\sin\theta_k)^k$$

is calculated as follows: The integral I_2 contains a product of elementary integrals of the kind $\int_0^{\pi} \mathrm{d}\theta (\sin\theta)^k$. These, in turn, are special cases of Euler's Beta function which is defined by

$$B(a,b) := \int_0^1 \mathrm{d}t\, t^{a-1}(1-t)^{b-1} = 2\int_0^{\pi/2} (\sin\phi)^{2a-1}(\cos\phi)^{2b-1}$$

Here, the first integral is the usual definition of the Beta function. The second one is obtained from it by the substitution $t = \sin^2\phi$. The Beta function can be expressed in terms of three Gamma functions,

$$B(a,b) = \frac{\Gamma(a)\Gamma(b)}{\Gamma(a+b)} ,$$

a form which makes its symmetry in a and b obvious.

In the present case one has $a = (k+1)/2$ and $b = 1/2$. As the cosine does not appear in the integrand at all, one can readily extend the integration over θ_k to the interval $[0,\pi]$. Thus one obtains

$$I_2 = 2\pi \prod_{k=1}^{n-2} \frac{\Gamma\left(\frac{k+1}{2}\right)\Gamma\left(\frac{1}{2}\right)}{\Gamma\left(1+\frac{k}{2}\right)}$$

Inserting the Γ-functions in the product and using the value $\Gamma(1/2) = \sqrt{\pi}$, one finds

$$\begin{aligned} I_2 &= 2\pi(\sqrt{\pi})^{n-2} \frac{\Gamma(\frac{2}{2})\Gamma(\frac{3}{2})\cdots\Gamma(\frac{n-1}{2})}{\Gamma(\frac{3}{2})\Gamma(\frac{4}{2})\cdots\Gamma(\frac{n-1}{2})\Gamma(\frac{n}{2})} \\ &= \frac{2\pi^{n/2}}{\Gamma(\frac{n}{2})} . \end{aligned}$$

Thus, the volume to be calculated is

$$V_R = I_1 I_2 = \frac{2\pi^{n/2}}{n\Gamma(\frac{n}{2})} R^n = \frac{\pi^{n/2}}{\Gamma(1+\frac{n}{2})} R^n \ .$$

An alternative derivation using the proof-by-induction method is the topic of Exercise 1.2. As a test, one verifies the result (1.8b) for $n = 2$, i.e. for the case of the plane in which case one finds the surface $V_R = \pi R^2$ of the circle with radius R. Likewise, for $n = 3$, one finds the volume of the ball in $\mathbb{R}^3$ to be $V_R = (4\pi/3)R^3$.

The volume in phase space is given by the integral

$$\widetilde{\Omega}_\Delta(E, N, V) = \int_V \mathrm{d}^{3N} q \int_{E-\Delta \le H \le E} \mathrm{d}^{3N} p \ ,$$

and is calculated as follows. Every molecule of the gas must be confined to the spatial volume V. This condition is met if one chooses the Hamiltonian function accordingly, i.e.

$$H = \sum_{k=1}^{N} \frac{1}{2m} p^{(k)\,2} + U \quad \text{with} \quad \begin{cases} U = 0 & \text{inside } V \\ U = \infty & \text{at the walls} \end{cases} \ .$$

The integral over the variables q then gives a factor V^N and one writes

$$\widetilde{\Omega}_\Delta(E, N, V) = V^N \omega(E) \ , \tag{1.9a}$$

where $\omega(E)$ is the volume in the space of momenta which is contained between the two spheres with radius $R_E - \delta = \sqrt{2m(E-\Delta)}$ and $R_E = \sqrt{\sum p^{(k)\,2}} = \sqrt{2mE}$, respectively. For this calculation one applies formula (1.8b) with $\delta = \sqrt{2mE} - \sqrt{2m(E-\Delta)}$ and $n = 3N$, viz.

$$V(R_E) - V(R_E - \delta) = \frac{\pi^{3N/2} R_E^{3N}}{\Gamma\left(1 + \frac{3N}{2}\right)} \left[1 - \left(1 - \frac{1}{3N} \frac{(3N)\delta}{R_E} \right)^{3N} \right] \ .$$

Using Gauss' formula for the exponential function

$$\lim_{n\to\infty} \left(1 + \frac{x}{n} \right)^n = \mathrm{e}^x$$

one finds that the second term in square brackets, for large values of N, is approximately equal to the exponential $\exp\{-(3N)\delta/R\}$. For very large numbers of molecules this term is negligible. Geometrically, this is equivalent to the observation that the volume enclosed between the two spheres is equal to the volume of the ball, to very good approximation. Thus, one obtains the result

$$\omega(E) \simeq \frac{\pi^{3N/2}}{\Gamma\left(1+\frac{3N}{2}\right)}(2mE)^{\frac{3N}{2}} \ . \tag{1.9b}$$

The total volume in phase space $\widetilde{\Omega}_\Delta$, for large N does not depend in an essential way on Δ. It is proportional to V^N and to $E^{3N/2}$,

$$\widetilde{\Omega}_\Delta(E,N,V) \simeq \widetilde{\Omega}(E,N,V) \propto V^N (mE)^{3N/2} \ . \tag{1.9c}$$

The physical dimension of this quantity is

$$\left(\text{length}^3\right)^N \cdot (\text{momentum})^{3N} = \text{action}^{3N} \ .$$

Of course, the molecules of an ideal gas must be described by quantum mechanics, not by classical mechanics. Because of Heisenberg's uncertainty relation one certainly cannot localize any single molecule within a reference volume of the order of $\omega_0 = h^3$ where h is Planck's constant. Therefore it seems reasonable to compare the volume for N molecules as calculated above to $(\omega_0)^N$. Furthermore, in counting the admissible microstates, one must take into account the fact that the particles in the gas are indistinguishable and that states which are dynamically identical but differ only by the exchange of two particles should not be counted twice. With this in mind one defines the following dimensionless quantity,

$$\Omega(E,N,V) := \frac{1}{N!h^{3N}}\widetilde{\Omega}(E,N,V) \ , \tag{1.10}$$

with $\widetilde{\Omega}(E,N,V)$ as given in (1.9c).

We will note below in the analysis of the ideal gas, (1.17), that without the factor $N!$ in the denominator one would run into an inconsistency called Gibbs' paradox. This difficulty caused some confusion before quantum indistinguishability was discovered.

1.4 The Entropy, a First Approach

With the uncertainty relation in mind which says that it is impossible to localize a particle simultaneously in position and momentum, one subdivides the phase space $\mathbb{P}$ into elementary cells Z_i whose volume is h^{3N}. One then calculates the probability to find the microstate in a cell Z_i which is given by

$$w_i = \int_{Z_i} \mathrm{d}x \ \varrho(x) \ , \tag{1.11a}$$

with $x = (q,p)^T \in \mathbb{P}$ a point in the $6N$-dimensional phase space. This probability, for all i, has a value between 0 and 1,

$$0 \le w_i \le 1 \quad \text{for all } w_i \ . \tag{1.11b}$$

The entropy of the probability distribution is defined as follows.[3]

Definition 1.6 (Entropy) The function

$$\sigma := -\sum_i w_i \ln w_i \tag{1.12}$$

is called the entropy of the probability distribution $\varrho(q,p)$.

This is the entropy in the sense of statistical mechanics.

The essential properties of the so-defined function σ can best be understood in a model which assumes the number of cells Z_i to be finite. Numbering the cells by 1 to k we write

$$\sigma^{(k)}(w_1, w_2, \dots, w_k) = -\sum_{i=1}^{k} w_i \ln w_i \ , \tag{1.13a}$$

and note the normalization condition

$$\sum_{i=1}^{k} w_i = 1 \ . \tag{1.13b}$$

By its definition one sees that $\sigma^{(k)}(w_1, w_2, \dots, w_k)$ has the following properties:

(i) The function $\sigma^{(k)}(w_1, w_2, \dots, w_k)$ is totally symmetric in all its arguments,

$$\begin{aligned}&\sigma^{(k)}(w_1, \dots, w_i, \dots, w_j, \dots w_k)\\ &= \sigma^{(k)}(w_1, \dots, w_j, \dots, w_i, \dots w_k) \ .\end{aligned} \tag{1.14a}$$

The w_i may be interchanged arbitrarily because the function (1.13a) does not depend on how one has numbered the cells.

(ii) If one of the weights w_i is equal to 1, while all others are zero, the function $\sigma^{(k)}$ vanishes,

$$\sigma^{(k)}(w_1 = 1, 0, \dots, 0) = 0 \ . \tag{1.14b}$$

---

[3] I am using the notation w_i etc. and not $\mathfrak{p}_i$ or the like for "probability" because the w_i can also be weights by which specific states "i" are contained in the ensemble.

A state compatible with the uncertainty relation which is completely known, has entropy zero. Note that for $x \to 0$ the function $x \ln x$ is defined to be zero.

(iii) If one adds to a system originally consisting of k cells, one more cell, say cell number $k+1$, but allows only for states of the new system which do not lie in the extra cell Z_{k+1}, then the entropy does not change,

$$\sigma^{(k+1)}(w_1, \ldots, w_k, 0) = \sigma^{(k)}(w_1, w_2, \ldots, w_k) \,. \tag{1.14c}$$

(iv) If all weights are equal and, thus, by the normalization condition (1.13b) are equal to $1/k$, the entropy takes its largest value

$$\sigma^{(k)}(w_1, w_2, \ldots, w_k) \le \sigma^{(k)}\left(\frac{1}{k}, \ldots, \frac{1}{k}\right) \,. \tag{1.14d}$$

The strict "smaller than" sign holds whenever at least one of the weights is different from $1/k$.

(v) Consider two independent systems (1) and (2) which have entropies

$$\sigma_1^{(k)} = -\sum_{i=1}^{k} w_i^{(1)} \ln w_i^{(1)}$$

$$\sigma_2^{(l)} = -\sum_{j=1}^{l} w_j^{(2)} \ln w_j^{(2)} \,,$$

respectively. The probability for system (1) to lie in the domain $Z_i^{(1)}$ and at the same time, for system (2) to lie in the domain $Z_j^{(2)}$ is equal to the product $w_i^{(1)} w_j^{(2)}$. The entropy of the combined system is

$$\sigma^{(k+l)} = -\sum_{i=1}^{k}\sum_{j=1}^{l} w_i^{(1)} w_j^{(2)} \left(\ln w_i^{(1)} + \ln w_j^{(2)}\right) = \sigma_1^{(k)} + \sigma_2^{(l)} \,, \tag{1.14e}$$

where we have inserted the normalization conditions

$$\sum_{i=1}^{k} w_i^{(1)} = 1 \quad \text{and} \quad \sum_{j=1}^{l} w_j^{(2)} = 1 \,.$$

In other terms, as long as the two systems are independent of each other, their entropies are added.

While the properties (i)–(iii) and (v) are read off from the definition (1.12), and, hence, are more or less obvious, the property (iv) needs to be proven. The proof goes as follows:

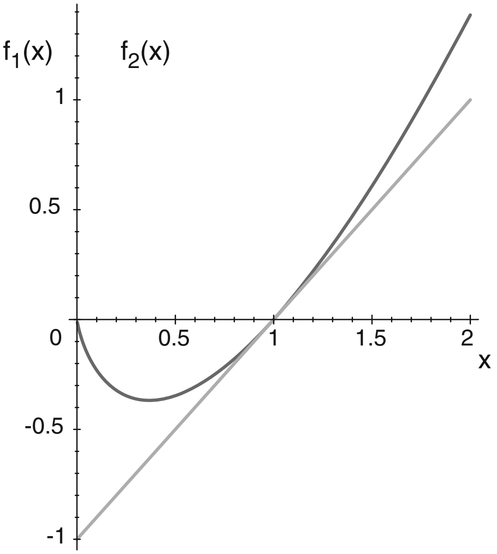

Fig. 1.3 Graphs of the functions $f_1(x) = x \ln x$ and $f_2(x) = x - 1$ with reference to the proof of property (iv) of the entropy

One studies the functions $f_1(x) = x \ln x$ and $f_2(x) = x - 1$ with real argument and shows that

$$f_1(x) \geq f_2(x) \quad \text{for all} \quad x \geq 0 \,,$$

the equal sign applying when $x = 1$, see Fig. 1.3. As the derivative is $f_1'(x) = \ln x + 1$, the function f_1 has an absolute minimum at $x_0 = \mathrm{e}^{-1}$. At this value of the argument the function f_1 has the value $f_1(x_0) = -1/\mathrm{e}$. This is larger than $f_2(x_0) = 1/\mathrm{e} - 1$ because of the numerical inequality $1 > 2/\mathrm{e} \simeq 0.73576$. For all $x \leq 1$ the derivatives fulfill the inequality $f_1'(x) \leq f_2'(x)$ the equal sign holding at $x = 1$. For all $x > 1$, in turn, one has $f_1'(x) > f_2'(x)$. The second derivative of $f_1(x)$, $f_1''(x) = 1/x$, is positive for all $x > 0$. Therefore, the function $f_1(x)$ is convex. The straight line $f_2(x)$ describes its tangent at $x = 1$ from below. This proves the asserted inequality.

This inequality, written in the form

$$-\ln x \leq \frac{1}{x} - 1 \,, \tag{1.15}$$

is applied to every individual term in (1.12),

$$\begin{aligned} &-w_i \ln w_i - \left(-w_i \ln\left(\frac{1}{k}\right)\right) = w_i \left[-\ln\left(\frac{w_i}{1/k}\right)\right] \\ &\leq w_i \left(\frac{1/k}{w_i} - 1\right) = \frac{1}{k} - w_i \;. \end{aligned}$$

After summation over all values of i the right-hand side gives zero,

$$\sum_{i=1}^{k} \frac{1}{k} - \sum_{i=1}^{k} w_i = 0 \,,$$

and one concludes

$$-\sum_{i=1}^{k} w_i \ln w_i \leq -\sum_{i=1}^{k} w_i \ln\left(\frac{1}{k}\right) = -\ln\left(\frac{1}{k}\right) = -\sum_{i=1}^{k} \frac{1}{k} \ln\left(\frac{1}{k}\right) .$$

This is the property (1.14d).

Remarks

i) The properties (i) and (ii) admit a first interpretation: $\sigma^{(k)}$ is a measure for disorder of the system. In other terms, the function $\sigma^{(k)}$ expresses our lack of knowledge of the actual state of the system. This interpretation is compatible with the properties (iii) and (iv), the latter of which says that our ignorance is greatest when all possible states of the system are equally probable.

ii) The number $\sigma^{(k)}(w_1, \ldots, w_k)$ may also be interpreted as a quantitative measure for the lack of knowledge *before* an experiment determines which of the k possibilities is realized. Alternatively, $\sigma^{(k)}$ may be understood as a gain of information if such a measurement is performed.

iii) Property (v) says that after two independent measurements the gain of information is equal to the sum of the increments of information in the two independent measurements.

Example 1.1 (Microcanonical Distribution and Ideal Gas)

Suppose a domain of phase space is defined by the requirement that it contain all energies within an interval $(E - \Delta, E)$. Assume this domain to be subdivided into k cells. For a microcanonical distribution in the sense of Definition 1.5 one has

$$w_i^{\mu\text{-can.}} = \frac{1}{k} \quad \text{and} \quad \sigma^{(k)}_{\mu\text{-can.}} = -\sum_{i=1}^{k} \frac{1}{k} \ln\left(\frac{1}{k}\right) = \ln k \,. \tag{1.16}$$

Let the (spatial) volume V contain N particles. If one made use of the result (1.9a) and (1.9b), with a size of the cells h^3, the total number of cells would be

$$k = \frac{\widetilde{\Omega}_\Delta(E, N, V)}{h^{3N}} = \frac{\pi^{3N/2}}{\Gamma(1 + 3N/2)} \left(\frac{2mE}{h^2}\right)^{3N/2} V^N = N!\Omega \,,$$

with Ω as defined in (1.10). This would lead to a formula for the entropy $\sigma^{(k)}_{\mu\text{-can.}}$ which would exhibit an inconsistency. Indeed, calculating

$$\ln k = N \ln\left(V\left(\frac{2\pi mE}{h^2}\right)^{3/2}\right) - \ln\Gamma\left(1+\frac{3N}{2}\right) ,$$

letting N become very big, and using Stirling's formula for the asymptotics at large x,

$$\ln\Gamma(x) \sim x(\ln x - 1) + \mathcal{O}(\ln x) \qquad (x \to \infty) ,$$

one obtains

$$\begin{aligned}\ln k &= N\left\{\ln V + \frac{3}{2}\ln\left(\frac{2\pi mE}{h^2}\right)\right\} - \left(1+\frac{3N}{2}\right)\left\{\ln\left(1+\frac{3N}{2}\right) - 1\right\}\\ &= N\left\{\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{4\pi mE}{3h^2N}\right) + \frac{3}{2}\right\} + N\ln N + \mathcal{O}(\ln N) .\end{aligned}$$

Keeping the volume per particle V/N and the energy per particle E/N fixed, $\sigma^{(k)}_{\mu\text{-can.}}$ should be proportional to N because entropy is an extensive quantity. However, the result obtained above contains the product $N\ln N$ in its second term which is in obvious conflict with this simple reasoning. This contradiction is known as *Gibbs' paradox.*

The paradox is resolved if instead of $\widetilde{\Omega}_\Delta$ one uses the modified function $\Omega(E, N, V)$ defined in (1.10) and if one takes account of the indistinguishability of the particles. In calculating $\ln(k/N!)$ an additional term $\ln N! = N(\ln N - 1) + \mathcal{O}(\ln N)$ is subtracted from the inconsistent result above so that one obtains

$$\begin{aligned}\sigma^{(k)}_{\mu\text{-can.}} &= \ln\Omega(E, N, V)\\ &= N\left\{\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{4\pi mE}{3h^2N}\right) + \frac{5}{2}\right\} + \mathcal{O}(\ln N) .\end{aligned} \tag{1.17}$$

This is in agreement with the additivity of entropy.

Theorem 1.1 *The entropy of a closed system is maximal if and only if the distribution of the microstates is microcanonical.*

Proof Take the difference of the microcanonical entropy and the entropy of the closed system, remembering the condition $\sum_{i=1}^{\Omega} w_i = 1$,

$$\sigma^{(k)}_{\mu\text{-can.}} - \sigma = \ln\Omega + \sum_{i=1}^{\Omega} w_i \ln w_i = \frac{1}{\Omega}\sum_{i=1}^{\Omega}(w_i\Omega)\ln(w_i\Omega) ,$$

and make use of the subsidiary condition $\sum_{i=1}^{\Omega} w_i\Omega = \Omega$. Subtracting this condition in the form of

$$\frac{1}{\Omega}\sum_{i=1}^{\Omega}(w_i\Omega - 1) = 0$$

from $\sigma^{(k)}_{\mu\text{-can.}} - \sigma$, one obtains

$$\sigma^{(k)}_{\mu\text{-can.}} - \sigma = \frac{1}{\Omega}\sum_{i=1}^{\Omega}\{(w_i\Omega)\ln(w_i\Omega) - (w_i\Omega - 1)\} \ .$$

In the expression in curly brackets the function $x\ln x$ is compared with the function $x - 1$, here with $x = w_i\Omega$. In the context of the property (iv) of the entropy, Eq. (1.14d), we showed that for positive-semidefinite x, $x \geq 0$, the inequality $x\ln x \geq x - 1$ holds true. Therefore $\sigma^{(k)}_{\mu\text{-can.}} - \sigma \geq 0$, the equal sign holding if $w_i = 1/\Omega$. This proves the theorem.

Remark In the literature it is often postulated that the entropy of the microcanonical distribution is the logarithm of the number of microstates, $S = \ln\Omega$. On the other hand it is immediately clear that after having divided the phase space into k cells, the state of equal probabilities for these cells has maximal entropy. By the formulae (1.16) and (1.17) one sees that, indeed, $\sigma^{(k)}_{\mu\text{-can.}} = \ln k = \ln\Omega$. The entropy of a microcanonical ensemble is maximal for a closed system.

1.5 Temperature, Pressure and Chemical Potential

Assume two closed systems Σ_1 and Σ_2 are given which at the start are in independent equilibrium states (E_1, N_1, V_1) and (E_2, N_2, V_2), respectively. These systems are brought to contact in various ways as follows.

1.5.1 Thermal Contact

In this case there is only exchange of energy. The volumes and particle numbers of the two individual systems remain unchanged, see Fig. 1.1. After a while, when the combined system has reached a new equilibrium state, the total energy and the total entropy are given by, respectively,

$$E = E_1 + E_2 = E_1' + E_2' \ , \tag{1.18a}$$

$$\ln\Omega_{12} = \ln\Omega_1(E_1', N_1, V_1) + \ln\Omega_2(E_2', N_2, V_2) \ . \tag{1.18b}$$

The primed state variables are the ones which are reached after the combined system has reached an equilibrium state. The maximum of $\ln \Omega_{12} = \sigma_1(E'_1) + \sigma_2(E'_2)$ is easily determined. The condition reads

$$\left[\frac{\partial \sigma_1}{\partial E_1} \mathrm{d}E_1 + \frac{\partial \sigma_2}{\partial E_2} \mathrm{d}E_2\right]_{\mathrm{d}E_1 + \mathrm{d}E_2 = 0} = 0$$

or with $\mathrm{d}E_2 = -\mathrm{d}E_1$

$$\frac{\partial \sigma_1}{\partial E_1}(E'_1, N_1, V_1) = \frac{\partial \sigma_2}{\partial E_2}(E'_2, N_2, V_2) \,. \tag{1.18c}$$

The partial derivative of σ by E, with fixed values of particle number N and volume V, defines a new state variable $\tau(E, N, V)$,

$$\frac{1}{\tau(E, N, V)} := \frac{\partial \sigma(E, N, V)}{\partial E} \,. \tag{1.19}$$

As the entropy σ as well as the energy E are *extensive* quantities the variable τ must be an *intensive* quantity. The condition (1.18c), written in a slightly different form,

$$\tau_1(E'_1, N_1, V_1) = \tau_2(E'_2 = E - E'_1, N_2, V_2) \tag{1.20}$$

says that in an equilibrium state the two systems have taken the same value of τ. Before reaching that equilibrium the infinitesimal change of entropy is given by

$$\mathrm{d}\sigma_{12} = \left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right)(\mathrm{d}E_1) > 0 \,,$$

from which follow the inequalities

$$\tau_2 > \tau_1 \;:\; \mathrm{d}E_1 > 0 \,, \quad \text{or} \quad \tau_2 < \tau_1 \;:\; \mathrm{d}E_1 < 0 \,.$$

The system with the higher value of τ transmits energy to the system with the lower value of that state variable until both systems have reached the same value of τ.

These elementary considerations suggest to interpret the variable $\tau(E, N, V)$ as a measure for the empirical temperature. It is sufficient to introduce a smooth function $f(\tau)$ which grows monotonously with τ, to gauge this function by the choice of a convention and to choose a suitable unity. The simplest such convention is certainly given by an affine form for $f^{(\mathrm{A})}(\tau) =: T^{(\mathrm{A})}$, viz.

$$T^{(\mathrm{A})} = c^{(\mathrm{A})} \cdot \tau + d^{(\mathrm{A})} \,, \tag{1.21a}$$

where the letter A symbolizes the definition, while $c^{(A)}$ and $d^{(A)}$ are dimensionful constants. Given the ansatz (1.21a) it suffices to fix two points F_1 and F_2, singled out by physics and to fix the scale by defining the unit of temperature.

For example the *Celsius scale* uses the freezing point of water under normal pressure, $F_1 = 0\,°\mathrm{C}$, as the first point of reference, and the boiling point of water, $F_2 = 100\,°\mathrm{C}$, as the second. The scaling interval is defined by $\Delta T^{(C)} = (F_2 - F_1)/100$.

The *Fahrenheit scale* which was proposed by Daniel Gabriel Fahrenheit in 1724, was originally based on the lowest temperature to which he could cool *brine* (a mixture of ice, water and salt) as the lower point of reference. In the Celsius scale the point $F_1^{(F)} = 0\,°\mathrm{F}$ lies at approximately $-17.8\,°\mathrm{C}$. For the second point of reference a value was chosen that was thought to be the normal body temperature of a person in good health, $35.6\,°\mathrm{C}$ (although this value seems a bit low), and was taken to be $F_2 = 96\,°\mathrm{F}$. The unit on the Fahrenheit scale is $(F_2 - F_1)/96$. As a rule of thumb these definitions yield the relation

$$T^{(F)} \simeq 1.8\, T^{(C)} + 32$$

between the two scales. Nowadays the Fahrenheit scale is *defined* by the relation

$$T^{(F)} = 1.8\, T^{(C)} + 32\,. \tag{1.21b}$$

It is the official temperature scale in use in the United States of America and a few other countries. The freezing point in Celsius lies at $32\,°\mathrm{F}$ in Fahrenheit, the boiling point of water lies at $212\,°\mathrm{F}$ in Fahrenheit. The two scales intersect at the point $-40\,°\mathrm{C} = -40\,°\mathrm{F}$.

There is an *absolute temperature* which, in fact, is a *thermodynamic temperature,* in the sense that it plays a distinguished role in physics. It is defined by

$$\tau = kT \tag{1.22}$$

where k is Boltzmann's constant,

$$k = 1.3806505(24) \times 10^{-23}\,\mathrm{J\,K}^{-1}\,. \tag{1.23}$$

The letter K stands for the temperature scale *Kelvin* which is defined such that the absolute zero is $F_1^{(K)} = 0\,\mathrm{K}$, while the triple point of water is $F_2^{(K)} = 273.16\,\mathrm{K}$, the subdivision of the scale being the same as in the Celsius scale. In other terms, if in (1.21a) τ is replaced by the absolute temperature then $c^{(C)} = 1$, $d^{(C)} = -273.16\,°\mathrm{C}$.

Remarks

i) As mentioned above, the origin of the Celsius scale is taken to be the freezing point of water at normal pressure, i.e. at the mean atmospheric pressure at sea level. In fact, this value is lower by 0.01 K than the triple point of water.
ii) Still another scale was in use in France, the *Réaumur scale,* officially until 1794 when it was replaced by the Celsius scale by a convention. However, in practice, it was used until about the middle of the nineteenth century. This scale differs from the Celsius scale by the choice of the boiling point of water, $F_2^{(\mathrm{R})} = 80\,^\circ\mathrm{R}$ (the melting point remaining the same) and by the scale interval $(F_2^{(\mathrm{R})} - F_1^{(\mathrm{R})})/80$.
iii) The absolute zero is a lower limit of temperature which can never be reached exactly. This fact suggests still another choice of empirical temperature. If one chose a logarithmic scale this physically singular point would be at minus infinity. Such a scale was proposed by Rudolf Plank[4] but was not adopted in practice.

Definition 1.7 (Thermodynamic Entropy) The *thermodynamic entropy* is defined as the product

$$S := k\sigma \tag{1.24}$$

where σ is the entropy (1.12) as defined in the framework of statistical mechanics, and k is Boltzmann's constant.

Remark The statistical function σ is dimensionless. Therefore, the thermodynamic entropy takes the physical dimension of the Boltzmann constant, $[S] = [k] = \mathrm{J/K}$ (energy over temperature). Furthermore, the Eq. (1.19) shows that τ has dimension energy, $[\tau] = [E]$. Hence, also kT is an energy. Given the numerical value (1.23) of Boltzmann's constant one can convert energies kT to units eV etc. One has

$$k = 8.617343(15) \times 10^{-5}\,\mathrm{eV\,K^{-1}}\ . \tag{1.25a}$$

This value follows from the conversion of mechanical units of energy to electromagnetic units,

$$1\,\mathrm{eV} = 1.60217653(14) \times 10^{-19}\,\mathrm{J}\ . \tag{1.25b}$$

For example, the *cosmic background radiation* of 2.725 K corresponds to an energy 0.2348 meV. Another example is boiling water whose temperature, $T \simeq 373\,\mathrm{K}$, corresponds to about 32 meV. A conversion formula which is equivalent to (1.25a),

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[4] Aloys Valerian Rudolf Plank, 1886–1973.

reads:

$$\text{at} \quad T = 300\,\mathrm{K} \quad \text{one has} \quad kT = \frac{1}{38.682}\mathrm{eV}\,. \tag{1.25c}$$

The definition (1.19) yields the relation between the temperature T in the Kelvin scale

$$\frac{1}{T} = \frac{\partial S}{\partial E}\,, \tag{1.26}$$

the thermodynamic entropy S and the energy E. This relation holds with particle number N and volume V fixed.

Example 1.2 (The Ideal Gas) On the basis of the formula (1.17) the entropy is given by

$$\begin{aligned} S(E,N,V) = k \ln \Omega(E,N,V) &= Nk \ln V + \frac{3}{2} Nk \ln E \\ &+ \text{ terms independent of } V \text{ and } N\,. \end{aligned} \tag{1.27}$$

The definition (1.26) leads to the important relation

$$E = \frac{3}{2} NkT\,. \tag{1.28}$$

If two ideal gases are brought to thermal contact, the entropy becomes

$$S_{12} = \frac{3k}{2}\left(N_1 \ln E_1 + N_2 \ln E_2\right) + \ldots\,,$$

where all terms were omitted which do not depend on E_1 and E_2. The entropy takes its maximum value if the condition

$$\frac{\partial S_{12}}{\partial E_1} = \frac{3k}{2}\left(\frac{N_1}{E_1} - \frac{N_2}{E_2}\right) = 0$$

is fulfilled, i.e. if

$$E_1^{(0)} = \frac{N_1}{N_1 + N_2} E\,, \qquad E_2^{(0)} = \frac{N_2}{N_1 + N_2} E\,.$$

The energies of the subsystems 1 and 2 are proportional to their particle numbers.

1.5.2 Thermal Contact and Exchange of Volume

Besides letting the temperatures of the two subsystems match we will now allow for their volumes V_1 and V_2 to adjust such that the entropy

$$S = S_1\,(E_1, N_1, V_1) + S_2\,(E_2, N_2, V_2)$$

reaches a maximum. Their total volume shall remain unchanged. The maximum is assumed under the subsidiary conditions

$$\mathrm{d}E_1 + \mathrm{d}E_2 = 0\,, \quad \mathrm{d}V_1 + \mathrm{d}V_2 = 0 \quad \text{and} \quad T_1 = T_2\,.$$

The condition which guarantees this, reads

$$\mathrm{d}S = \left(\frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2}\right)\mathrm{d}V_1 + \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2}\right)\mathrm{d}E_1 = 0\,. \tag{1.29a}$$

In the equilibrium state the temperatures are equal. Therefore, by (1.26), the second term of this equation vanishes and there remains the condition

$$\frac{\partial S_1}{\partial V_1} = \frac{\partial S_2}{\partial V_2}\,. \tag{1.29b}$$

If the volumes can adjust to each other then, in the equilibrium phase, the pressure $p(E, N, V)$ must be the same everywhere. The physical dimension of the product of entropy S and temperature T is the same as the one of the product of pressure p and volume V, $[S \cdot T] = [p \cdot V] =$ energy. This observation, the condition (1.29a) and relation (1.26) lead to a further definition:

Definition 1.8 (Pressure) The *pressure* as a state variable $p(E, N, V)$ is defined by

$$p(E, N, V) := \frac{\partial S(E, N, V)}{\partial V}\,T(E, N, V)\,, \tag{1.30}$$

i.e. as the product of the temperature and the partial derivative of the entropy by the volume.

In equilibrium the pressures in the two subsystems are equal $p_1(E_1, N_1, V_1) = p_2(E_2, N_2, V_2)$. Before reaching that state one has, e.g., $p_1 > p_2$ and therefore

$$\mathrm{d}S = \frac{1}{T}(p_1 - p_2)\,\mathrm{d}V_1 > 0 \quad \text{as well as} \quad \mathrm{d}V_1 > 0\,.$$

The subsystem "1" expands at the expense of the subsystem "2" until the same pressure is reached in both systems.

Example 1.3 (Ideal Gas) If one takes account only of the terms in formula (1.17) which depend on V, then $S(E, N, V) = k(N \ln V + \ldots)$ and

$$\frac{p}{T} = \frac{\partial S(E, N, V)}{\partial V} = \frac{kN}{V} \,.$$

Writing this somewhat differently one obtains the important relation

$$pV = kNT \tag{1.31}$$

which holds for the ideal gas. In this case the isothermals are branches of hyperbolas. This is illustrated by the example shown in Fig. 1.2.

1.5.3 Exchange of Energy and Particles

If one allows the two subsystems to exchange both energy as well as particles but keeps the *total* number of particles fixed, then the subsidiary conditions read $\mathrm{d}N_1 + \mathrm{d}N_2 = 0$, $\mathrm{d}E_1 + \mathrm{d}E_2 = 0$. The condition for the entropy to be maximal in the equilibrium state takes the form

$$\mathrm{d}S = \left(\frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2}\right) \mathrm{d}N_1 + \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2}\right) \mathrm{d}E_1 = 0 \,. \tag{1.32a}$$

As the temperatures are equal, $T_1 = T_2$, one concludes

$$\frac{\partial S_1}{\partial N_1} = \frac{\partial S_2}{\partial N_2} \,. \tag{1.32b}$$

This partial derivative defines a new state variable, the *chemical potential* $\mu_C(E, N, V)$

Definition 1.9 (Chemical Potential)

$$\mu_C(E, N, V) := -\frac{\partial S(E, N, V)}{\partial N} T(E, N, V) \,. \tag{1.32c}$$

Obviously, the condition (1.32b) says that equilibrium is reached when the chemical potentials of the two subsystems are equal,

$$\mu_C^1(E_1, N_1, V_1) = \mu_C^2(E_2, N_2, V_2) \,. \tag{1.32d}$$

The nomenclature and also the sign in (1.32c) are plausible if one realizes that the chemical potential has physical dimension of energy, $[\mu_C] = \mathrm{E}$, and that a difference in chemical potential causes a flow of particles from the subsystem with the higher chemical potential to the subsystem with the lower chemical potential. If, for example, one has $\mu_C^2 > \mu_C^1$ and $T_2 = T_1$, then

$$\mathrm{d}S = \frac{1}{T}\left(\mu_C^2 - \mu_C^1\right)\mathrm{d}N_1 > 0 \quad \text{and hence} \quad \mathrm{d}N_1 > 0\,.$$

Example 1.4 (Ideal Gas) Also in this case the new definition may be tried on the example of the ideal gas by studying the terms of the entropy (1.17) which depend on the particle number N,

$$S = kN\left\{\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{4\pi mE}{3Nh^2}\right) + \frac{5}{2}\right\} + \mathcal{O}(\ln N)\,.$$

To leading order in the particle number N it follows from the definition (1.32c)

$$\mu_C = kT\ln\left(\frac{N}{V}\right) - \frac{3}{2}kT\left(\frac{4\pi mE}{3Nh^2}\right)\,. \tag{1.33}$$

For large values of particle number the chemical potential is proportional to the logarithm of N/V.

1.6 Gibbs Fundamental Form

Given a microcanonical ensemble let $\Omega(E, N, V)$ be the volume in phase space. The state variables temperature, pressure and chemical potential can be calculated from the entropy function $S(E, N, V) = k\ln\Omega(E, N, V)$ as follows. By the definitions (1.19) and (1.26), respectively, one has $T^{-1} = \partial S/\partial E$, the definition (1.30) yields $p/T = \partial S/\partial V$, and, finally, the definition (1.32c) yields $-\mu_C/T = \partial S/\partial N$. All three equations have in common that the product $T\,\mathrm{d}S$ is expressed by the change $\mathrm{d}E$ of the energy (with N and V fixed), the change $p\,\mathrm{d}V$ (with fixed E and N) and the change $-\mu_C\,\mathrm{d}N$ (with E and V fixed). These relations can be summarized in a common one-form, i.e. as a total differential,

$$T\,\mathrm{d}S = \mathrm{d}E + p\,\mathrm{d}V - \mu_C\,\mathrm{d}N\,. \tag{1.34a}$$

Solving for the term $\mathrm{d}E$ one obtains what is called *Gibbs fundamental form*

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu_C\,\mathrm{d}N\,, \tag{1.34b}$$

which, mathematically speaking, is a one-form and whose physical interpretation is as follows: The fundamental form shows quantitatively in which ways the system can exchange energy with its neighbourhood: by a change of entropy, or of volume, or of particle number. In particular, keeping two of the state variables fixed, one obtains the conditional equations

$$T = \frac{\partial E}{\partial S} \,, \quad p = -\frac{\partial E}{\partial V} \quad \text{and} \quad \mu_C = \frac{\partial E}{\partial N} \,. \tag{1.35}$$

All three partial derivatives have an obvious interpretation.

One concludes from this summary of the definitions (1.26), (1.30) and (1.32c) that the knowledge of one of the two functions $E(S, N, V)$ *or* $S(E, N, V)$ is sufficient for the calculation of all other state variables which characterize the system in equilibrium. For this reason every such function on the manifold Σ which characterizes the system in equilibrium, is called *thermodynamic potential.*

Remarks

i) Obviously, the differential (1.34b) is a closed form, $\mathrm{d} \circ \mathrm{d}E = 0$. If, in addition, the system is closed then one has $\mathrm{d}E = 0$ which is an expression of the first law of thermodynamics. The three individual terms in (1.34b), $T\,\mathrm{d}S$, pdV and $\mu_C\,\mathrm{d}N$, in general, are no total differentials.

ii) Special cases of the formula (1.34b) are

- $\mathrm{d}S = 0$ and $\mathrm{d}V = 0$: In this case $\mathrm{d}E = \mu_C\,\mathrm{d}N$, there is exchange of chemical energy only;
- $\mathrm{d}S = 0$ and $\mathrm{d}N = 0$: In this case $\mathrm{d}E = -p\,\mathrm{d}V$, only mechanical energy is being exchanged;
- $\mathrm{d}N = 0$ and $\mathrm{d}V = 0$: In this case $\mathrm{d}E = T\,\mathrm{d}S$, there is exchange of heat only.

iii) As we mentioned in relation with (1.2) the state variables appear as *energy-conjugate pairs*,

$$(T, S) \,, \quad (p, V) \quad \text{and} \quad (\mu_C, N) \,.$$

The product of the partners in each pair has physical dimension (energy). The first variable in a pair is an *intensive* quantity, the second is an *extensive* one. (See also the remark following (1.2).)

iv) If there are more than one kind of particles in a system, Gibb's fundamental form generalizes to

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \sum_i \mu_C^i\,\mathrm{d}N_i \,, \tag{1.36}$$

where μ_C^i denotes the chemical potential for the particles of the kind "*i*".

1.7 Canonical Ensemble, Free Energy

Consider a thermodynamic system Σ_1 immersed in a heat bath Σ_0 whose temperature is T. The combined system $\Sigma = \Sigma_0 + \Sigma_1$ is taken to be closed. The energy E_0 of the heat bath is assumed to be much larger than the energy E_1 of the system Σ_1, so that the temperature T does not change appreciably if energy is taken from or is delivered to the immersed system. This model arrangement is sketched symbolically in Fig. 1.4.

As we learnt earlier it is meaningful to divide the phase space $\mathbb{P}$ of Σ_1 into cells of size h^{3N}. With $\varrho(q,p)$ denoting the classical probability density the quantum description suggests to identify microstates which lie in the same cell Z_i. This means that instead of $\varrho(q,p)$ one should better use the function

$$\bar{\varrho}_i(q,p) := \frac{1}{h^{3N}} \iint\limits_{Z_i} \mathrm{d}^{3N}q' \, \mathrm{d}^{3N}p' \; \varrho(q',p') \tag{1.37}$$

which describes the probability to find a microstate in the cell Z_i around the point $(q,p)^T \in \mathbb{P}$.

In this model the aim is to determine the probability for a microstate, as a function of the energy E_1 of the immersed system Σ_1, and of T, the temperature of the heat bath Σ_0. This probability must be proportional to the number of microstates of the surrounding system Σ_0 which have the energy $E_0 = E - E_1$, E denoting the constant total energy of the system Σ_1 and the heat bath Σ_0. By summing over all microstates of Σ_0 which meet this condition one generates the probability

$$\varrho_{\text{can.}} \propto \Omega_0(E_0 = E - E_1, N_0, V_0) \quad \text{i. e.}$$
$$\varrho_{\text{can.}} \propto \mathrm{e}^{S_0(E_0=E-E_1,N_0,V_0)/k} \, .$$

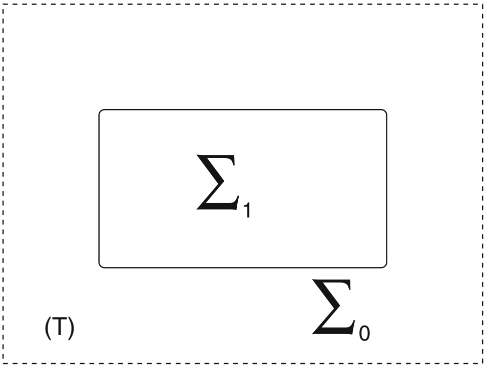

Fig. 1.4 A thermodynamic system Σ_1 is immersed in a heat bath Σ_0 whose temperature is T

As by assumption $E_1 \ll E$ the entropy S_0 can be expanded in terms of the energy variable around the total energy E,

$$S_0(E - E_1, N_0, V_0) \simeq S_0(E, N_0, V_0) - E_1 \left. \frac{\partial S_0}{\partial E_0} \right|_{E_0=E} + \frac{1}{2} E_1^2 \left. \frac{\partial^2 S_0}{\partial E_0^2} \right|_{E_0=E} .$$

In the first term on the right-hand side we have

$$\left. \frac{\partial S_0}{\partial E_0} \right|_{E} \simeq \left. \frac{\partial S_0}{\partial E_0} \right|_{E_0} = \frac{1}{T_0} \equiv \frac{1}{T} ,$$

while the second term as well as all higher terms are of order $\mathcal{O}(1/N_0)$ or smaller and, hence, are negligible. In this way one finds the probability density to be proportional to a weight factor

$$\varrho_{\text{can.}} \propto \mathrm{e}^{-E_1/kT} \equiv \mathrm{e}^{-\beta E_1} , \tag{1.38a}$$

$$\text{where} \quad \beta := \frac{1}{kT} . \tag{1.38b}$$

This quantity is called the *Boltzmann factor*. One is dealing here with the immersed system Σ_1. The heat bath only serves the purpose of defining the temperature T and to keep it constant. As one is not interested in the certainly very large number of particles in the bath, one may write N_1 simply as $N \equiv N_1$. Furthermore, one can replace the energy E_1 of Σ_1 by the Hamiltonian function $H(q, p) = E_1$, thus obtaining

$$\varrho_{\text{can.}}(q, p) = \left(N! h^{3N} Z \right)^{-1} \mathrm{e}^{-\beta H(q,p)} . \tag{1.39}$$

In this formula Z is a normalization constant which is fixed by the requirement

$$\iint \mathrm{d}^{3N} q \, \mathrm{d}^{3N} p \, \varrho_{\text{can.}}(q, p) = 1 .$$

Definition 1.10 (Partition Function) The partition function which normalizes the probability density (1.39) to 1, is given by

$$Z(\beta, N, V) = \frac{1}{N! h^{3N}} \iint \mathrm{d}^{3N} q \, \mathrm{d}^{3N} p \, \mathrm{e}^{-\beta H(q,p)} . \tag{1.40}$$

An ensemble which is in equilibrium with a heat bath of given temperature is called a *canonical ensemble*:

Definition 1.11 (Canonical Ensemble) A canonical ensemble is the set of all microstates which, for given temperature T, particle number N and volume V, arises with probability density $\varrho_{\text{can.}}(q, p)$, .

Remarks

i) Note that in a *microcanonical* ensemble all microstates which belong to the same energy, have equal probability. In contradistinction, in a *canonical* ensemble these states are weighted by the Boltzmann factor $\mathrm{e}^{-\beta H(q,p)}$, where $\beta = 1/(kT)$.

ii) The probability to find the canonical system Σ_1 with a given value E of the energy, is given by

$$\frac{1}{Z}\Omega(E,N,V)\,\mathrm{e}^{-\beta E} = \frac{1}{Z}\mathrm{e}^{-\beta E + S(E,N,V)/k} \ . \tag{1.41}$$

Here, we write E instead of E_1. The function $\Omega(E,N,V)$ is the number of states with energy E.

The energy of the systems that we dealt with up till now is also called inner energy. In contrast to this notion one also defines what is termed the *free energy* as follows:

Definition 1.12 (Free Energy) The free energy is a function of temperature, particle number and volume, and is defined by

$$F(T,N,V) := E(T,N,V) - TS(T,N,V) \tag{1.42a}$$

where

$$\frac{1}{T} = \frac{\partial S(E,N,V)}{\partial E} \ . \tag{1.42b}$$

The relevance of the specific construction in (1.42a) becomes clearer if one realizes that the free energy $F(T,N,V)$ is obtained from the entropy $S(E,N,V)$ by Legendre transformation in the variable E in favour of the variable $1/T$. We return to this construction in more detail below. Furthermore, one easily sees that the probability (1.41) to find the system Σ_1 with energy E_1, is the largest when the free energy $F(E_1,N_1,V_1)$ takes a minimum as a function of E_1. Indeed one then has

$$\frac{\mathrm{d}F}{\mathrm{d}E_1} = 1 - T\frac{\partial S}{\partial E_1} = 0 \quad \text{or}$$
$$T = \left(\frac{\partial S}{\partial E_1}\right)^{-1} = T_1 \ .$$

(Remember that T was the temperature of the heat bath while $T_1 = (\partial S/\partial E_1)^{-1}$ is the temperature of the immersed system.)

1.8 Excursion: Legendre Transformation of Convex Functions

The relation between the entropy function $S(E, N, V)$ and the free energy $F(T, N, V)$ provides an example for an important application of Legendre transformation, a method that the reader may know from mechanics. As she or he will realize, Legendre transformation is of paramount importance in thermodynamics, too, and is the key for understanding the role of thermodynamic variables. Therefore, a short summary of this concept, supplemented by a gentle generalization, may be useful here.

Let $f(x; u_1, \ldots, u_n)$ be a function which is at least C^2 in the variable x. This variable is the one with respect to which the transformation is carried out, while u_1 to u_n are "spectator variables" which move along unchanged while the original function goes over into the image function. Let

$$z := \frac{\partial f}{\partial x} \quad \text{and assume that} \quad \frac{\partial^2 f}{\partial x^2} \neq 0 \, .$$

The inverse function of $z = \partial f / \partial x$ whose existence is guaranteed by the assumption $\partial^2 f / \partial x^2 \neq 0$, is denoted by

$$x = g(z; u_1, \ldots, u_n) \; .$$

The Legendre transform of f is obtained by the following construction: Define

$$(\mathcal{L}f)\,(x) \equiv F(x, z) := x \frac{\partial f}{\partial x} - f(x; \ldots) = xz - f(x; \ldots) \, . \tag{1.43a}$$

Replacing the variable x in $F(x, z)$ by g, and the partial derivative $\partial f / \partial x$ by the function z, one obtains

$$\mathcal{L}f(z) = g(z; u_1, \ldots, u_n) z - f\left(g(z; u_1, \ldots); u_1, \ldots, u_n\right) \; . \tag{1.43b}$$

This is the Legendre transform of $f(x; u_1, \ldots, u_n)$. By the same assumption as above, $\partial^2 f / \partial x^2 \neq 0$, the inverse function exists also and is equal to the original function. Define

$$\phi(z, x) = \mathcal{L}f(z) = x(z; \ldots) z - f\left(x(\ldots); \ldots\right) \; . \tag{1.44a}$$

Then one has

$$\mathcal{L}\mathcal{L}f(z; u_1, \ldots, u_n) = z \frac{\partial \phi}{\partial z} - \phi = zx - xz + f = f(x; u_1, \ldots, u_n) \; . \tag{1.44b}$$

The Legendre transformation is bijective. In other terms, in a more formal language, if $f \to \mathcal{L}f$ is interpreted as what is called a $*$-operation, Legendre transformation is said to be *involutive.*

A geometric interpretation of Legendre transformation is obtained by comparing the graphs of the two functions $y = f(x; u_1, \dots, u_n)$ and $y = zx$ for fixed values of z. An example is shown in Fig. 1.5. According to (1.43a) the partial derivative of $F(x, z)$ by the variable x yields the inverse function $z = \partial f / \partial x$ at the point where the derivative vanishes,

$$\frac{\partial F(x, z)}{\partial x} = 0 \quad \Longrightarrow \quad z = \frac{\partial f(x; u_1, \dots, u_n)}{\partial x} .$$

For fixed value of z, this means that $x_0 = x(z)$ is the point where the two graphs have the largest vertical distance. (In the example I have chosen $f(x) = (1/2)x^2$ and $z = 1$. In this case $x_0 = x(z) = 1$.)

This construction shows that the function need not necessarily be continuously differentiable everywhere. It is sufficient to require that it be *continuous*, but only arc-wise continuously differentiable, provided it is *convex*. An example is shown in Fig. 1.6. In this case one defines the Legendre transform by means of the supremum

$$\sup_x F(x, z) = \sup_x \bigl[xz - f(x; u_1, \dots, u_n) \bigr] \tag{1.45}$$

and uses this condition to determine x as a function of z.

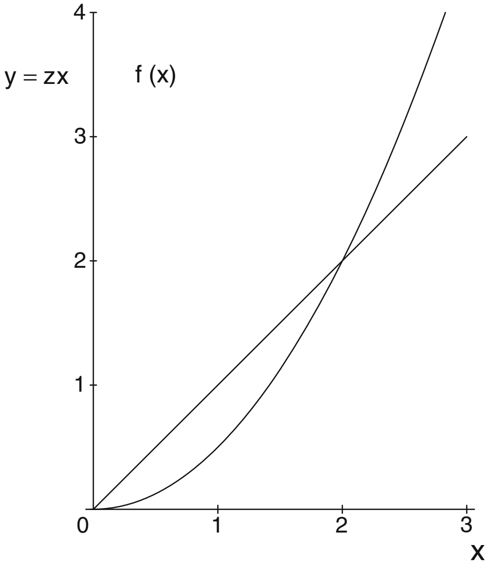

Fig. 1.5 Geometric illustration of Legendre transformation: graphs of the functions $y = f(x; \dots)$ and $y = zx$ for fixed z. The point $x_0 = x(z)$ is the value of the abscissa where the two curves have maximal vertical distance

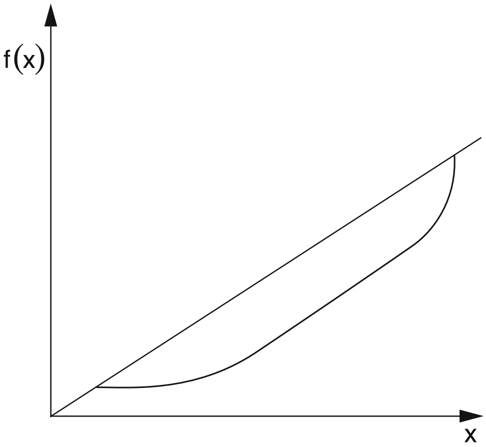

Fig. 1.6 Example of a continuous but only piecewise differentiable function whose Legendre transform is obtained from the condition (1.45)

Definition 1.13 (Convex Functions)

i) A function $f(x)$ which is continuous in the interval $x \in (x_1, x_2)$, is said to be *convex* if

$$f\big(tx_b + (1-t)x_a\big) \le tf(x_b) + (1-t)f(x_a) \tag{1.46}$$
$$\text{for all} \quad x_a, x_b \in [x_1, x_2] \quad \text{and all} \quad t \in (0,1)\,.$$

ii) If the function $f(x)$, in addition, is continuously differentiable, then the following criterion applies: For two arbitrary, non coinciding points $x_a < x_b$ in the interval (x_1, x_2) the function $f(x)$ is convex if

$$f'(x_a)(x_b - x_a) \le f(x_b) - f(x_a)\,, \tag{1.47}$$

that is to say, if the tangent of the curve $f(x)$ in the point x_a has a gradient which is smaller than or equal to the gradient of the straight line through $f(x_a)$ and $f(x_b)$.

Remarks

i) The graphs in Figs. 1.5 and 1.6 illustrate the first criterion: The right-hand side of (1.46) is the straight line joining the points $(x_1, f(x_1))$ and $(x_2, f(x_2))$ while the left-hand side is the value of the function at the point $x = tx_2 + (1-t)x_1$, with $x_1 \le x \le x_2$, which must be below the straight line.
ii) The second criterion (1.47) which applies to the case of a differentiable function, has a more strongly localized form. The equivalence to the first criterion is easily

established: Define

$$v(t) := tf(x_b) + (1-t)f(x_a) - f\bigl(tx_b + (1-t)x_a\bigr) \, ,$$
$$w(x_a, x_b) := f(x_b) - f(x_a) - f'(x_a)(x_b - x_a) \, .$$

As the function f is convex, the function v is positive-definite, $v \geq 0$, for all pairs $x_a \neq x_b$ in the interval (x_1, x_2). The derivative of $v(t)$ by t is

$$\frac{\mathrm{d}v(t)}{\mathrm{d}t} = f(x_b) - f(x_a) - \frac{\mathrm{d}f(tx_b + (1-t)x_a)}{\mathrm{d}x} \cdot (x_b - x_a) \, .$$

In particular, at the point $t = 0$ one has $\mathrm{d}v(t)/\mathrm{d}t|_{t=0} = w(x_a, x_b)$. Furthermore, v vanishes both at $t = 1$ and at $t = 0$, $v(t = 1) = 0 = v(t = 0)$. As f is convex, $v(t) \geq 0$ is positive-semidefinite in the interval $0 \leq t \leq 1$. For any choice of the pair (x_a, x_b) one concludes that, indeed, $w(x_a, x_b) = v'(0) \geq 0$.[5]

iii) In general, thermodynamic potentials will be continuous in their arguments but will not be differentiable everywhere. However, if they are convex functions—by the criterion (1.46)—then the general condition (1.45) has a unique solution so that the existence of Legendre transformation is assured.

iv) The Legendre transform of $f(x)$ [also called the function conjugate to $f(x)$] is given by

$$f^*(z; u_1, \dots, u_n) = \sup_x \bigl[xz - f(x; u_1, \dots, u_n)\bigr] \, . \tag{1.48}$$

One shows that this function is convex as well if the original f was convex. We will return to this in Sect. 5.2.1 below.

v) Clearly, these definitions and results can equally well be applied to *concave* functions. For this purpose, it is sufficient to apply a reflection to such functions so as to transform them to convexity.

Example 1.5 (Free Energy as Thermodynamic Potential) If one starts from the entropy $S(E, N, V)$ as a thermodynamic potential, while particle number and volume are spectator variables, $u_1 \equiv N$, $u_2 \equiv V$, then by solving for the variable E, using $\partial S/\partial E = 1/T$, the energy emerges as a function of temperature and of the spectators N and V, $E = E(T, N, V)$. Following the construction of Legendre transformation

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[5] For more details in the analysis of differentiable convex functions, as well as other criteria for convexity, we refer to the mathematical literature.

one obtains

$$(\mathcal{L}S)\,(E) = E\frac{\partial S}{\partial E} - S(E, N, V) \tag{1.49a}$$

$$= E(T, N, V)\frac{1}{T} - S\,(E(T, N, V), N, V) = \mathcal{L}S(T)\ . \tag{1.49b}$$

Multiplying this result by the temperature T yields the free energy (1.42a).

Example 1.6 (Free Energy of an Ideal Gas) For the case of an ideal gas in contact with a heat bath, the partition function is given by

$$Z = \frac{1}{N!h^{3N}} \iint \mathrm{d}^{3N}q\,\mathrm{d}^{3N}p\ \mathrm{e}^{-\beta\sum_{i=1}^{N} p^{(i)2}/(2m)}$$

where the q-coordinates of every particle must be integrated over the volume V, whereas the momenta must be integrated over the whole momentum space. The first group of integrations yields a factor V^N. In doing the second group of integrations one makes use of the elementary integral

$$\int_{-\infty}^{+\infty} \mathrm{d}x\ \mathrm{e}^{-x^2} = \sqrt{\pi} \quad \text{with} \quad x = p_k^{(i)}\sqrt{\frac{\beta}{2m}}\ , \quad k = 1, 2, 3\ .$$

From this one obtains

$$Z = \frac{V^N}{N!h^{3N}}\,(2\pi mkT)^{3N/2}\ . \tag{1.50}$$

The probability to find the canonical system with the value E of the energy is given by the formula (1.41). As we noted in relation with (1.42b) the free energy has a minimum at this point. Remember that the system consists of very many particles. Therefore, the probability above is very close to the value 1, i.e. one has $\mathrm{e}^{-\beta F}/Z \simeq 1$. Using the asymptotic formula $\ln N! \simeq N(\ln N - 1) + \mathcal{O}(\ln N)$ one concludes

$$\begin{aligned}
-\beta F = \ln Z &= N\left\{\ln V + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right)\right\} - \ln N! \\
&= N\left\{\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + 1\right\} + \mathcal{O}(\ln N)\ .
\end{aligned}$$

Using this, the free energy is written somewhat differently

$$F = -kTN \left\{ \ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + 1 \right\} + \mathcal{O}(\ln N)\,. \tag{1.51}$$

This formula allows to calculate the energy and the other state variables

$$\begin{aligned} \langle H \rangle &= \iint \mathrm{d}^{3N}q\,\mathrm{d}^{3N}p\ \varrho_{\text{kan.}}(q,p)H(q,p) \\ &= \frac{1}{ZN!h^{3N}} \iint \mathrm{d}^{3N}q\,\mathrm{d}^{3N}p\ H(q,p)\,\mathrm{e}^{-\beta H(q,P)} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \\ &= -\frac{\partial}{\partial \beta}\ln Z = \frac{3N}{2}\frac{1}{\beta} = \frac{3}{2}NkT\,, \end{aligned} \tag{1.52a}$$

$$p = -\frac{\partial F}{\partial V} = \frac{kTN}{V} \quad \text{oder} \quad pV = NkT\,, \tag{1.52b}$$

$$\begin{aligned} S &= -\frac{\partial F}{\partial T} = kN\left\{ \ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + \frac{5}{2} \right\} \\ &= kN\left\{ \ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{4\pi mE}{3Nh^2}\right) + \frac{5}{2} \right\}\,. \end{aligned} \tag{1.52c}$$

The last of these equations, (1.52c), coincides with (1.17). The formula (1.52a) is identical with (1.28), Eq. (1.52b) is the same as formula (1.31).

Example 1.7 (Maxwell's Velocity Distribution) Imagine a gas consisting of N identical particles of mass m which is in an equilibrium state with a heat bath of temperature T. Assume that the interaction of the particles among themselves is described by a (mechanical) potential such that the Hamiltonian function is

$$H = \sum_{i=1}^{N} \frac{p^{(i)\,2}}{2m} + U(q_1, \ldots, q_N)\,.$$

One wishes to know the probability to find an arbitrary particle of the gas, say particle number 1, with absolute value of its momentum $|p_1|$ between p and $p + \mathrm{d}p$.

The answer to this question is obtained by integration of $\varrho_{\text{can.}}$ over all variables except for the modulus $p \equiv |p_1|$ of p_1. On the basis of (1.39) and using spherical polar coordinates one finds

$$\mathrm{d}w(p) = \frac{1}{Z_1} 4\pi\,\mathrm{e}^{-\beta p^2/(2m)}\,p^2\,\mathrm{d}p\,, \tag{1.53a}$$

up to a normalization factor which must be determined such that $\int \mathrm{d}w(p) = 1$ is obtained. (The variables q_i are to be integrated over the volume V. Given the potential in the exponential function the integration $\int \mathrm{d}^{3N}q\cdots$ yields a constant.) With $x := p\sqrt{\beta/(2m)} = p(2mkT)^{-1/2}$ the normalization factor is found to be

$$\begin{aligned} Z_1 &= 4\pi \int_0^\infty p^2\,\mathrm{d}p\ \mathrm{e}^{-\beta p^2/(2m)} = \frac{4\pi(2m)^{3/2}}{\beta^{3/2}} \int_0^\infty x^2\,\mathrm{d}x\ \mathrm{e}^{-x^2} \\ &= \frac{\pi^{3/2}(2m)^{3/2}}{\beta^{3/2}} = (2\pi mkT)^{3/2}\ . \end{aligned} \tag{1.53b}$$

This result is independent of the interactions which are summarized in the (mechanical) potential $U(q_1,\ldots,q_N)$. This also applies to the mean value of the kinetic energy,

$$\begin{aligned} \left\langle p^2/(2m)\right\rangle &= \int \mathrm{d}w(p)\frac{p^2}{2m} \\ &= \frac{4\pi}{2m(2\pi mkT)^{3/2}} \int_0^\infty p^4\,\mathrm{d}p\ \mathrm{e}^{-\beta p^2/(2m)} \\ &= \frac{4\pi}{\pi^{3/2}}kT \int_0^\infty x^4\,\mathrm{d}x\ \mathrm{e}^{-x^2} = \frac{3}{2}kT\ . \end{aligned} \tag{1.53c}$$

In obtaining these formulas use was made of the integrals

$$\int_0^\infty x^2\,\mathrm{d}x\ \mathrm{e}^{-x^2} = \frac{1}{4}\sqrt{\pi} \quad \text{and} \quad \int_0^\infty x^4\,\mathrm{d}x\ \mathrm{e}^{-x^2} = \frac{3}{8}\sqrt{\pi}$$

both of which are obtained from Gauss' integral

$$\int_{-\infty}^\infty \mathrm{d}x\ \mathrm{e}^{-x^2} = \sqrt{\pi}$$

(see, e.g. Quantum Physics, Sect. 1.3.3) by partial integrations.

In the example of the ideal gas which, by definition, consists of noninteracting particles, the potential U is identically zero and the energy is

$$E = \langle H\rangle = N\frac{3}{2}kT\ .$$

Maxwell's velocity distribution is shown in Fig. 1.7 in the analytic form

$$f(x,T) = \frac{4}{\sqrt{\pi}}\left(\frac{T_0}{T}\right)^{3/2} x^2\,\mathrm{e}^{-x^2 T_0/T} \tag{1.53d}$$

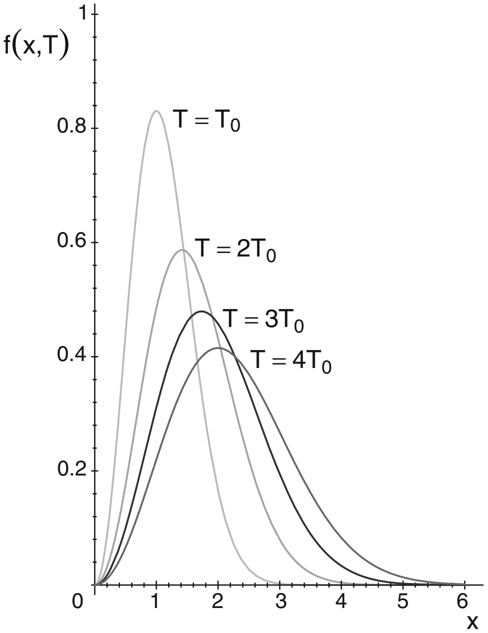


Fig. 1.7 Maxwell distribution of the modulus of the momentum of a particle in the analytic form (1.53d), for four different temperatures T_0, $2T_0$, $3T_0$ and $4T_0$

as a function of the variable $x = p(2mkT_0)^{-1/2}$ and of the ratio T/T_0 of the temperature T and some reference temperature T_0, for the cases $T = T_0$, $T = 2T_0$, $T = 3T_0$ and $T = 4T_0$. The position and height of the maximum are, respectively,

$$x_{\max}(T) = \sqrt{\frac{T}{T_0}} \quad \text{and} \quad f(x_{\max}, T) = \frac{4}{\mathrm{e}\sqrt{\pi}}\sqrt{\frac{T_0}{T}} .$$

Every distribution is normalized to 1, $\int_0^\infty \mathrm{d}x\, f(x,T) = 1$.

Remarks

i) Of course, quantum mechanics is the *correct* theoretical framework which must the basis of thermodynamics whenever microscopic or macroscopic quantum effects become important. If this is the case the Hamiltonian function H must be replaced by the Hamilton operator $\underline{H}$, the particle number N must be replaced by the operator $\underline{N}$ whose eigenvalues are the particle numbers. The variables E and N which are relevant in describing a classical macroscopic system, then are the expectation values $E = \langle \underline{H} \rangle$ of the Hamilton operator and $N = \langle \underline{N} \rangle$ of the particle number operator, respectively.

ii) In a quantum mechanical description the probability density (1.39) must be replaced by

$$\varrho_{\text{can.}}(E_n) = \frac{1}{Z} \mathrm{e}^{-\beta E_n} \quad \text{with} \quad E_n \in \text{Spec}\,(H)\,. \tag{1.54}$$

In the case of a discrete spectrum the partition function is given by

$$Z(\beta) = \sum_n \mathrm{e}^{-\beta E_n} = \mathrm{tr}\left(\mathrm{e}^{-\beta H}\right)\,. \tag{1.55}$$

As long as the interaction with the heat bath is weak these formulae may also be used in describing microscopic systems such as, e.g., individual atoms.

Thermodynamics: Classical Framework

2

2.1 Introduction

This chapter starts with a summary of the thermodynamic potentials and the relationships between them which are obtained from Legendre transformation. This is followed by an excursion to some important global properties of materials such as specific heat, expansion coefficients and others. The thermodynamic relations provide the basis for a discussion of continuous changes of state which are illustrated by the Joule-Thomson effect and the Van der Waals gas. These are models which are more realistic than the ideal gas. The discussion of Carnot cycles leads to and illustrates the second and third laws of thermodynamics. The chapter closes with a discussion of entropy as a concave function of thermodynamic variables.

2.2 Thermodynamic Potentials

The aim of this section is to become more familiar with the notion of thermodynamic potential and to develop some systematics in the various defining equations for state variables. The key in this endeavour is Legendre transformation in one variable, as introduced in the preceding section, which allows to pass from one thermodynamic potential to another one in a unique and invertible way. To start with we consider the example of the energy function $E(S, N, V)$, expressed in terms of entropy, number of particles and volume.

2.2.1 Transition to the Free Energy

Let a system in equilibrium be described by the thermodynamic potential $E(S, N, V)$ where S is the entropy, N the number of particles and V the volume. If this function

F. Scheck, *Statistical Theory of Heat*, Graduate Texts in Physics,
DOI 10.1007/978-3-319-40049-5_2

is concave (or convex) in the variable S one defines

$$T = \frac{\partial E}{\partial S} \tag{2.1a}$$

and solves this implicit equation for the entropy. By this way of proceeding the entropy becomes a function of T and of the spectator variables N and V, viz. $S(T, N, V)$. Applying now Legendre transformation (in S in favor of T) one obtains the *free energy* (also called *Helmholtz energy*)

$$-F(T, N, V) = TS(T, N, V) - E\left(S(T, N, V), N, V\right) \ , \tag{2.1b}$$

as it was defined in (1.42a). The function $F(T, N, V)$ is a new thermodynamic potential which may be used as an alternative to $E(S, N, V)$. By making use of the Gibbs fundamental form (1.34b) its total differential is given by

$$\mathrm{d}F = \mathrm{d}E - T\,\mathrm{d}S - S\,\mathrm{d}T = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu_C\,\mathrm{d}N \tag{2.1c}$$

from which follow three defining equations,

$$\frac{\partial F}{\partial T} = -S\left(E(T, N, V), N, V\right) \equiv -S(T, N, V) \ , \tag{2.2a}$$

$$\frac{\partial F}{\partial V} = -p(T, N, V) \ , \tag{2.2b}$$

$$\frac{\partial F}{\partial N} = \mu_C(T, N, V) \ . \tag{2.2c}$$

As anticipated in (1.2) the state variables come in energy conjugate pairs: the entropy S with the temperature T, the pressure p with the volume V, the chemical potential μ_C with the particle number N. The first in each of these pairs is an *intensive*, the second is an *extensive* quantity.

2.2.2 Enthalpy and Free Enthalpy

Consider now the Legendre transformation which replaces the variable V by the pressure p, and vice versa. Starting again from $E(S, N, V)$ as the thermodynamic potential, one takes the partial derivative

$$p = -\frac{\partial E(S, N, V)}{\partial V} \tag{2.3a}$$

and then solves this implicit equation for $V = V(S, N, p)$. This is possible in an invertible and unique way provided $E(S, N, V)$ is either convex or concave in the variable V. In this way one defines the *enthalpy* as follows:

Definition 2.1 (Enthalpy) Let the energy be defined as a thermodynamic potential, $E = E(S, N, V)$ and assume the implicit equation (2.3a) to be solved for the volume V. Then the *enthalpy* is defined by

$$H(S,N,p) := V(S,N,p)\,p + E\,(S,N,V(S,N,p)) \; . \tag{2.3b}$$

It is a function of the entropy, the particle number and the pressure.

The total differential of $H(S,N,p)$, that is to say, the one-form $\mathrm{d}H$, follows from the defining equation (2.3b), by inserting the Gibbs fundamental form (1.34b). It reads

$$\begin{aligned} \mathrm{d}H &= V\,\mathrm{d}p + p\,\mathrm{d}V + T\,\mathrm{d}S - p\,\mathrm{d}V + \mu_C\,\mathrm{d}N \\ &= T\,\mathrm{d}S + V\,\mathrm{d}p + \mu_C\,\mathrm{d}N \, . \end{aligned} \tag{2.3c}$$

From this expression follow the defining equations

$$\frac{\partial H}{\partial S} = T(S,N,p) \; , \tag{2.4a}$$

$$\frac{\partial H}{\partial p} = V(S,N,p) \; , \tag{2.4b}$$

$$\frac{\partial H}{\partial N} = \mu_C(S,N,p) \; . \tag{2.4c}$$

If, as an alternative, one seeks a thermodynamic potential which depends on the variables T, N and p, there are two possibilities for the choice of the Legendre transformation: Either one starts from the free energy and transforms in the variables V versus p,

$$F(T,N,V) \longrightarrow G(T,N,p) \quad \text{with} \quad p := -\frac{\partial F}{\partial V} \; , \tag{2.5a}$$

or one makes use of the enthalpy (2.3b) and transforms in S versus T,

$$H(S,N,p) \longrightarrow G(T,N,p) \quad \text{with} \quad T := -\frac{\partial H}{\partial S} \; . \tag{2.5b}$$

In either way one obtains the

Definition 2.2 (Free Enthalpy) The *free enthalpy* is a thermodynamic potential which depends on the state variables temperature T, number of particles N and pressure p;

$$G(T,N,p) := E(T,N,p) - TS + pV \; . \tag{2.5c}$$

Thereby, the potential $E(S,N,V)$ from which we started, was transformed twice such that S is replaced by T and V by p. (As a physicist, by insouciance, I am using the same function symbol!) The total differential of $G(T,N,p)$ is calculated as before by making use of the Gibbs fundamental form (1.34b) for dE

$$\begin{aligned} \mathrm{d}G &= \mathrm{d}E - T\,\mathrm{d}S - S\,\mathrm{d}T + p\,\mathrm{d}V + V\,\mathrm{d}p \\ &= -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu_C\,\mathrm{d}N\;. \end{aligned} \tag{2.5d}$$

This yields the equations

$$\frac{\partial G}{\partial T} = -S\;, \tag{2.6a}$$

$$\frac{\partial G}{\partial p} = V\;, \tag{2.6b}$$

$$\frac{\partial G}{\partial N} = \mu_C\;. \tag{2.6c}$$

In each case the remaining two variables are kept fixed.

2.2.3 Grand Canonical Potential

One further thermodynamic potential needs to be introduced if one decides to use the temperature T, the chemical potential μ_C and the volume V as the state variables. For that purpose and under the assumption that the free energy is convex (or concave) it is sufficient to perform the Legendre transformation

$$N \mapsto \mu_C \;:\; F(T,N,V) \longrightarrow K(T,\mu_C,V)$$

in which case one has

$$\mu_C = \frac{\partial F}{\partial N}\;, \tag{2.7a}$$

$$K(T,\mu_C,V) := E\,(T,N(T,\mu_C,V),V) - TS - \mu_C N\;. \tag{2.7b}$$

The first of these must be solved for N. The somewhat complicated notation of the second argument of the energy is meant to point out that the desired function $E(T,\mu_C,V)$ is obtained from $E(S,N,V)$ by a twofold transformation, viz. via $S \mapsto T$ (in the free energy) and $N \mapsto \mu_C$ (see above). As in the previous case one constructs the one-form

$$\begin{aligned} \mathrm{d}K &= (T\,\mathrm{d}S - p\,\mathrm{d}V + \mu_C\,\mathrm{d}N) - T\,\mathrm{d}S - S\,\mathrm{d}T - \mu_C\,\mathrm{d}N - N\,\mathrm{d}\mu_C \\ &= -p\,\mathrm{d}V - S\,\mathrm{d}T - N\,\mathrm{d}\mu_C\;, \end{aligned} \tag{2.7c}$$

from which one obtains the defining equations

$$\frac{\partial K}{\partial V} = -p \,, \tag{2.8a}$$

$$\frac{\partial K}{\partial T} = -S \,, \tag{2.8b}$$

$$\frac{\partial K}{\partial \mu_C} = -N \,. \tag{2.8c}$$

Thus, one is dealing here with a system for which temperature, chemical potential and volume are kept fixed while the system may exchange energy and/or particles with its environment.

One is now in a position to give a precise definition of the *grand canonical ensemble:*

Definition 2.3 (Grand Canonical Ensemble) A grand canonical ensemble is the set of all microstates in phase space which belong to the same macrostate with given temperature T, chemical potential μ_C and volume V.

Like in the case of the canonical ensemble, Sect. 1.7, we assume a thermodynamic system Σ_1 which is immersed in a large heat bath Σ_0 with energy E_0 and number of particles N_0. The temperature T_0 and the chemical potential μ_C^0 of the bath are assumed to be given. The immersed system can exchange energy and particles with the bath but the total energy as well as the total particle number are fixed. By analogy to the canonical ensemble we have

$$\begin{aligned}\varrho_{\text{grd.can.}} &\propto \Omega_2\left(E_2 = E_0 - E_1, N_2 = N_0 - N_1, V_1\right) \quad \text{i.e.} \\ \varrho_{\text{grd.can.}} &\propto \mathrm{e}^{S_2(E_2=E_0-E_1, N_2=N_0-N_1, V_1)/k} \,.\end{aligned}$$

Expanding, as before, in the variables energy and number of particles around the values E_0 and N_0, respectively,

$$S_2(E_2, N_2, V_1) \simeq S_2(E_0, N_0, V_1) - E_1 \left.\frac{\partial S_2}{\partial E_2}\right|_{E_0} - N_1 \left.\frac{\partial S_2}{\partial N_2}\right|_{N_0} \,,$$

and making use of the defining equations

$$\frac{\partial S}{\partial E} = \frac{1}{T} \quad \text{and} \quad \frac{\partial S}{\partial N} = -\frac{\mu_C}{T} \,,$$

one obtains

$$S_2(E_2, N_2, V_1) \simeq S_2(E_0, N_0, V_1) - \frac{E_1}{T_0} + \frac{N_1 \mu_C^0}{T_0} \,.$$

The probability to find the immersed system with energy E_1 and particle number N_1, is

$$\begin{aligned} w &= \frac{1}{Z}\Omega_1(E_1, N_1, V_1)\,\mathrm{e}^{-\beta(E_1-\mu_0 N_1)} \\ &= \frac{1}{Z}\,\mathrm{e}^{S(E_1,N_1,V_1)/k}\,\mathrm{e}^{-\beta(E_1-\mu_C^0 N_1)} \\ &= \frac{1}{Z}\,\mathrm{e}^{-\beta(E_1-T_0S_1-\mu_C^0 N_1)} \quad \text{where} \quad \beta = \frac{1}{kT_0}\ . \end{aligned}$$

This probability is maximal when the grand canonical ensemble (2.7b) assumes a minimum in the variables E_1 and N_1. This is the case if

$$\begin{aligned} &\frac{\partial K(E_1, \mu_C^1, V_1)}{\partial E_1} = 1 - T_0\frac{\partial S_1}{\partial E_1} = 0 \quad \text{and} \\ &\frac{\partial K}{\partial N_1} = -\mu_C^0 - T_0\frac{\partial S_1}{\partial N_1} = 0\ . \end{aligned}$$

Replacing the partial derivatives on the right-hand sides of these equations by the definitions (1.26) and (1.32c), respectively, one obtains the conditions

$$1 - \frac{T_0}{T_1} = 0 \quad \text{and} \quad -\mu_C^0 + T_0\frac{\mu_C^1}{T_1} = 0$$

and from these

$$T_1 = T_0\ , \qquad \mu_C^1 = \mu_C^0\ . \tag{2.9}$$

The immersed system takes the temperature and the chemical potential of the heat bath.

By analogy to the Definition 1.10 one defines the partition function of the grand canonical ensemble

$$Y(T, \mu_C, V) = \sum_{N=0}^{\infty} \frac{1}{N!h^{3N}} \iint \mathrm{d}^{3N}q\,\mathrm{d}^{3N}p\ \mathrm{e}^{-\beta(H(q,p)-\mu_C N)}\ , \tag{2.10}$$

thus obtaining

$$\varrho_{\text{grd.can.}}(q, p) = \frac{1}{YN!h^{3N}}\,\mathrm{e}^{-\beta(H(q,p)-\mu_C N)}\ . \tag{2.11}$$

Remarks

i) The canonical ensemble and the grand canonical ensemble may now be compared as follows:

   In a *canonical ensemble* one wishes to know the probability for the system Σ_1 to have the energy E. Since for large particle numbers there is a sharp maximum, one must have approximately

$$\frac{1}{Z}\,\mathrm{e}^{-\beta F(T,N,V)} \simeq 1 \;.$$

   From this one concludes that the partition function may be taken to be

$$Z = \mathrm{e}^{-\beta F(T,N,V)} \quad \text{or} \quad -\beta F(T,N,V) = \ln Z(T,N,V) \;, \tag{2.12}$$

   to a very good approximation.

   In a *grand canonical ensemble* one asks for the probability to find the system Σ_1 with energy E and chemical potential μ_C. Therefore, one has

$$\frac{1}{Y}\,\mathrm{e}^{-\beta K(T,\mu_C,V)} \simeq 1$$

   —again in a very good approximation—and from this

$$Y = \mathrm{e}^{-\beta K(T,\mu_C,V)} \quad \text{or} \quad -\beta K(T,\mu_C,V) = \ln Y(T,\mu_C,V) \;. \tag{2.13}$$

ii) In a quantum mechanical description the Hamiltonian function is replaced by the Hamilton operator $\underline{H}$, the particle number is replaced by the corresponding operator $\underline{N}$. In the case of a canonical ensemble one then has

$$Z = \sum_n \mathrm{e}^{-\beta E_n} = \mathrm{tr}\left(\mathrm{e}^{-\beta \underline{H}}\right) \;, \tag{2.14}$$

   where tr denotes the trace of the matrix $\mathrm{e}^{-\beta \underline{H}}$.

   Likewise, in a grand canonical ensemble, one has

$$Y = \sum_n \mathrm{e}^{-\alpha N_n - \beta E_n} = \mathrm{tr}\left(\mathrm{e}^{-\alpha \underline{N} - \beta \underline{H}}\right) = \mathrm{tr}\left(\mathrm{e}^{-\beta(\underline{H} - \mu_C \underline{N})}\right) \;. \tag{2.15}$$

   In these formulae the parameters are given by

$$\beta = \frac{1}{kT} \;, \qquad \alpha = -\frac{\mu_C}{kT} = -\beta \mu_C \;.$$

   For the sake of simplicity, for both cases it is assumed that the spectrum of the Hamilton operator is purely discrete.

iii) It depends on the macroscopic conditions imposed on the system which of the thermodynamic potentials introduced above should be used. The variables of the potentials $S(E,N,V)$, $F(T,N,V)$, $H(S,N,p)$, $G(T,N,p)$ or $K(T,\mu_C,V)$ indicate the representation that one should use. The transition between any two representations is given uniquely by Legendre transformation.

2.3 Properties of Matter

An equilibrium state of a macroscopic system is described by means of three state variables, one of which is taken from one of the energy conjugate pairs

$$(T,S)\ , \quad (p,V)\ , \quad (\mu_C,N)\ . \tag{2.16}$$

In addition, in its macroscopic behaviour, the system as a whole is characterized by certain *properties of matter* which can be measured and which are related to the thermodynamic potentials. Of specific importance are various forms of specific heat.

Definition 2.4 (Specific Heat) The specific heat is the quantity of heat $T\,\mathrm{d}S$ that must be transmitted to the system for its temperature to rise by the amount $\mathrm{d}T$. Two cases are to be distinguished:

(a) If the particle number and the volume of the system stay constant one defines

$$C_V := T\frac{\partial S(T,N,V)}{\partial T} = -T\frac{\partial^2 F(T,N,V)}{\partial T^2}\ . \tag{2.17a}$$

In the second step (2.2a) was inserted.

(b) If particle number and pressure are kept constant one defines

$$C_p := T\frac{\partial S(T,N,p)}{\partial T} = -T\frac{\partial^2 G(T,N,p)}{\partial T^2}\ . \tag{2.17b}$$

In the second step (2.6a) was used.

If N and V are kept constant then one concludes from (2.1b) and from (2.2a)

$$-S = \frac{\partial F}{\partial T} = -T - \frac{\partial S}{\partial T} + \frac{\partial E(T,N,V)}{\partial T}\ .$$

This yields

$$C_V = \frac{\partial E(T,N,V)}{\partial T}\ . \tag{2.18}$$

If, in turn, $\mathrm{d}V = 0$ and $\mathrm{d}N = 0$ are required, then Gibbs' fundamental form (1.34b) yields $\mathrm{d}E = T\,\mathrm{d}S$ so that one obtains

$$C_V = T\frac{\partial S(T,N,V)}{\partial T} \ .$$

In a similar way, for the case ($\mathrm{d}V = 0$, $\mathrm{d}p = 0$) one starts from the free enthalpy (2.5c) and calculates

$$\frac{\partial G}{\partial T} = \frac{\partial}{\partial T}(E + pV) - S - T\frac{\partial S}{\partial T} \ .$$

The left-hand side is $-S$, the third term on the right-hand side is the specific heat C_p. Thus, one obtains the relation

$$C_p = \frac{\partial}{\partial T}(E + pV) \ . \tag{2.19}$$

Further properties of matter comprise the isothermal compressibility and the isobaric expansion coefficient which are defined by, respectively,

Definition 2.5 (Isothermal Compressibility) The *isothermal compressibility* is given by

$$\kappa_T := -\frac{1}{V}\left.\frac{\partial V(T,N,p)}{\partial p}\right|_T = -\frac{1}{V}\left.\frac{\partial^2 G(T,N,p)}{\partial p^2}\right|_T \ . \tag{2.20}$$

In the second step the isothermal compressibility is expressed in terms of the free enthalpy by means of relation (2.6b).

Definition 2.6 (Isobaric Expansion Coefficient) The *isobaric expansion coefficient* (also called *coefficient of thermal expansion*) is defined by

$$\alpha := \frac{1}{V}\left.\frac{\partial V(T,N,p)}{\partial T}\right|_p = \frac{1}{V}\left.\frac{\partial^2 G(T,N,p)}{\partial p\,\partial T}\right|_p \ . \tag{2.21}$$

In the second step relation (2.6b) for the free enthalpy was used again.

Although this information is already contained in (2.20) this formula emphasizes once more that the temperature is kept constant. An analogous remark applies to (2.21) with regard to pressure.

Example 2.1 (Ideal Gas) The ideal gas provides an instructive illustration for these notions. One starts from the formulae (1.28) and (1.31) that were proven in Sect. 1.2,

$$E = \frac{3}{2}NkT \; , \qquad pV = kNT \; .$$

From (2.18) and from (2.19) one obtains the formulae

$$C_V = \frac{3}{2}Nk \; , \quad C_p = \frac{5}{2}Nk \; , \quad C_p - C_V = Nk \; . \tag{2.22a}$$

Using $V = NkT/p$ the isothermal compressibility and the isobaric expansion coefficient can readily be computed. From the definitions (2.20) and (2.21) one obtains for the ideal gas

$$\kappa_T = \frac{NkT}{Vp^2} = \frac{1}{p} \; , \quad \text{and} \quad \alpha = \frac{Nk}{Vp} = \frac{1}{T} \; , \text{ respectively.} \tag{2.22b}$$

A remarkable result is

$$\frac{TV\alpha^2}{\kappa_T} = \frac{TNkT(1/T^2)}{p(1/p)} = Nk \; ,$$

which is equal to $C_p - C_V$. Indeed, in an exercise further below we will show that this is a relation that holds more generally,

$$C_p - C_V = \frac{TV\alpha^2}{\kappa_T} \; , \tag{2.23}$$

and is not limited to the ideal gas.

Remarks

i) Customarily the specific heat is defined with respect to a mole. In this case

$$N_0 = 6.0221415(10) \times 10^{23}\,\mathrm{mol}^{-1} \; , \tag{2.24a}$$

$$R = kN_0 = 8.3144727\,\mathrm{JK}^{-1}\mathrm{mol}^{-1} \; . \tag{2.24b}$$

The first of these numbers is the Avogadro-Loschmidt number, the second is called the gas constant. The specific heats referring to a mole are denoted by lower case letters, c_V and c_p. For the example of the ideal gas one then has

$$c_V = \frac{3}{2}R \; , \quad c_p = \frac{5}{2}R \quad \text{and} \quad c_p - c_V = R \; . \tag{2.25a}$$

ii) it is instructive to calculate the volume taken by a mole of an ideal gas. One has

$$V_0 = N_0 k = 22.414 \times 10^{-3}\,\mathrm{m}^3\,\mathrm{mol}^{-1} \; .$$

This holds at the temperature $T = 273.15\,\mathrm{K}$ and at the pressure $p = 101{,}325\,\mathrm{Pa}$ (i.e. at 1 atm).

iii) In what follows we will use the notation c_V, c_p and V_0, respectively. For the ideal gas the relations (1.28) and (1.31) then read

$$E = \frac{3}{2}RT \quad \text{and} \quad pV_0 = RT\ . \tag{2.25b}$$

2.4 A Few Thermodynamic Relations

To start with we add still another definition which complements the Definition 2.5: Instead of the temperature one may equally well require the entropy to be constant. This requirement leads to what is called the *adiabatic compressibility*

$$\kappa_S = -\frac{1}{V}\left.\frac{\partial V(T,N,p)}{\partial p}\right|_S\ . \tag{2.26}$$

As a first résumé the description of thermodynamical systems in equilibrium may be described as shown in Table 2.1:

Table 2.1 Important ensembles of thermodynamics

Ensemble	Potential
Microcanonical	$S(E,N,V) = k\ln\Omega(E,N,V)$
Canonical	$F(T,N,V) = -kT\ln Z(T,N,V)$
Grand canonical	$K(T,\mu_C,V) = -kT\ln Y(T,\mu_C,V)$

The function Ω for the microcanonical ensemble is defined in (1.10); the partition function Z of the canonical ensemble is defined in (1.40); the partition function for the grand canonical ensemble is defined in (2.10). The thermodynamic potentials, the relevant state variables, the Gibbs fundamental form and its analogues are listed in the overview given in Table 2.2:

Table 2.2 Thermodynamic potentials: energy E, free energy F, enthalpy H, free enthalpy G and grand canonical potential K

Potential	Variables	Differential relation
E	(S,N,V)	$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu_C\,\mathrm{d}N$
$F = E - TS$	(T,N,V)	$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu_C\,\mathrm{d}N$
$H = E + pV$	(S,N,p)	$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \mu_C\,\mathrm{d}N$
$G = E - TS + pV$	(T,N,p)	$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu_C\,\mathrm{d}N$
$K = E - TS - \mu_C N$	(T,μ_C,V)	$\mathrm{d}K = -S\,\mathrm{d}T - p\,\mathrm{d}V - N\,\mathrm{d}\mu_C$

All of the matter properties (2.17a), (2.17b), (2.20), (2.21) and (2.26) are proportional to partial derivatives by the state variables pressure, temperature and volume. Furthermore, there are relations via thermodynamic potentials such as, for example,

$$\left(\frac{\partial S}{\partial p}\right)\bigg|_T = -\frac{\partial^2 G}{\partial p \partial T} = -\left(\frac{\partial V}{\partial T}\right)\bigg|_p ,$$

which follows from the Definition 2.2, (2.5c). For example, making use of the Jacobian for two functions of two variables,

$$\begin{aligned}\frac{\partial\left(u(x,y), v(x,y)\right)}{\partial(x,y)} &= \det\begin{pmatrix}\partial u/\partial x & \partial u/\partial y\\ \partial v/\partial x & \partial v/\partial y\end{pmatrix}\\ &= \frac{\partial u(x,y)}{\partial x}\frac{\partial v(x,y)}{\partial y} - \frac{\partial u(x,y)}{\partial y}\frac{\partial v(x,y)}{\partial x} ,\end{aligned} \tag{2.27}$$

the specific heats may be written as follows

$$c_p = T\frac{\partial\left(S,p\right)}{\partial(T,p)} , \quad c_V = T\frac{\partial\left(S,V\right)}{\partial(T,V)} .$$

In this way one proves the general relations between the specific heats c_p and c_V, the compressibilities κ_T and κ_S, and the isobaric expansion coefficient α

$$\frac{c_p}{c_V} = \frac{\kappa_T}{\kappa_S} , \tag{2.28a}$$

$$c_p - c_V = V_0 T\frac{\alpha^2}{\kappa_T} . \tag{2.28b}$$

The proof of these formulae is deferred to exercise 2.9.

2.5 Continuous Changes of State: First Examples

Let Σ be a thermodynamic system. One distinguishes *continuous* changes of state where the values of the state variables may change but the system remains qualitatively the same, from changes of state whereby the system changes to some other state of matter. An example for the first type is the expansion of an isolated gas into a larger volume; examples for the second kind are the transition from ice to water, or from liquid to gas. Continuous changes are called *processes*, the discontinuous ones are called *phase transitions*. In this section we deal exclusively with *processes*, i.e. we discuss changes of state where the state variables are continuous functions.

Let the number of particles of the system Σ be fixed. The process is said to be

- *isothermal,* if the temperature remains constant, $T = \text{const}$;
- *isobaric,* if the pressure is constant, $p = \text{const}$;
- *isochoric,* if the volume remains constant, $V = \text{const}$;
- *isentropic,* if the entropy is constant, $S = \text{const}$;
- *isoenergetic,* if the energy is constant, $E = \text{const}$.

For example, note that an isothermal process in an ideal gas, by the relation (1.28), is also an isoenergetic process.

When a given system Σ undergoes a process, its entropy S may remain unchanged, it may increase or may decrease. In the latter case one must distinguish whether the change of entropy occurs *within* the system or by exchange with its environment. We will distinguish these possibilities by the notation $\mathrm{d_i}S$ (with "i" for "inner") and $\mathrm{d_o}S$ (with "o" for "outer"), respectively. In this context, the following terminology will be important:

Definition 2.7 (Change of Entropy in Processes) Processes for which $\mathrm{d_i}S = 0$, are said to be *reversible,* processes where $\mathrm{d_i}S > 0$ are said to be *irreversible.*

If the entropy changes by some exchange with the environment then processes for which $\mathrm{d_a}S = 0$, are called *adiabatic*. Correspondingly, processes for which $\mathrm{d_a}S \neq 0$ are *nonadiabatic*.

Example 2.2 (System in a Heat Bath) Figure 2.1 shows a vessel Σ filled with an ideal gas with momentary values T of temperature, p of pressure and V of volume, immersed in a large heat bath. The pressure p within the vessel differs from the pressure p' of its environment. However, the system is provided with a movable piston so that it may expand or contract until inner and outer pressures are equal. The difference in pressure is assumed to be small so that the system is in equilibrium

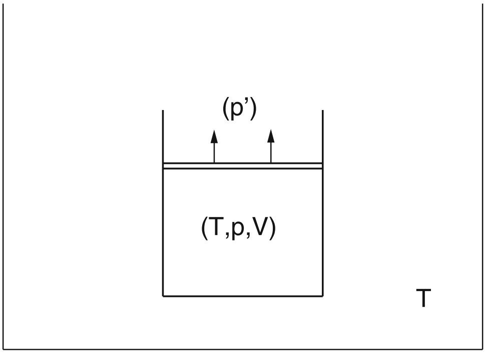


Fig. 2.1 A system Σ, described by state variables T, p and V, is immersed in a heath bath of temperature T whose pressure p' is slightly different from p. The system is closed from above by a piston which moves until $p = p'$ is reached

at any time. In case $p' < p$ the system expands. Its energy changes according to the formula

$$\Delta E = -\int_{V_1}^{V_2} \mathrm{d}V\, p = -NkT \int_{V_1}^{V_2} \mathrm{d}V\, \frac{1}{V} = -NkT \ln\left(\frac{V_2}{V_1}\right) .$$

As $V_2 > V_1$ one has $\Delta E < 0$. The system delivers mechanical work by shifting the piston upwards in the figure. The heat bath, in turn, guarantees that both the temperature and the energy stay constant. This means that the system receives the amount of heat

$$Q = \int_{S_1}^{S_2} \mathrm{d}S\, T = T(S_2 - S_1) = NkT \ln\left(\frac{V_2}{V_1}\right) \equiv T\Delta S .$$

The last step of these equations follows from (1.27), $S(E, N, V) = Nk \ln V + \cdots$, where the dots stand for terms which are independent of V.

If the outer pressure is larger than the inner one, $p' > p$, the piston moves downwards in the figure. The work that it delivers, is positive, $\Delta E > 0$. In this case the amount of heat Q is detracted from the system and is delivered to the heat bath. In both cases the exchange of mechanical energy is correlated with addition or subtraction of heat via the change of entropy and of volume. This process is reversible but not adiabatic.

In other, more general cases than the example just described, the exchange of energy of the system Σ with the environment, or within itself, is controlled by Gibbs' fundamental form,

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu_C\,\mathrm{d}N .$$

The first term $T\,\mathrm{d}S$ describes the exchange of heat, the second term $-p\,\mathrm{d}V$ describes the exchange of mechanical work, the third term $\mu_C\,\mathrm{d}N$ describes the exchange of chemical energy. As an example for an exchange of entropy within the system proper, imagine an isolated gas expanding into a larger vessel. In this case one has $\mathrm{d_i}S > 0$, but $\mathrm{d_a}S = 0$. A process of this kind is irreversible and adiabatic.

Example 2.3 (Reversible-Adiabatic Expansion) Let an ideal gas expand in a reversible and adiabatic manner. As, by assumption, $\mathrm{d}S = 0$ and $\mathrm{d}N = 0$, we have

$$\mathrm{d}E = -p\,\mathrm{d}V = -NkT\frac{\mathrm{d}V}{V} , \tag{2.29a}$$

$$\mathrm{d}E = \frac{3}{2}Nk\,\mathrm{d}T \tag{2.29b}$$

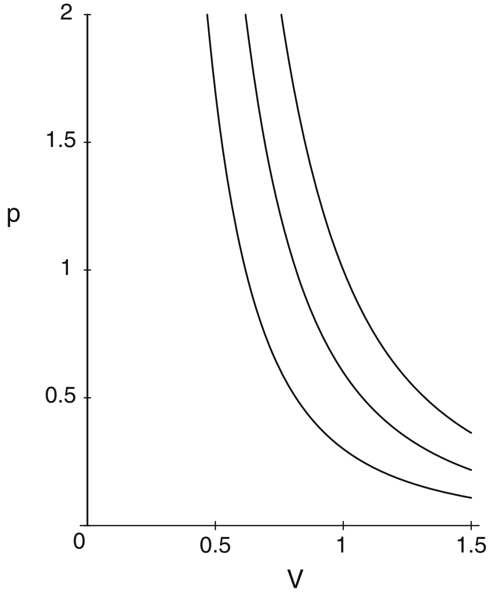


Fig. 2.2 Three examples for adiabatics, (2.30b), for the case of reversible–adiabatic expansion of an ideal gas

From this one concludes:

$$\frac{3}{2}\frac{\mathrm{d}T}{T}+\frac{\mathrm{d}V}{V}=0 \quad \text{or} \quad \mathrm{d}\ln\left(T^{3/2}V\right)=0\ .$$

As an important result, one obtains the relation

$$T^{3/2}V=\text{const.} \tag{2.30a}$$

Inserting the relation (1.31), $pV = kNT$, for the ideal gas, the above relation takes the alternative form

$$pV^{5/3}=\text{const.}\ . \tag{2.30b}$$

The curves defined by this equation are called *adiabatics*, they are illustrated in Fig. 2.2. The reader is invited to compare them with the isothermals shown in Fig. 1.2.

Example 2.4 (Joule-Thomson Process) This process consists in the following idealized set-up: The two chambers in Fig. 2.3 are separated by a throttle. Each one of them is equipped with a movable piston. A gas or a liquid which fills the left chamber with volume V_1 and pressure p_1, is forced through the throttle into the chamber on the right of the figure. The pressure in this part of the system is p_2. The two pistons are shifted in such a way that the pressures p_1 and p_2 stay constant. Furthermore, the whole system is assumed to be thermally isolated. The

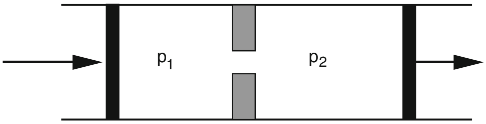


Fig. 2.3 Joule-Thomson effect: a gas or a liquid is pushed from the *left* chamber to the *right* chamber through a throttle in such a way that the pressures $p_1 > p_2$ stay constant. If the temperature in the *left* chamber is given, does the temperature in the *right* chamber rise or fall?

temperature in the left chamber is fixed, the temperature in the right chamber is to be measured. In the controlled decompression from (V_1, p_1) to (V_2, p_2) the amount of work $A = p_1V_1 - p_2V_2$ is delivered. As the system is thermally isolated this is also the change of inner energy $\Delta E = A$. Therefore, the enthalpy (2.3b) remains unchanged, $H_1 = H_2$.

One then calculates the change in temperature induced by this process. One has

$$\mathrm{d}T = \left(\frac{\partial T}{\partial p}\right)_H \mathrm{d}p = -\frac{(\partial H/\partial p)_T}{(\partial H/\partial T)_p}\,\mathrm{d}p\,. \tag{2.31}$$

The second formula is a simple consequence of the formula for the product of two Jacobi determinants, viz.

$$\frac{\partial(x,z)}{\partial(y,z)} = \frac{\partial(x,z)}{\partial(x,y)}\frac{\partial(x,y)}{\partial(y,z)}\,,$$

which yields the relation

$$\left.\frac{\partial x}{\partial y}\right|_z = -\left.\frac{\partial z}{\partial y}\right|_x \left.\frac{\partial x}{\partial z}\right|_y\,.$$

The denominator of the right-hand side of (2.31), by the differential condition (2.3c) and normalizing to one mole of the gas (or liquid), is equal to c_p,

$$\left.\frac{\partial H}{\partial T}\right|_p = T\frac{\partial S}{\partial T} = c_p\,.$$

The numerator can also be calculated from (2.3c), making use of (2.6a) and of (2.6b). One concludes that

$$\frac{\partial V}{\partial T} = \frac{\partial^2 G(T,N,p)}{\partial T\partial p} = -\frac{\partial S}{\partial p}$$

and, therefore,

$$\left(\frac{\partial H}{\partial p}\right)_T = V + T\left(\frac{\partial S}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p .$$

From this and from (2.21) one obtains the result

$$\mu_{\mathrm{JT}} := \left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{c_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right] = \frac{V_0}{c_p}\left[T\alpha - 1\right] . \tag{2.32}$$

Thus, the increase or decrease of the temperature is related to the specific heat c_p and to the isobaric expansion coefficient α. The quantity μ_{JT} is called the *Joule-Thomson coefficient.*

Note, however, that for the example of an ideal gas the result (2.32) is somewhat disappointing because according to Example 2.1, (2.22b), one has $\alpha = 1/T$ and, therefore, there is no change of temperature. This is not so for *real* gases. In this case there are domains in the (T, p)-plane where $-\,\partial T/\partial p|_H$ is positive, i.e. where there is warming up, and there are domains where this quantity is negative, i.e. where cooling takes place. Such domains are separated by what is called an *inversion curve*.

Example 2.5 (Van der Waals Gas) There is a classical model for real gases which can be treated analytically on the basis of the previous example: The *Van der Waals Gas*. This model is characterized by two parameters a and b the first of which appears in the formula for the pressure and is due to the interaction of the gas molecules within the gas and with the walls. The second parameter characterizes the finite extension of the molecules. In this model the simple relation (2.25b) for pressure and volume of the ideal gas is replaced by the *Van der Waals equation*

$$\left(p + \frac{a}{V_0^2}\right)\left(V_0 - b\right) = RT . \tag{2.33}$$

The parameter a, called *cohesiveness,* describes the attraction among the molecules, the parameter b, called *co-volume*, is related to the finite extension of the molecules. The physical picture behind this ansatz is as follows. If b is the average volume of a single molecule its motion in the gas is confined to the space $(V_0 - b)$. On the other hand the mutual attraction of the molecules acts like an increase in pressure. This increase is proportional to the square of the density of the molecules in the gas, this density being proportional to $1/V_0$. This is the reason for the additional term in the pressure p.

We move on to calculate the inversion curve for this model as well as a few more characteristic quantities. The isothermals are obtained by solving the Van der Waals

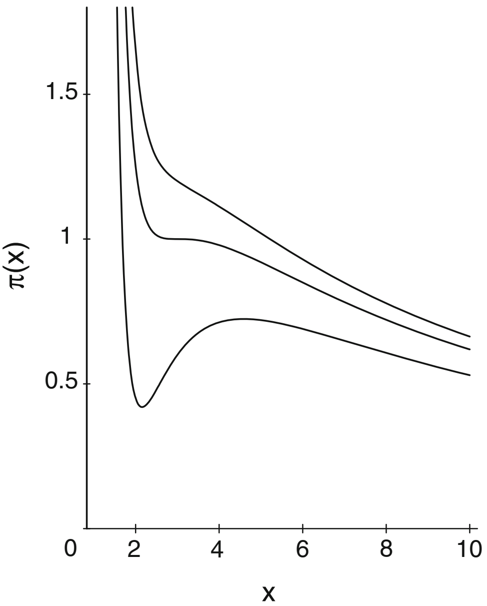


Fig. 2.4 Three isothermals of a Van der Waals gas with $T = 1,05T_{\text{crit}}$ (*upper curve*), $T = T_{\text{crit}}$ (*middle curve*) and $T = 0,9T_{\text{crit}}$ (*lower curve*). The figure shows the function $\pi(x) = p/p_{\text{crit}}$ in terms of the dimensionless variable $x = V/b$

equation (2.33) for $p(V)$,

$$p(V) = \frac{RT}{V_0 - b} - \frac{a}{V_0^2} \,. \tag{2.34a}$$

The temperature T is chosen as the parameter characterizing the individual curves in Fig. 2.4. The derivative of p by V, for constant T, tells us whether the isothermal has an extremum, i.e. either a minimum or maximum, or a saddle point, or no extremum at all,

$$\left.\frac{\mathrm{d}p(V)}{\mathrm{d}V}\right|_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} \,.$$

This is zero if

$$\frac{(1-x)^2}{x^3} = \frac{bRT}{2a} \quad \text{where} \quad x := \frac{V}{b} \,. \tag{2.34b}$$

The left-hand side of this equation has its maximum at $x_{\max} = 3$ where it has the value $4/27$. Therefore, there are extrema only if RT stays smaller than or equal to the critical value

$$RT_{\text{crit}} = \frac{8a}{27b} \,. \tag{2.34c}$$

If $T < T_{\text{crit}}$ there is a minimum and a maximum, if $T = T_{\text{crit}}$ one finds a saddle point, while for $T > T_{\text{crit}}$ there is no extremum. At the saddle point where $V = 3b$ and $T = T_{\text{crit}}$, the pressure has the value

$$p_{\text{crit}} = \frac{a}{27b^2} \,. \tag{2.34d}$$

It is appropriate to define dimensionless variables using the parameter b and the values (2.34c) and (2.34d):

$$x := \frac{1}{b}V \,, \quad \pi := \frac{p}{p_{\text{crit}}} \,, \quad \tau := \frac{RT}{RT_{\text{crit}}} \tag{2.35}$$

Figure 2.4 shows three isothermals in the representation $\pi(x)$ as a function of x, for one value below, one value above the critical temperature, respectively, as well as for $T = T_{\text{crit}}$.

In order to obtain the inversion curve one must first calculate the derivative of (2.33) by the temperature T, at fixed pressure p,

$$-(V-b)\frac{2a}{V^3}\left.\frac{\partial V}{\partial T}\right|_p + \left(p + \frac{a}{V^2}\right)\left.\frac{\partial V}{\partial T}\right|_p = R \quad \text{or}$$
$$T\left.\frac{\partial V}{\partial T}\right|_p \left(p - \frac{a}{V^2} + \frac{2ab}{V^3}\right) = RT \,.$$

According to (2.32) we must have $\mu_{\text{JT}} = 0$ and therefore

$$T\left.\frac{\partial V}{\partial T}\right|_p - V = 0 \quad \text{or}$$
$$RT\left(p - \frac{a}{V^2} + \frac{2ab}{V^3}\right)^{-1} - V = 0 \,.$$

In a next step one replaces the numerator RT by the Van der Waals equation (2.33) thus obtaining the condition

$$\left(\frac{2a}{V} - \frac{3ab}{V^2} - bp\right)\left(p - \frac{a}{V^2} + \frac{2ab}{V^3}\right)^{-1} = 0 \quad \text{or}$$
$$p = \frac{2a}{bV} - \frac{3a}{V^2} \,.$$

By transforming to the dimensionless variables (2.35) one obtains the equation

$$\pi(x) = \frac{27}{x^2}(2x-3) \,. \tag{2.36a}$$

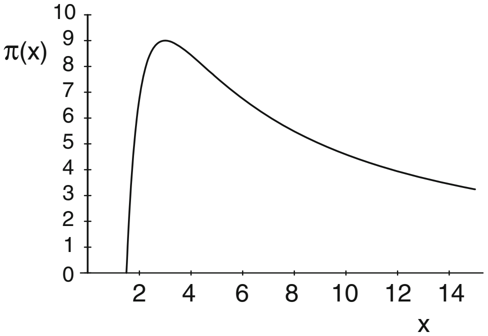


Fig. 2.5 The inversion curve of the Van der Waals gas in the (V,p)-plane. Here the function $\pi(x) = p/p_{\text{crit}}$ is plotted as a function of $x = V/b$

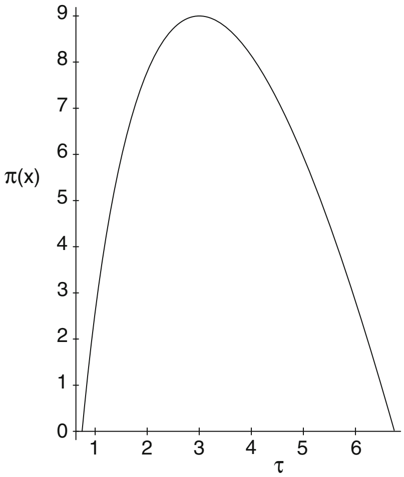


Fig. 2.6 Inversion curve of the Van der Waals gas in the (T,p)-plane. In this diagram $\tau(x) = T/T_{\text{crit}}$ is the abscissa while $\pi(x) = p/p_{\text{crit}}$ is the ordinate

Figure 2.5 shows this curve in a (x,π)- or (V,p)-diagram.

The effect becomes more clearly visible by drawing the inversion curve in a (T,p)-diagram. This diagram is obtained by solving the Van der Waals equation (2.33) for $\tau(x) = T/T_{\text{crit}}$ as a function of $x = V/b$ and by replacing p/p_{crit} by (2.36a),

$$\tau(x) = \frac{27}{4x^2}(x-1)^2 \,. \tag{2.36b}$$

The inversion curve in the (T,p)-diagram of Fig. 2.6 which shows π as a function of τ, is obtained in parametric representation from (2.36a) and (2.36b).

A comment on this figure may be useful: The left intersection point of the curve with the horizontal axis is reached for $x = 3/2$. At this point the variable τ has the value $\tau_{\text{m}} = 3/4$. Expressed in terms of the temperature one has

$$RT_{\text{m}} = \frac{2a}{9b} \,. \tag{2.37a}$$

The intersection point to the right is reached when x tends to infinity, $x \to \infty$. One then has $\tau_{\mathrm{M}} = 27/4$, the temperature is obtained from

$$RT_{\mathrm{M}} = \frac{2a}{b} \,. \tag{2.37b}$$

Clearly, the maximum of the inversion curve is reached at $\tau_0 = 3$, or $RT_0 = 8a/(9b)$, it has the value $\pi_0 = 9$ or $p_0 = 9a/(27b^2)$. Typical values for a and b, as obtained from measurements of the critical temperature and the critical pressure, are

$$\begin{aligned} a &= 0.04 \times 10^6 \div 4 \times 10^6 \,\mathrm{Atm\, cm^6\, Mol^{-2}} \,, \\ b &= 23 \div 43 \,\mathrm{cm^3\, Mol^{-1}} \,. \end{aligned} \tag{2.38}$$

In the domain enclosed by the inversion curve the derivative $(\partial T/\partial p)_H$ is positive. As the difference of pressure between left and right chambers in Fig. 2.3 is negative, the difference in temperature is also negative. Throttled expansion leads to *cooling*. Outside this domain the quantity $(\partial T/\partial p)_H$ is negative, the gas grows warm. Thus, if one wishes to obtain a cooling effect one must choose temperatures and pressures which are below T_{M} and below p_0, respectively.

2.6 Continuous Changes of State: Circular Processes

This section deals with idealized thermodynamic circular processes, or *cycles,* where thermal energy is converted to work (steam engines) or work is converted to thermal energy (heat pumps). One must keep in mind, though, that notions such as “heat” and “entropy” are defined only with respect to a macroscopic observer, very much like the notion of “work” alludes to macroscopic processes such as, for example, the motion of a piston rod. In a microscopic perspective heat is kinetic energy of the constituents of a substance. One can only distinguish ordered motion from chaotic motion.

2.6.1 Exchange of Thermal Energy Without Work

In a first step we consider two thermodynamic systems $\Sigma^{(1)}$ and $\Sigma^{(2)}$ which are assumed to have the constant volumes V_1 and V_2, respectively, but equal numbers of particles, $N_1 = N_2$, and the same specific heat, $c_V^{(1)} = c_V^{(2)}$. These two systems are coupled by thermic exchange in such a way that the total system $\Sigma^{(1)} + \Sigma^{(2)}$ remains an isolated system. Furthermore, if the specific heat is constant in the range of temperatures one considers, then from

$$c_V = T_1 \frac{\partial S_1(T_1, N_1, V_1)}{\partial T} = T_2 \frac{\partial S_2(T_2, N_1, V_2)}{\partial T}$$

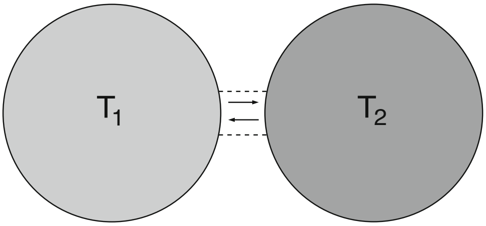


Fig. 2.7 Two initially isolated systems which have the same specific heat c_V, are brought to thermal contact

one deduces a logarithmic dependence of the entropy on temperature,

$$S_i(T, N_i, V_i) = \int_{T_0}^{T} \mathrm{d}T \, \frac{c_V}{T} = c_V \ln\left(\frac{T}{T_0}\right) + S_0^{(i)} \,, \tag{2.39}$$

$i = 1, 2$. T_0 is an arbitrary reference temperature, $S_0^{(1)}$ and $S_0^{(2)}$ are the corresponding values of the entropy at T_0. If the two systems have thermal contact as sketched in Fig. 2.7, both take on the same temperature T_Ω. This temperature is calculated from the conservation of energy: *Before* and *after* connecting the systems, one has, respectively,

$$E = c_V(T_1 + T_2) = 2c_V T_\Omega \,,$$

from which

$$T_\Omega = \frac{1}{2}(T_1 + T_2) \,. \tag{2.40}$$

The total entropy of the separated systems is

$$S_A = S_1(T_1) + S_2(T_2) = c_V \ln\left(\frac{T_1 T_2}{T_0^2}\right) + S_0^{(1)} + S_0^{(2)} \,. \tag{2.41a}$$

In contact and after reaching thermal equilibrium the total entropy is

$$S_\Omega = S_1(T_\Omega) + S_2(T_\Omega) = 2c_V \ln\left(\frac{T_\Omega}{T_0}\right) + S_0^{(1)} + S_0^{(2)} \,. \tag{2.41b}$$

From this and from (2.40) the change of the entropy $\Delta S \equiv S_\Omega - S_A$ is calculated to be

$$\Delta S = 2c_V \ln\left(\frac{T_\Omega}{\sqrt{T_1 T_2}}\right) = 2c_V \ln\left(\frac{T_1 + T_2}{2\sqrt{T_1 T_2}}\right) \,. \tag{2.41c}$$

The conclusion is simple: As $T_1 + T_2 \geq 2\sqrt{T_1 T_2}$, the equal sign applying only when $T_1 = T_2$, one obtains

$$\Delta S > 0 \quad \text{for} \quad T_1 \neq T_2 \,. \tag{2.41d}$$

For $T_1 \neq T_2$ the process described above is always *irreversible.*

2.6.2 A Reversible Process

In a second step we assume the idealized set-up to be constructed such that the thermal balance is effected by a *reversible* process. The difference between the total energy of the initially isolated systems, $E_A = c_V(T_1 + T_2)$, and the smaller energy, $E_\Omega = 2c_V\sqrt{T_1 T_2}$, after thermalization,

$$\Delta E = E_A - E_\Omega = 2c_V \left\{ \frac{1}{2}(T_1 + T_2) - \sqrt{T_1 T_2} \right\} \,,$$

must have been compensated by work delivered to the outside. This is the purpose of the machine M which is inserted between the two systems and which is represented by the black box in Fig. 2.8.

Using a differential form let $\alpha_1 = -T\,\mathrm{d}S = -c_V\,\mathrm{d}T$ be the amount of thermal energy delivered by the system Σ_1 by a change $\mathrm{d}T$ of its temperature. While cooling from T_1 to T_Ω the system delivers the amount of heat

$$Q_1 = -\int_{T_1}^{T_\Omega} \mathrm{d}T\, c_V = c_V\,(T_1 - T_\Omega) \,. \tag{2.42a}$$

In a similar way the differential thermal energy that the second system receives from the machine M is equal to $\alpha_2 = c_V\,\mathrm{d}T$. Altogether the machine M delivers the thermal energy

$$Q_2 = \int_{T_2}^{T_\Omega} \mathrm{d}T\, c_V = c_V\,(T_\Omega - T_2) \tag{2.42b}$$

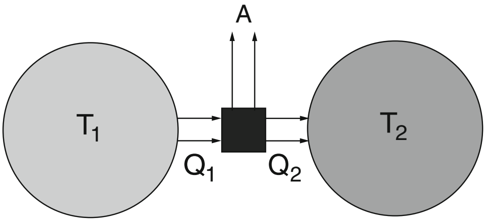


Fig. 2.8 An engine is inserted between the two systems of Fig. 2.7 which converts the excess energy into work

to the system Σ_2. Expressed differently this means that the part

$$A = Q_1 - Q_2 = 2c_V \left\{ \tfrac{1}{2} (T_1 + T_2) - T_\Omega \right\} \tag{2.42c}$$

is delivered in the form of work. At the same time this is the maximal portion of the released heat which can be converted to work. The same conclusion is obtained from the change of entropy (2.41c) and from the inequality

$$\sqrt{T_1 T_2} \le T_\Omega \le \tfrac{1}{2} (T_1 + T_2) \ , \tag{2.43}$$

which, obviously, holds generally. At the lower bound no entropy is created, the maximal amount of heat is converted to work. The process is reversible. At the upper bound of the inequality, in turn, the generation of entropy is maximal, no work is produced at all.

These somewhat schematic considerations of principle lead to a definition of heat and work engines that we will make use of in the sequel.

Definition 2.8 (Thermal Efficiency) The *thermal efficiency* (in the case of heat engines) or *coefficient of performance* (in the case of heat pumps) for the schematic set-up sketched in Fig. 2.8 is defined by

$$\eta := \frac{A}{Q_1} \ . \tag{2.44}$$

If there is no production of entropy this coefficient takes the maximal value

$$\eta_C = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_\Omega - T_2}{T_1 - T_\Omega} \ . \tag{2.45}$$

This value is called *Carnot efficiency.*

2.6.3 Periodically Working Engines

The diagram in Fig. 2.9 describes schematically a periodically working engine which functions between two isothermals T_A and T_B and between to adiabatics (with entropies S_A and S_B, respectively). During the motion from A_1 to A_2 isothermal expansion takes place from the volume V_1 to the volume V_2, whereby the heat reservoir Σ_1 delivers the thermal energy Q_1. This is followed by adiabatic expansion to the volume V_3 during which work is delivered to the outside. The energy decreases until the lower temperature T_2 of the second reservoir Σ_2 is reached. The next phase is isothermal compression from volume V_3 to volume V_4 with the thermal energy Q_2 being delivered to the system Σ_2. Finally, in returning from B_2 to A_1 adiabatic compression takes place until the temperature T_1 is reached again. This idealized elementary cycle is called *Carnot process* or *Carnot cycle.*

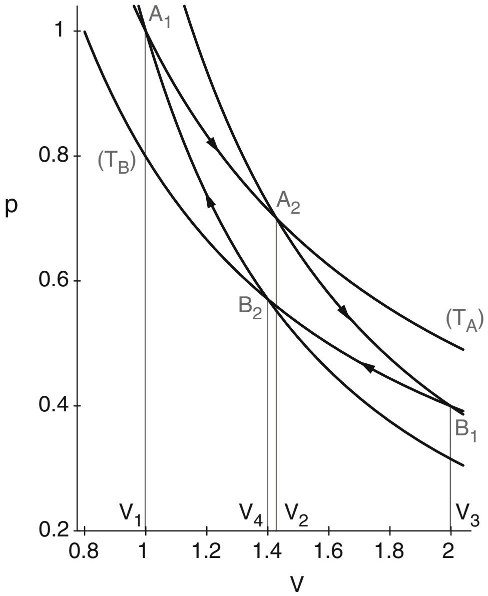


Fig. 2.9 A periodically working machine: isothermal expansion from A_1 to A_2, then adiabatic expansion from A_2 to B_1; isothermal compression from B_1 to B_2, finally, adiabatic compression from B_2 back to A_1

There is a general rule regarding the efficiency of heat engines. This rule applies equally well to the thermal efficiency of heat engines and to the coefficient of performance of heat pumps. Therefore, for short, we will use the terms *efficiency* for both cases, and the term *heat engine* for classical steam-engines and heat pumps.

Theorem 2.1 (Efficiency of Heat Engines) *The efficiency of a Carnot cycle is the best possible. All heat engines working in a reversible mode between two reservoirs* Σ_A *and* Σ_B *have the same efficiency.*

Proof The two reservoirs Σ_A and Σ_B in Fig. 2.10 have the temperatures T_A and T_B, respectively, with $T_A > T_B$. They are coupled by means of a Carnot machine M_{C} which works as a heat pump, and by a second, arbitrary device M'. The amounts of heat and of work, respectively, which are delivered or absorbed in the successive phases, are recorded in Fig. 2.10. The Carnot pump absorbs the work

$$A = \eta_{\mathrm{C}} Q_1 = \frac{\eta_{\mathrm{C}}}{1-\eta_{\mathrm{C}}} Q_2 \,. \tag{2.46a}$$

Denoting the efficiency of the arbitrary (possibly imperfect) machine M' by η, and using the notations of the figure, one has

$$A' = \eta Q_1' \quad \text{and} \quad \eta = 1 - \frac{Q_2'}{Q_1'} \,. \tag{2.46b}$$

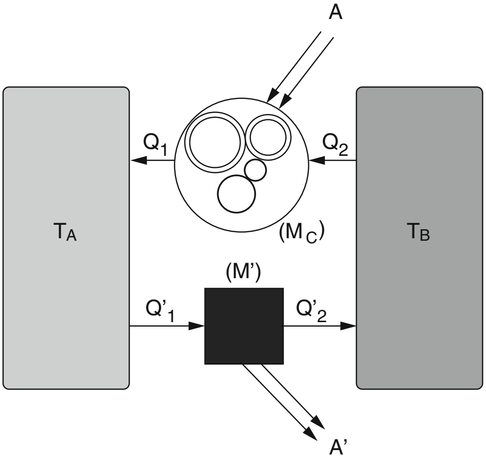


Fig. 2.10 Between two heat reservoirs with temperatures $T_A > T_B$ a Carnot engine M_{C} and some other, arbitrary engine M' are inserted. The Carnot engine works as a heat pump (maximal efficiency), the arbitrary machine M' has the efficiency η'

The purpose of the Carnot engine is to pump back the heat Q'_2 to the system Σ_A where Q'_2 is the amount of heat that the machine M' delivers to the system Σ_B with the lower temperature. Therefore, one has

$$A = \frac{\eta_{\mathrm{C}}}{1-\eta_{\mathrm{C}}} Q'_2 = \frac{\eta_{\mathrm{C}}}{1-\eta_{\mathrm{C}}} (1-\eta) Q'_1 \ . \tag{2.46c}$$

The total amount of work gained or lost by the combination of the two machines is given by

$$\Delta A = A' - A = \left\{ \eta - \frac{\eta_{\mathrm{C}}(1-\eta)}{1-\eta_{\mathrm{C}}} \right\} Q'_1 = \frac{\eta - \eta_{\mathrm{C}}}{1-\eta_{\mathrm{C}}} Q'_1 \ . \tag{2.46d}$$

By the second law of thermodynamics this work must be smaller than or equal to zero, $\Delta A \leq 0$. This law says that there can be no machine in *perpetual motion.* Indeed, in one of its formulations, the second law reads:

There is no periodically working machine which has no other effect than to generate positive work by cooling a heat reservoir.

Since $\eta_{\mathrm{C}} < 1$ and $Q'_1 > 0$ one concludes

$$\eta \leq \eta_{\mathrm{C}} \ . \tag{2.47}$$

Therefore the Carnot efficiency is the best possible.

For the proof of the second part of the theorem we assume that the whole set-up now follows a *reversible* cycle in which the machine M' works as a heat pump, while the Carnot engine works as a heat engine. By the same argument as above one now finds $\eta_{\mathrm{C}} \leq \eta$. The conclusion from this and from (2.47) is, obviously, that a reversible realization of the set-up must have the Carnot efficiency,

$$\eta = \eta_C \quad \text{(for the reversible process).} \tag{2.48}$$

All reversibly working heat engines have the same efficiency. This efficiency is the Carnot efficiency (2.45).

Remark Whenever the total process is not reversible the efficiency η is genuinely smaller than η_C. If such is the case the irreversibility stems from the unknown component M'.

2.6.4 The Absolute Temperature

The constructions described in the preceding section and the second law of thermodynamics we made use of there, show that there must be an absolute temperature. The argument goes as follows: Theorem 2.1 implies that in all *reversibly* working machines containing two reservoirs with temperatures τ_1 and τ_2, respectively, the ratio Q_1/Q_2 is a universal function of τ_1 and τ_2,

$$\frac{Q_1}{Q_2} = f(\tau_1, \tau_2) \; .$$

Consider a set-up consisting of three heat reservoirs coupled through two Carnot engines as sketched in Fig. 2.11 and choose the latter so that $Q_2' = Q_2$. One concludes

$$\frac{Q_1}{Q_2} = f(\tau_1, \tau_2) \; , \quad \frac{Q_2}{Q_3} = f(\tau_2, \tau_3) \quad \text{and} \quad \frac{Q_1}{Q_3} = f(\tau_1, \tau_3) \; ,$$

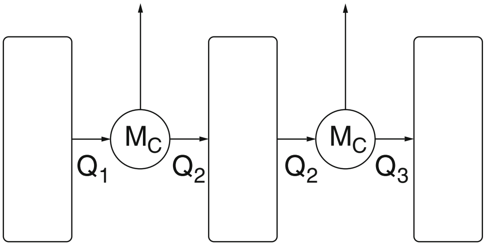


Fig. 2.11 Three heat reservoirs τ_1, τ_2 and τ_3 (from the *left*) are coupled by means of two Carnot engines such that the heat Q_2' delivered to the right by the middle reservoir equals the amount of heat Q_2 that it receives from the *left*, $Q_2' = Q_2$. This schematic set-up leads to the conclusions (2.49) and (2.51)

thus obtaining the functional equation

$$f(\tau_1, \tau_2) f(\tau_2, \tau_3) = f(\tau_1, \tau_3) \ . \tag{2.49}$$

Define then

$$T(\tau) := f(\tau, \tau_0) \tag{2.50}$$

where τ_0 is an arbitrary reference temperature. One concludes from (2.49) that

$$f(\tau, \tau') = \frac{T(\tau)}{T(\tau')} \ , \tag{2.51}$$

where $T(\tau)$ is a monotonously rising function of the temperature τ.

The *absolute temperature* is defined in such a way that it is proportional to the function $T(\tau)$. Let T denote again the absolute temperature. Then one has

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \quad \text{and} \quad \eta_\mathrm{C} = 1 - \frac{T_2}{T_1} \ . \tag{2.52}$$

By the second law of thermodynamics $\eta_\mathrm{C} < 1$. Therefore T is always positive.

2.7 The Laws of Thermodynamics

A first and important rule of thermodynamics was formulated in Sect. 1.2. This rule is often described as "zeroth" law of thermodynamics: Systems in equilibrium have the same temperature. Formulated more explicitly, this rule says that thermal equilibrium is a transitive property. If two systems Σ_1 and Σ_2 each are in thermal equilibrium with a third system Σ_3, then they are in thermal equilibrium with each other.

In the preceding section we also made use of the second law. This section gives a complete description of the laws of thermodynamics in a more precise formulation.

The first law is the thermodynamic version of the law of conservation of energy. It reads

Theorem 2.2 (First Law of Thermodynamics) *The energy of a closed thermodynamic system is a conserved quantity. It is constant in time.*

On the basis of the schematic models described in Sect. 2.6 we start from an *adiabatically closed system* Σ. Denoting two different states of this system symbolically by Z_1 and Z_2, respectively, "adiabatically closed" means that there is a process only producing or consuming work (but no heat) which converts Z_1 to Z_2 or, vice versa, Z_2 to Z_1. The positive or negative amount of work $A(Z_1 \leftrightarrow Z_2)$ which is needed for this transformation, depends only on the two states but is independent of the nature of the process. (For this reason we need not qualify details of such a process, and we may let it work in the background.) This idea suggests that the state function "energy" is defined with respect to a reference state Z_0 whose energy is E_0,

$$E(Z) := E_0 + A\,(Z_0 \to Z)\ . \tag{2.53}$$

In the case of an arbitrary system which is not adiabatically closed, the change of energy in going from an initial state Z_1 to the final state Z_2 is equal to the sum of work produced or consumed, and of the amount of heat which is absorbed or released,

$$\Delta E(Z_1 \to Z_2) = A(Z_1 \to Z_2) + Q(Z_1 \to Z_2)\ . \tag{2.54}$$

This is the most general expression of the first law.

The second law of thermodynamics makes a statement of central importance about the increase of disorder in thermodynamic systems. There are a number of different formulations of this law whose equivalence must be proven in detail. I choose here a formulation which is inspired by the statistical interpretation of the theory of heat. One distinguishes the differential amount of heat

$$\mathrm{d}Q = T\,\mathrm{d}S \tag{2.55a}$$

which is absorbed or produced, from the differential amount of work $\mathrm{d}A$ which is produced or consumed. The latter has the general form

$$\mathrm{d}A = \sum_{\alpha} \xi_\alpha\,\mathrm{d}X_\alpha\ , \tag{2.55b}$$

where ξ_α is an *intensive* quantity, X_α is an *extensive* quantity, the two forming an energy-conjugate pair of state variables, cf. (1.2). Examples known to the reader are $p\,\mathrm{d}V$ and $\mu_C\,\mathrm{d}N$, with p the pressure, V the volume, μ_C the chemical potential and N the number of particles. Further examples are $E \cdot \mathrm{d}P$ and $\Phi\,\mathrm{d}Q$, where E is the electric field, P is the electric polarization, Φ is an electric potential and Q is the charge. With this notation the second law reads as follows

Theorem 2.3 (Second Law of Thermodynamics) *Thermodynamic systems in equilibrium are characterized by an intensive quantity, the temperature T, and by an extensive quantity, the entropy S, in such a way that a change of their energy is given by the formula*

$$\mathrm{d}E = T\,\mathrm{d}S + \sum_{\alpha} \xi_\alpha\,\mathrm{d}X_\alpha\ . \tag{2.55c}$$

The first term on the right-hand side describes the amount of heat, the second term describes the amount of work. The entropy of a closed system never decreases. It reaches its maximal value in the equilibrium state.

Remarks

i) There are other, more phenomenologically oriented formulations of the second law, among them the impossibility of perpetual motion. Two more are described in exercise 2.3.
ii) Equation (2.55c), in fact, is a relation between one-forms on the manifold Σ described by coordinates T and S (and a third variable). The question of what kind these one-forms are, whether exact or closed forms, will be dealt with in more detail in the next chapter.

The existence of an absolute temperature rests primarily on the second law, cf. Sect. 2.6.4. As a consequence there exists a point zero of this temperature. Intuitively, and in a purely classical picture, this origin might be thought of as the point on the temperature scale where all motions at the atomic or molecular level have come to a rest. It is the third law of thermodynamics which controls the behaviour of the entropy close to the absolute zero.

Theorem 2.4 (Third Law of Thermodynamics) *In approaching the absolute zero $T = 0$ from above, i.e. from positive absolute temperatures, the entropy of a system in equilibrium tends to the smallest possible value S_0, also from above. This value is independent of all state variables.*

The lowest value of the entropy is finite and nonzero if the ground state of the system is degenerate in energy. Otherwise it has the value $S_0 = 0$.

For example, if the system consists of N molecules and if its ground state has the degree of degeneracy κ, then

$$S_0 \equiv S(T=0) = kN \ln \kappa \quad \text{or} \quad S_0 = R \ln \kappa \ . \tag{2.56}$$

Note that here one is referring to one mole.

For what follows let us assume that the ground state carries no degeneracy, $\kappa = 1$ and, therefore, that $S_0 = 0$. In approaching the absolute zero from above (i.e. by lowering the temperature through positive values) there follow the limits:

$$\lim_{T \to 0} c_p(T) = 0 \ , \tag{2.57a}$$

$$\lim_{T \to 0} c_V(T) = 0 \ , \tag{2.57b}$$

$$\lim_{T\to 0} \alpha = 0 , \tag{2.57c}$$

$$\lim_{T\to 0} \frac{1}{T}\left[c_p(T) - c_V(T)\right] = 0 . \tag{2.57d}$$

In these expressions c_p and c_V are the specific heats (referring to a mole) and α is the isobaric expansion coefficient (2.21). In proving these relations the following considerations are useful. At first, the entropy as a thermodynamic potential is a function of the energy, the particle number and the volume, $S(E, N, V)$. The Legendre transformation (1.42a) which effects the transition from entropy to free energy, transforms the entropy to a function of T, N and V,

$$S(E, N, V) \longrightarrow S(T, N, V) = -\frac{\partial F}{\partial T} .$$

When the temperature tends to zero, $T \to 0$, the third law implies also

$$\lim_{T\to 0} S(T, N, V) = 0 . \tag{2.58a}$$

Furthermore, returning once more to the free enthalpy (2.5c) one concludes

$$\lim_{T\to 0} S(T, N, p) = -\frac{\partial G}{\partial T} = 0 \tag{2.58b}$$

where S is now a function of temperature, number of particles and pressure p. The two properties (2.58a) and (2.58b) tell us that, along with the temperature, the entropy tends to zero, independently of the path along which one is reaching this limit. In particular, the partial derivatives of S by p and by V must tend to zero as well. This is sufficient for proving the statements (2.57a)–(2.57d):

By (2.17b) the entropy can be written as

$$S(T, N, p) = \int_0^T \mathrm{d}T' \, \frac{1}{T'} c_p(T') .$$

For $T \to 0$ this integral exists only if $c_p(T)$ goes to zero in this limit. As by (2.28b) the specific heat c_V is always smaller than the specific heat c_p, $0 < c_V < c_p$, c_V also tends to zero in the limit $T \to 0$. This proves the limits (2.57a) and (2.57b).

The isobaric expansion coefficient α which was defined in (2.21), may be expressed in terms of a partial derivative of S by p,

$$\alpha = \frac{1}{V}\frac{\partial V(T, N, p)}{\partial T} = \frac{1}{V}\frac{\partial^2 G}{\partial p \partial T} = -\frac{1}{V}\frac{\partial S}{\partial p} .$$

The limit (2.57c) follows from this. The limit (2.57d), finally, is proven by making use several times of the formula (2.27) for Jacobi determinants. In a first step one sees that the definitions (2.17a) and (2.17b) (with reference to one mole) can be written as Jacobi determinants, viz.

$$c_p = T\frac{\partial(S,p)}{\partial(T,p)} \quad \text{and} \quad c_V = T\frac{\partial(S,V)}{\partial(T,V)} \ .$$

The second of these is rewritten as follows

$$\begin{aligned} c_V &= T\left(\frac{\partial(T,V)}{\partial(T,p)}\right)^{-1}\left(\frac{\partial(S,V)}{\partial(T,p)}\right) \\ &= T\frac{1}{\partial V/\partial p|_T}\left\{\left.\frac{\partial S}{\partial T}\right|_p \left.\frac{\partial V}{\partial p}\right|_T - \left.\frac{\partial S}{\partial p}\right|_T \left.\frac{\partial V}{\partial T}\right|_p\right\} \\ &= T\left\{\left.\frac{\partial S}{\partial T}\right|_p + \left(\left.\frac{\partial V}{\partial T}\right|_p\right)^2 \frac{1}{\partial V/\partial p|_T}\right\} \ , \end{aligned}$$

where use was made of the relation

$$\left.\frac{\partial S}{\partial p}\right|_T = -\frac{\partial^2 G}{\partial p \partial T} = -\left.\frac{\partial V}{\partial T}\right|_p \ ,$$

that follows from (2.5c). The difference of c_p and c_V then becomes

$$c_p - c_V = -T\left(\left.\frac{\partial V}{\partial T}\right|_p\right)^2 \frac{1}{\left.\frac{\partial V}{\partial p}\right|_T} \ .$$

From the general formula (2.27) one concludes

$$\left.\frac{\partial V}{\partial T}\right|_p = -\left.\frac{\partial V}{\partial p}\right|_T \left.\frac{\partial p}{\partial T}\right|_V \quad \text{and hence}$$

$$c_p - c_V = T\left.\frac{\partial V}{\partial T}\right|_p \left.\frac{\partial p}{\partial T}\right|_V \ .$$

Furthermore, from the Definition 2.2, (2.5c), there follows $S = -\partial G/\partial T$, $V = \partial G/\partial p$ and, hence, also

$$\left.\frac{\partial V}{\partial T}\right|_p = -\left.\frac{\partial S}{\partial p}\right|_T \ .$$

Finally, the Definition 2.3 and (2.7c) yield the formulae $p = -\partial K/\partial V$ and $S = -\partial K/\partial T$, which give

$$\left.\frac{\partial p}{\partial T}\right|_V = -\left.\frac{\partial S}{\partial V}\right|_T .$$

This shows that the difference of c_p and c_V, divided by T, depends on partial derivatives of the entropy by V and p, respectively, taken at constant temperature,

$$\frac{1}{T}\left(c_p - c_V\right) = \left.\frac{\partial S}{\partial p}\right|_T \left.\frac{\partial S}{\partial V}\right|_T .$$

This yields the limit (2.57d). The four results (2.57a)–(2.57d) are proven.

Let $S^{(X)}(T) = S(T, N, X)$ be the function that one generates if besides the number of particles N one fixes the variable X. By the third law—and with the same assumption as before (nondegenerate ground state)—this curve tends to the origin of the (T, S)-plane for all admissible values of the variable X. For example, for two values X_1 and X_2 of X this could look as sketched in Fig. 2.12. If one now tries to reach the origin $(S_0 = 0, T_0 = 0)$ by moving back and forth between these two curves, by following alternatively adiabatics and isothermals, the drawing suggests that this might not be possible with a finite number of steps. Although this is not a real proof it seems plausible that the absolute zero remains unreachable.

Remarks

i) It is instructive to realize that this heuristic reasoning is applicable also when the lowest value of the entropy is different from zero, $S_0 \neq 0$. In the case of a degenerate ground state, too, the absolute zero $T_0 = 0$ cannot be reached in a finite number of steps.

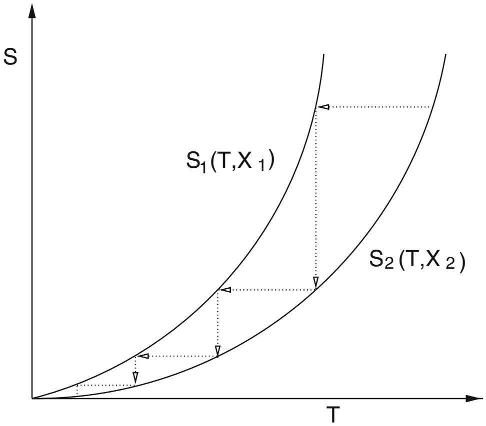


Fig. 2.12 A system moves between two curves with fixed values X_1 and X_2 of the variable X, respectively, alternatively along adiabatics and along isothermals, towards the absolute zero

ii) If it is true that the absolute zero cannot be reached in a finite number of steps then it follows that there is no Carnot engine in which the absolute temperature of the "lower" reservoir is equal to zero. If this were so, yet, the thermal efficiency (2.45) of the Carnot engine would be

$$\eta_C(T_1, T_2 = 0) = 1 - \left.\frac{\sqrt{T_1 T_2} - T_2}{T_1 - \sqrt{T_1 T_2}}\right|_{T_2=0} = 1 \; .$$

Expressed differently this means: There is no Carnot cycle whose efficiency is equal to 1. The efficiency η_C is always truly smaller than one.

2.8 More Properties of the Entropy

In this section we summarize a few more properties of the entropy function. It will turn out that the most important property is that this function is a *concave* function.

Starting from the differential form (1.34a),

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}E + \frac{p}{T}\,\mathrm{d}V - \frac{\mu_C}{T}\,\mathrm{d}N \; , \tag{2.59}$$

which is equivalent to the Gibbs fundamental form (1.34b), one notices that the function S grows monotonously both with the energy E and with the volume V: Indeed, one has

$$\left.\frac{\partial S}{\partial E}\right|_{(N,V)} = \frac{1}{T} \quad \text{and} \quad \left.\frac{\partial S}{\partial V}\right|_{(E,N)} = \frac{p}{T} \; .$$

As the temperature is always positive, the function S, at fixed number of particles N and fixed volume V, grows monotonously with the energy. If the pressure p is positive then S grows monotonously also with V, while E and N have fixed values.

The entropy is an extensive quantity, i.e. it is additive in its arguments. Another way of expressing this is to say it is *homogeneous of degree 1*. The reader is reminded here of the definition of homogeneous functions:

Definition 2.9 (Homogeneous Function of Degree N) A continuous function $f(X)$ is said to be *homogeneous of degree N*, if it fulfills the condition

$$f(\lambda X) = \lambda^N f(X) \quad \text{for} \quad \lambda > 0 \; . \tag{2.60}$$

Here the argument X may be a tuple of the kind $X = (x_1, x_2, \ldots, x_n)$.

Homogeneous functions have the property

$$\sum_{i=1}^{n} x_i \frac{\partial f}{\partial x_i} = Nf(X) \; ; \tag{2.61}$$

(This is Euler's theorem for homogeneous functions). With the entropy function in mind let X denote all of its arguments, i.e. $X = (E, N, V)$. The function S being homogeneous means that we have

$$S(\lambda X) = \lambda S(X) \; , \quad \lambda > 0 \; , \quad \text{and} \tag{2.62a}$$

$$E\frac{\partial S}{\partial E} + N\frac{\partial S}{\partial N} + V\frac{\partial S}{\partial V} = S(E, N, V) \; . \tag{2.62b}$$

From (2.59) and (2.62b) follows a simple functional dependence of S,

$$S = \frac{1}{T}\left\{E + pV - \mu_C N\right\} \; . \tag{2.63}$$

This relation is called the *homogeneity relation.*

To conclude this section we prove that the entropy is a *concave* function

Theorem 2.5 *If X denotes the state variables of a thermodynamic system then for all $t \in [0, 1]$ and for any two states X_1 and X_2 of the system*

$$S\big(tX_2 + (1-t)X_1\big) \geq tS(X_2) + (1-t)S(X_1) \; . \tag{2.64}$$

The entropy is a concave function of its variables.

Proof Consider two thermodynamic systems Σ_1 and Σ_2 which consist of the same substance—a gas, for example,—and which are in the states X_1 and X_2, respectively. The fact that the substance is the same in both, means that the entropy $S(X)$ is the same *function* for both systems. As long as the systems are isolated from each other their total entropy is equal to the sum $S(X_1) + S(X_2)$. However, if they are in contact, the entropy is $S(X_1 + X_2)$. By the second law we have

$$S(X_1 + X_2) \geq S(X_1) + S(X_2) \; . \tag{2.65a}$$

Furthermore, as the function S is homogeneous of degree 1, this implies

$$S\left(\tfrac{1}{2}(X_1 + X_2)\right) = \frac{1}{2}S(X_1 + X_2) \geq \frac{1}{2}\left\{S(X_1) + S(X_2)\right\} \; . \tag{2.65b}$$

In a next step consider the function $S(t(n,p)X_2 + [1 - t(n,p)]X_1)$ at the values

$$t(n,p) = \frac{p}{2^n} \quad \text{with} \quad n \in \mathbb{N}_0 \quad \text{and} \quad p = 0, 1, \ldots, 2^n \; .$$

The values of $t(n,p)$ for the first three values of n are listed in the following scheme

p n	0	1	2	3	4
0	0	1			
1	0	$\frac{1}{2}$	1		
2	0	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	1

If t equals zero or one, the inequality (2.64) is trivially true. For $t = 1/2$ it was already verified by (2.65b). Therefore, it holds for the values $n = 0$ and $n = 1$. This may be used to construct a proof by induction:

Assume that the inequality is fulfilled for an arbitrary, finite number n and for all $p \in [0, 1, \ldots, 2^n]$,

$$S\left(t(n,p)X_2 + [1 - t(n,p)]X_1\right) \geq t(n,p)S(X_2) + [1 - t(n,p)]S(X_1) \; .$$

As $t(n+1,p) = t(n,p)/2$ the inequality (2.65b) yields

$$\begin{aligned}
&S\left(t(n+1,p)X_2 + [1 - t(n+1,p)]X_1\right) \\
&\quad = S\left(\tfrac{1}{2}\left\{t(n,p)X_2 + [2 - t(n,p)]X_1\right\}\right) \\
&\quad \geq \tfrac{1}{2}\left\{S(t(n,p)X_2) + S([2 - t(n,p)]X_1)\right\}
\end{aligned}$$

The function S is homogeneous of degree 1. Therefore, the right-hand side of this inequality is

$$\begin{aligned}
&\tfrac{1}{2}\left\{S(t(n,p)X_2) + S([2 - t(n,p)]X_1)\right\} \\
&\quad = \tfrac{1}{2}t(n,p)S(X_2) + \left(1 - \tfrac{1}{2}t(n,p)\right)S(X_1) \\
&\quad = t(n+1,p)S(X_2) + \left(1 - t(n+1,p)\right)S(X_1) \; .
\end{aligned}$$

As this holds for all n and for all p and as the entropy S is a continuous function, the inequality (2.64) is true for all values of $t \in [0, 1]$. This proves the theorem.

In conclusion, we note that the entropy is a *concave* function of its arguments (see also the Definition 1.13). In proving this property we used only the continuity of the function S but we did not assume that it were differentiable.

Geometric Aspects of Thermodynamics

3

3.1 Introduction

This chapter deals with mathematical aspects of thermodynamics most of which will be seen to be primarily of geometrical nature. Starting with a short excursion to differentiable manifolds we summarize the properties of functions, of vector fields and of one-forms on thermodynamic manifolds. This summary centers on exterior forms over Euclidean spaces and the corresponding differential calculus. In particular, one-forms provide useful tools for the analysis of thermodynamics. A theorem by Carathéodory is developed which is closely related to the second law of thermodynamics. The chapter closes with a discussion of systems which depend on two variables and for which there is an interesting analogy to classical mechanics.

3.2 Motivation and Some Questions

As was seen in the first two chapters, thermodynamical systems in equilibrium are described mathematically by low-dimensional differentiable *manifolds* M_Σ. One defines a theoretical framework which serves to formulate thermodynamics and statistical mechanics in mathematical terms. The first questions to answer are: Of what kind are the appropriate physical objects and what are the observables which are defined on these manifolds? The *variables* S (entropy), E (energy), T (temperature) etc. which characterize a specific thermodynamical state, in general, are piecewise continuous *functions* on M_Σ.

The differential forms $\mathrm{d}E$, $T\,\mathrm{d}S$, $p\,\mathrm{d}V$, $\mu_C\,\mathrm{d}N$, …, are *one-forms* on M_Σ. For example the one-form $T\,\mathrm{d}S =: \alpha$ describes an amount of heat, $p\,\mathrm{d}V =: \omega$ an amount of work, delivered by or taken from the system, both of which appear in the first law,

$$\mathrm{d}E = \alpha + \omega \tag{3.1}$$

F. Scheck, *Statistical Theory of Heat*, Graduate Texts in Physics,
DOI 10.1007/978-3-319-40049-5_3

(the number of particles being held fixed). The way they are constructed they are fairly simple: The one-form $T\,\mathrm{d}S$, for instance, contains the function $T(S, N, V)$ as a coefficient and $\mathrm{d}S$ as a base one-form. In (3.1) neither α nor ω are *closed,* i.e. there are no functions $f^{(\alpha)}$ or $f^{(\omega)}$ such that α or ω could be written as their total differentials,

$$\alpha \neq \mathrm{d}f^{(\alpha)} \quad \text{or} \quad \omega \neq \mathrm{d}f^{(\omega)} \,.$$

In contrast, according to (3.1), their sum is an *exact* form and therefore is closed, $\mathrm{d} \circ \mathrm{d}E = \mathrm{d}\alpha + \mathrm{d}\omega = 0$. This is a mathematical expression of the first law of thermodynamics.

In the description of thermodynamical processes the calculation of the increase of entropy involves integrals of the form

$$\Delta S = \int_\gamma \frac{\alpha}{T} \quad \text{or} \quad \oint_\gamma \frac{\alpha}{T} \,, \tag{3.2a}$$

i.e. open or closed path integrals for processes or cycles, respectively. Similarly, in calculating the amount of heat that is absorbed or delivered in a process, one calculates integrals of the form

$$Q(\gamma) = \int_\gamma \alpha \,. \tag{3.2b}$$

In either case these are integrals of one-forms which are evaluated along paths on M_Σ.

In Chap. 2 we also studied the role of coordinate transformations in thermodynamics. These are changes of variables of state, effected by means of Legendre transforms relating convex (or concave) functions. This tells us that the formulae of classical thermodynamics which, at first sight, may seem somewhat confusing, build on a differential geometric structure which basically is simple. For example, traditional concepts like the notion of “latent heat” have a simple and perspicuous definition in differential geometric terms. Without prior knowledge of and reference to this underlying mathematical structure this term would require a lengthy and fairly complicated definition.

The purpose of the next section is, firstly, to summarize some important definitions of differential geometry, and, secondly, to formulate thermodynamics as we know it up to this point, in a novel and more transparent manner before proceeding to the statistical aspects of the theory of heat.

3.3 Manifolds and Observables

3.3.1 Differentiable Manifolds

There is a qualitative definition of a differentiable manifold which is simple and which is intuitively clear: An n-dimensional differentiable manifold is a space which *locally* “looks like an $\mathbb{R}^n$”. More precisely and in more detail this describes the following definition

Definition 3.1 (Smooth Manifold) A smooth manifold is a finite-dimensional topological space M with dimension $\dim M = n$ which can be covered by a countable set of open neighbourhoods U_i and for which there are charts (φ_i, U_i)

$$\varphi_i : U_i \longrightarrow \varphi_i(U_i) \subset \mathbb{R}^n , \tag{3.3}$$

such that the mappings φ_i are homeomorphisms while the transition mappings between any two charts $(\varphi_j \circ \varphi_i^{-1})$ are diffeomorphisms.

As a reminder note that every map φ_i is a homeomorphism, that is to say, is unique and invertible, and is continuous in either direction. Every transition map $(\varphi_k \circ \varphi_j^{-1})$ relates two copies of $\mathbb{R}^n$ and is not only bijective but is also differentiable in either direction. For the example of Fig. 3.1 two open neighbourhoods on a torus T^2 were chosen which overlap partially. The hatched areas in the two copies of

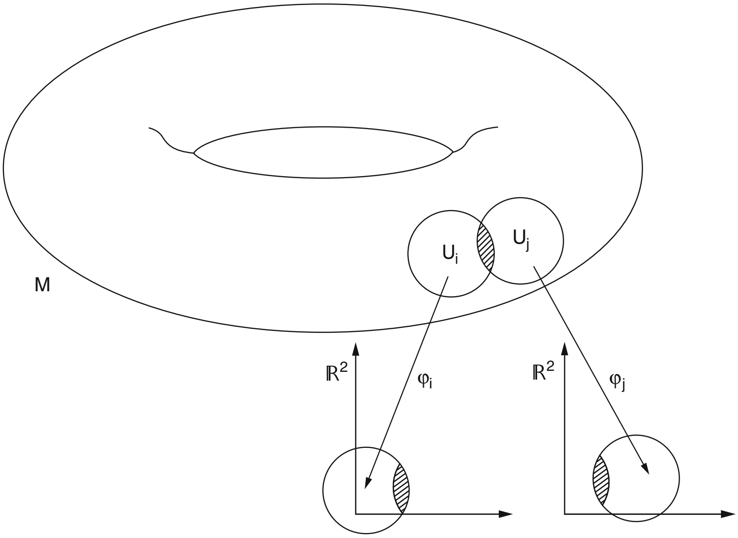


Fig. 3.1 The torus T^2 as an example for a differentiable manifold. In charts, any open neighbourhood on T^2 is mapped to an open neighborhood in the plane $\mathbb{R}^2$. If two such neighborhoods overlap so do their images

$\mathbb{R}^2$ are the images of this overlap in the two charts. In this common domain the two charts are interrelated by the diffeomorphism $(\varphi_i \circ \varphi_j^{-1})$ and its inverse $(\varphi_j \circ \varphi_i^{-1})$.

A *differentiable structure* $(M, \mathcal{A})$, built on M, needs an additional input: A *complete atlas* $\mathcal{A}$. This is defined as follows:

Definition 3.2 (Complete Atlas) A set $\mathcal{A}$ of charts on the smooth manifold M is a complete atlas if it fulfills the following conditions:

- (i) Every point $p \in M$ of the manifold is contained in at least one chart;
- (ii) Any two pairs of charts (φ_i, U_i) and (φ_k, U_k) are interrelated by a *smooth transition map*. If the two charts have no points in common, they are said to be smoothly overlapping by definition.
- (iii) Every chart which overlaps smoothly with all other charts, is already contained in the atlas.

Example 3.1 (Euclidean Space) The coordinates of a point of the manifold provide a simple example for functions on M. Let $p \in U \subset M$ be an arbitrary point within the domain of the chart (φ, U) (the index which served to distinguish the charts, for simplicity, is dropped here) such that one has

$$\varphi \,:\, U \to \mathbb{R}^n \,:\, p \mapsto \varphi(p) = \left(x^1_{(\varphi)}(p), \ldots, x^n_{(\varphi)}(p)\right)^T \ .$$

The coordinate number k of p in $\mathbb{R}^n$ is represented by $x^k_{(\varphi)}(p)$. Therefore, considering the mapping

$$f^k \,:\, \mathbb{R}^n \to \mathbb{R} \,:\, \varphi(p) \mapsto x^k_{(\varphi)}(p)$$

one sees that the composition of φ and of f^k, $(f^k \circ \varphi)$, is a function on $U \subset M$,

$$\begin{aligned} &\left(f^k \circ \varphi\right) \text{ is } \varphi \,:\, U \to \mathbb{R}^n \ , \text{ followed by } f^k \,:\, \mathbb{R}^n \to \mathbb{R} \ , \\ &\text{with } \ p \mapsto \varphi(p) \quad \text{and} \quad \varphi(p) \mapsto x^k_{(\varphi)}(p) \ . \end{aligned}$$

It maps the point p onto its k-th coordinate.

If M itself is the Euclidian space $\mathbb{R}^n$, the set $(f^1, f^2, \ldots, f^n)$ yields the identical mapping id $: \mathbb{R}^n \to \mathbb{R}^n$. This yields an atlas which contains only one chart. Expressed differently, this means that the manifold $M = \mathbb{R}^n$ is identified with the chart $\mathbb{R}^n$. This reflects the well-known experience that the Euclidian space $\mathbb{R}^n$ can be described in the same kind of space. So to speak it is described “by itself”.

But is this atlas complete? In answering this question one realizes that the identity id together with all diffeomorphisms

$$\Phi \,:\, \mathbb{R}^n \longrightarrow \mathbb{R}^n \ ,$$

which are compatible with the identity, provide a complete atlas. This is the well-known assertion that all those local coordinate systems are admissible which are related smoothly to the identity and to all other local coordinate systems. Independently of which set of coordinates one chooses, one stays always within the same differentiable structure $(M, \mathcal{A})$.

3.3.2 Functions, Vector Fields, Exterior Forms

Functions on M play the familiar role of mappings from M to the real numbers

$$f : M \longrightarrow \mathbb{R} : p \longmapsto f(p) , \tag{3.4a}$$

—independently of whether M is a Euclidean space or not. However, in asking whether a function is differentiable one must be more careful: Indeed, if M is not a Euclidean space differentiability on M is not defined a priori. It is defined, however, on maps describing the manifold which, by definition, are Euclidean. Therefore, a function f is said to be *smooth* if

$$\left(f \circ \varphi^{-1}\right) : \varphi(U) \subset \mathbb{R}^n \longrightarrow \mathbb{R} \tag{3.4b}$$

is differentiable. As a rule, smooth functions on manifolds are even C^∞. This is a meaningful definition because the composite mapping $(f \circ \varphi^{-1})$ leads from a chart $\varphi(U) \subset \mathbb{R}^n$ to the reals $\mathbb{R}$, via the manifold, so that one can decide in the usual way whether it is smooth.

The set of all smooth functions on M is denoted by $\mathfrak{F}(M)$.

The definition of *vector fields* is modeled on the directional derivative of a function along vectors. For example, assume we are given a tangent vector v in the point p whose decomposition in an arbitrary basis $\{\hat{\boldsymbol{e}}_i\}$ has the components v^i, $v = \sum_{i=1}^n v^i \hat{\boldsymbol{e}}_i$. For $f : M \to \mathbb{R}$ the directional derivative along v is given by

$$v(f) \equiv \mathrm{d}f(v) = \sum_{i=1}^n v^i \left.\frac{\partial f}{\partial x^i}\right|_{x=p} . \tag{3.5}$$

By abstraction, one draws from this concrete example the characteristic properties of tangent vectors and, more generally, of vector fields, viz.

$$v\,(c_1 f_1 + c_2 f_2) = c_1 f(v_1) + c_2 f(v_2) \qquad (\mathbb{R}\text{-linearity}) ,$$

$$v(f_1 \cdot f_2) = f_1(p) v(f_2) + v(f_1) f_2(p) \qquad (\text{Leibniz rule}) .$$

By letting the point p scan the manifold M, the set of local tangent vectors becomes a vector *field*

$$V : \mathfrak{F}(M) \longrightarrow \mathfrak{F}(M) \,, \tag{3.6a}$$

whose action on smooth functions is defined locally by

$$\big(Vf\big)(p) := v_p(f) \,, \quad f \in \mathfrak{F}(M) \,, \quad \text{for all} \quad p \in M \,. \tag{3.6b}$$

This definition also answers the question of differentiability of vector fields in a clear and simple manner: A vector field is *smooth* if for all smooth functions f the function (Vf) is again a smooth function.

Locally, i.e. in charts, there exist bases $\{\hat{\boldsymbol{e}}_i\}$—as above—, or, as a special case, *base fields* $\{\partial_i\}$, with reference to a specific chart φ, which are given by

$$\partial_i^{(\varphi)} \quad \text{with} \quad \partial_i^{(\varphi)}\Big|_p (f) := \frac{\partial\left(f \circ \varphi^{-1}\right)}{\partial f^i}\,(\varphi(p)) \,. \tag{3.6c}$$

A smooth vector field V then has the local representation

$$v = \sum_{i=1}^{n} v^i \partial_i \,, \tag{3.6d}$$

the coefficients $v^i = v^i(p)$ being smooth functions. Of course, if M is a Euclidean space $\mathbb{R}^n$ the nested formula (3.6c) simplifies and becomes

$$\partial_i|_p\,(f) = \frac{\partial f}{\partial x^i}(p) \,.$$

As the Euclidean space can be described by means of a single chart, it is no longer necessary to refer to a local chart φ.

In the description of thermodynamic processes we will need another class of geometric objects: *exterior differential forms* and, in particular, among these the *one-forms*. In this case, too, the directional derivative (3.5) in the space $\mathbb{R}^n$ provides an instructive example. Indeed, this formula may be understood as the action of the total differential of a function f,

$$\mathrm{d}f = \sum_{i=1}^{n} \frac{\partial f}{\partial x^i}\,\mathrm{d}x^i,$$

on the tangent vector v along which the derivative is to be taken. Still another way of formulating this is the following: Suppose the smooth vector field V whose local representative is the tangent vector v, is the tangent vector field of a smooth *curve*

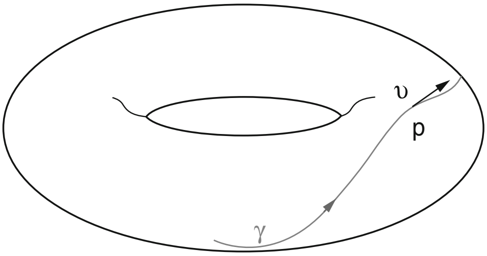


Fig. 3.2 Example for a curve on the torus T^2. In the point p it has the tangent vector v

γ on M

$$\gamma : \mathbb{R}_t \longrightarrow M \, . \tag{3.7}$$

As shown in Fig. 3.2 at $t = t_p$ the curve goes through the point p, the tangent vector in p is v. The directional derivative in the point p, taken along the vector v, is given by

$$\left.\frac{\mathrm{d}}{\mathrm{d}t} f(\gamma(t))\right|_{t=t_p} \equiv \mathrm{d}f(v)|_p \, . \tag{3.8}$$

Seen in a more formal way $\mathrm{d}f$ is a mapping which maps the element $v \in T_pM$ of the tangent space in p to a real number. Therefore, $\mathrm{d}f$ by itself is an element of the cotangent space T_p^*M, i.e. of the space which is the dual space of T_pM.

Like for local representations of vector fields, the coordinate functions of Example 3.1 play a special role. In a somewhat simplified notation one denotes them by x^i but one should keep in mind that they are coordinates in a local neighborhood U of a point $p \in M$. Their differentials $\mathrm{d}x^i$ yield a basis of T_p^*M, the cotangent space in the point p. This basis is dual to the basis $\{\partial_k\}$ of T_pM. This means that

$$\mathrm{d}x^i(\partial_k) = \delta^i_k = \frac{\partial x^i}{\partial x^k} = \partial_k(x^i) \, . \tag{3.9}$$

This prepares the ground for a definition of smooth one-forms:

Definition 3.3 (Smooth One-Forms) The locally defined forms $\{\mathrm{d}x^i\}$, $i = 1, \dots, n$, are called *base oneforms*. Every form which admits the local decomposition

$$\omega = \sum_{i=1}^{n} \omega_i(x) \, \mathrm{d}x^i \, , \tag{3.10a}$$

the coefficients $\omega_i(x)$ being smooth functions, is called a *smooth* differential form of degree 1 or, for short, a *smooth one-form*. The coefficients are obtained from the action of the one-form on the corresponding base fields, viz.

$$\omega_i(x) = \omega\left(\partial_i\right) \; . \tag{3.10b}$$

(The action of the one-form ω on the base field ∂_i yields the function $\omega_i(x)$.)

Example 3.2 (Two Simple Cases)

(i) Let g be a C^∞-function on $\mathbb{R}^n$. Its total differential reads

$$\mathrm{d}g = \sum_{i=1}^{n} \frac{\partial g}{\partial x^i} \mathrm{d}x^i \; .$$

Its coefficients in the basis $\mathrm{d}x^i$ are the partial derivatives $\partial g / \partial x^i$ which, by the assumption, are smooth functions. Hence, $\mathrm{d}g$ is a smooth one-form.

(ii) On the Euclidean space $M = \mathbb{R}^3$ let $\boldsymbol{V}$ be the tangent vector field of a smooth curve γ and let $\boldsymbol{F}$ be a physical, smooth force field. On Euclidean spaces and using Cartesian coordinates one can identify *contra*variant components F^i with *co*variant components F_i. Therefore the expression

$$\omega = \sum_{i=1}^{3} F_i(\boldsymbol{x})\, \mathrm{d}x^i$$

is a smooth one-form. Letting this form act on a vector field $\boldsymbol{V}$, one obtains

$$\omega(\boldsymbol{V}) = \sum_{i=1}^{3} F_i(\boldsymbol{x}) V^i(\boldsymbol{x}) = \boldsymbol{F} \cdot \boldsymbol{V} \; .$$

The physical interpretation of this formula is obvious: This is the work done by the force $\boldsymbol{F}$ in a motion along the curve γ.

3.3.3 Exterior Product and Exterior Derivative

One-forms may be used to construct skew-symmetric products which are defined as follows:

Definition 3.4 (Exterior Products of One-Forms) Let $\omega_1, \omega_2, \ldots, \omega_k$ be smooth one-forms, and let $V_1, V_2, \ldots, V_k$ be smooth vector fields on $\mathbb{R}^n$, where k should be smaller than or at most equal to n, $k \leq n$. The *exterior product* of the k one-forms, $\omega_1 \wedge \cdots \wedge \omega_k$, is defined by its action on k arbitrary smooth vector fields by the determinant

$$(\omega_1 \wedge \omega_2 \wedge \cdots \wedge \omega_k)\,(V_1, V_2, \ldots, V_k) \\ = \det \begin{pmatrix} \omega_1(V_1) & \omega_1(V_2) & \cdots & \omega_1(V_k) \\ \omega_2(V_1) & \omega_2(V_2) & \cdots & \omega_2(V_k) \\ \vdots & \vdots & \cdots & \vdots \\ \omega_k(V_1) & \omega_k(V_2) & \cdots & \omega_k(V_k) \end{pmatrix} . \tag{3.11}$$

Remarks

(i) For the example of two one-forms, $k = 2$, (3.11) gives

$$(\omega_1 \wedge \omega_2)\,(V_1, V_2) = \omega_1(V_1)\omega_2(V_2) - \omega_1(V_2)\omega_2(V_1)\ . \tag{3.11a}$$

In dimension 3 this is a formula which is closely related to the cross product in $\mathbb{R}^3$. For instance, consider the flux of a vector field $\boldsymbol{V}$ on $\mathbb{R}^3$ across the surface spanned by two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$,

$$\Phi_{\boldsymbol{V}}(\boldsymbol{a}, \boldsymbol{b}) = \boldsymbol{V} \cdot (\boldsymbol{a} \times \boldsymbol{b}) = V^1(a^2 b^3 - a^3 b^2) + \text{ cyclic perm. .} \tag{3.11b}$$

This expression suggests to define a two-form by means of the components of the vector field $\boldsymbol{V}$,

$$\eta_{\boldsymbol{V}} := V_1\, \mathrm{d}x^2 \wedge \mathrm{d}x^3 + V_2\, \mathrm{d}x^3 \wedge \mathrm{d}x^1 + V_3\, \mathrm{d}x^1 \wedge \mathrm{d}x^2\ . \tag{3.11c}$$

Indeed, by the action of this form on the pair $(\boldsymbol{a}, \boldsymbol{b})$ one obtains the function (3.11b).

(ii) The exterior product (3.11) is *totally antisymmetric*,

$$\omega_{\pi(1)} \wedge \omega_{\pi(2)} \wedge \cdots \wedge \omega_{\pi(k)} = (-)^{\pi} \omega_1 \wedge \omega_2 \wedge \cdots \wedge \omega_k\ , \tag{3.11d}$$

where π is a permutation of the numbers 1 to k, and $(-)^{\pi}$ is the sign of that permutation. This shows at once why one must have $k \le n$. For any k which is larger than n, the exterior product vanishes.

(iii) Note that in contrast to the cross product in $\mathbb{R}^3$, the exterior product is *associative*. This follows from the well-known properties of the determinant contained in the formula (3.11).

(iv) The one-forms $(\mathrm{d}x^1, \ldots, \mathrm{d}x^n)$ provide a basis for general smooth one-forms. In a similar way the exterior products $\mathrm{d}x^i \wedge \mathrm{d}x^k$ with $i < k$ form a basis for the expansion of two-forms. If the coefficients $\eta_{ik}(\boldsymbol{x})$ are smooth functions, then

$$\eta = \sum_{i<k=1}^{n} \eta_{ik}(\boldsymbol{x})\, \mathrm{d}x^i \wedge \mathrm{d}x^k \tag{3.11e}$$

is the local representation of a smooth two-form. This also tells us that the space $\Lambda^2(M)$ of two-forms over M has the dimension

$$\dim \Lambda^2(M) = \binom{n}{2} = \tfrac{1}{2}n(n-1)\,.$$

This is the number of possibilities to choose two different, ordered indices in the set $(1, 2, \dots, n)$.

This construction may be continued to forms of higher degree. For example the local k-forms $\mathrm{d}x^{i_1} \wedge \mathrm{d}x^{i_2} \wedge \dots \wedge \mathrm{d}x^{i_k}$, with $i_1 < i_2 < \dots < i_k$ an arbitrary choice of k indices from the set $(1, 2, \dots, n)$, form a basis of the space $\Lambda^k(M)$ of k-forms over M. The dimension of this space is the number of possibilities to choose the indices $i_1 < i_2 < \dots < i_k$ from the set $(1, 2, \dots, n)$, viz.

$$\dim \Lambda^k(M) = \binom{n}{k} = \frac{n(n-1)\cdots(n-k+1)}{k!}\,. \tag{3.11f}$$

With increasing k, from $k = 1$ on up, these numbers initially increase monotonously but then decrease again monotonously (they are entries of Pascal's triangle!). For $k = n$ they have decreased to $\dim \Lambda^n = 1$. This is to say that there is only one n-form.

We note, in addition, that functions may be interpreted as exterior forms of degree zero. This will become plausible in the context of the exterior derivative to be defined below.

Consider the space Λ^* of *all* exterior forms. Its dimension is seen to be

$$\begin{aligned}\dim \Lambda^* &= \binom{n}{0} + \binom{n}{1} + \binom{n}{2} + \dots \binom{n}{n-1} + \binom{n}{n} \\ &= (1+1)^n = 2^n\,.\end{aligned} \tag{3.11g}$$

The reader is invited to check this on the example of $\mathbb{R}^3$: In this case there is a single base form for zero-forms, there are three base forms for one- and for two-forms each, but only one for three-forms. In total, this gives 8, in accordance with (3.11g), $\dim \Lambda^* = 1 + 3 + 3 + 1 = 2^3$.

The generalization of the total derivative df of a smooth function f,

$$f \in \Lambda^0(M) \;:\; \mathrm{d}f \in \Lambda^1(M) \quad \text{with} \quad \mathrm{d}f = \sum_1^n \frac{\partial f}{\partial x^i}\,\mathrm{d}x^i\,, \tag{3.12}$$

to forms of higher degree is obtained by what is called the *exterior derivative* (also called *Cartan derivative*). It is defined as follows:

Definition 3.5 (Exterior Derivative) If $\overset{k}{\omega}$ is a smooth k-form, with $k < n$, the *exterior derivative* yields a map to an exterior form $\overset{k+1}{\omega}$ with degree one higher than the original form, viz.

$$\mathrm{d} : \Lambda^k(M) \longrightarrow \Lambda^{k+1}(M) \ : \ \overset{k}{\omega} \longmapsto \overset{k+1}{\omega} \ . \tag{3.13}$$

(a): For *functions* f it coincides with the total differential $\mathrm{d}f$;
(b): It fulfills the *graded* Leibniz rule:

$$\text{With } \overset{k}{\omega} \in \Lambda^k \quad \text{and} \quad \overset{l}{\omega} \in \Lambda^l \quad \text{one has}$$

$$\mathrm{d}\left(\overset{k}{\omega} \wedge \overset{l}{\omega}\right) = \left(\mathrm{d}\,\overset{k}{\omega}\right) \wedge \overset{l}{\omega} + (-)^k \overset{k}{\omega} \wedge \left(\mathrm{d}\,\overset{l}{\omega}\right) . \tag{3.14}$$

In a local coordinate representation of the k-form

$$\overset{k}{\omega} = \sum_{i_1 < \ldots < i_k} \omega_{i_1 \ldots i_k}(x)\, \mathrm{d}x^{i_1} \wedge \cdots \wedge \mathrm{d}x^{i_k} \tag{3.15a}$$

its exterior derivative yields the $(k+1)$-form

$$\mathrm{d}\,\overset{k}{\omega} = \sum_{i_1 < \ldots < i_k} \mathrm{d}\omega_{i_1 \ldots i_k}(x) \wedge \mathrm{d}x^{i_1} \wedge \cdots \wedge \mathrm{d}x^{i_k} \ . \tag{3.15b}$$

Remark The formula (3.15b) contains the exterior product of the total differential of the coefficient function $\omega_{i_1 \ldots i_k}(x)$ with the ordered base one-forms $\mathrm{d}x^{i_1}$ to $\mathrm{d}x^{i_k}$. This product generates a $(k+1)$-form, (3.15b). If one wishes to decompose this new form in terms of a linear combination of exterior products of $k+1$ base one-forms, one must express the total differential $\mathrm{d}\omega_{i_1 \ldots i_k}(x)$ in terms of partial differentials of $\omega_{i_1 \ldots i_k}(x)$, using (3.12), and of base one-forms. In a second step the base one-forms may be ordered in increasing degree from left to right.

Example 3.3 (Twofold Exterior Derivative) The exterior derivative of a smooth function yields its total differential

$$\mathrm{d}\,\overset{0}{\omega} = \sum_{i=1}^{n} \frac{\partial\,\overset{0}{\omega}}{\partial x^i}\,\mathrm{d}x^i \ .$$

Taking the exterior derivative of this new function one obtains

$$\mathrm{d}\left(\mathrm{d}\overset{0}{\omega}\right)=\sum_{i=1}^{n}\left(\mathrm{d}\frac{\partial\overset{0}{\omega}}{\partial x^i}\right)\wedge\mathrm{d}x^i=\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\partial^2\overset{0}{\omega}}{\partial x^j\partial x^i}\,\mathrm{d}x^j\wedge\mathrm{d}x^i$$
$$=\sum_{j<i=1}^{n}\left\{\frac{\partial^2\overset{0}{\omega}}{\partial x^j\partial x^i}-\frac{\partial^2\overset{0}{\omega}}{\partial x^i\partial x^j}\right\}\mathrm{d}x^j\wedge\mathrm{d}x^i=0\,.$$

Here use was made of the fact that the exterior product $\mathrm{d}x^j\wedge\mathrm{d}x^i$ is antisymmetric, while the mixed second derivatives are symmetric. Note that in the second term of the second line, the indices were interchanged.

This example illustrates a general property of the exterior derivative. If it is applied twice in succession the result is always zero,

$$\mathrm{d}^2\equiv\mathrm{d}\circ\mathrm{d}=0\,. \tag{3.16}$$

The formula (3.16) is the generalization of the formulae

$$\mathbf{rot}\,\mathbf{grad}=0\quad\text{and}\quad\mathbf{div}\,\mathbf{rot}=0\,,$$

that are well known from $\mathbb{R}^3$. The latter are the subject of the following example,

Example 3.4 (Exterior Forms on Euclidean $\mathbb{R}^3$) On the space $\mathbb{R}^3$ whose metric is $\mathbf{g}=\operatorname{diag}(1,1,1)$, there are four spaces of exterior forms $\Lambda^k(\mathbb{R}^3)$ whose dimensions are, respectively,

$$\dim\Lambda^0=1=\dim\Lambda^3\,,\quad\text{and}$$
$$\dim\Lambda^1=\binom{3}{1}=3=\binom{3}{2}=\dim\Lambda^2\,. \tag{3.17a}$$

The components of a given vector field $\boldsymbol{a}=\sum_{i=1}^{3}a^i(\boldsymbol{x})\partial_i$, by the identification $a_i(\boldsymbol{x})=a^i(\boldsymbol{x})$, may be used to construct the one-form

$$\overset{1}{\omega}_{\boldsymbol{a}}=\sum a_i(\boldsymbol{x})\,\mathrm{d}x^i\,. \tag{3.17b}$$

The exterior derivative of this form yields a two-form which is obtained be means of the rule (3.15b).

$$\begin{aligned}
\mathrm{d}\overset{1}{\omega}_{\boldsymbol{a}} &= \sum \mathrm{d}a_i(\boldsymbol{x}) \wedge \mathrm{d}x^i = \sum_{i,j} \frac{\partial a_i}{\partial x^j}\, \mathrm{d}x^j \wedge \mathrm{d}x^i \\
&= \left(-\frac{\partial a_1}{\partial x^2} + \frac{\partial a_2}{\partial x^1}\right) \mathrm{d}x^1 \wedge \mathrm{d}x^2 + \left(-\frac{\partial a_2}{\partial x^3} + \frac{\partial a_3}{\partial x^2}\right) \mathrm{d}x^2 \wedge \mathrm{d}x^3 \\
&\quad + \left(\frac{\partial a_3}{\partial x^1} - \frac{\partial a_1}{\partial x^3}\right) \mathrm{d}x^1 \wedge \mathrm{d}x^3 \qquad (3.17c) \\
&= (\nabla \times \boldsymbol{a})_3\, \mathrm{d}x^1 \wedge \mathrm{d}x^2 + (\nabla \times \boldsymbol{a})_1\, \mathrm{d}x^2 \wedge \mathrm{d}x^3 + (\nabla \times \boldsymbol{a})_2\, \mathrm{d}x^3 \wedge \mathrm{d}x^1 \,.
\end{aligned}$$

The coefficients of this two-form are seen to be the components of the curl of $\boldsymbol{a}$, $\nabla \times \boldsymbol{a}$. Taking, as a special case, $\boldsymbol{a} = \nabla f$ with f a smooth function, one has $\mathrm{d}f = \overset{1}{\omega}_{\nabla f}$. By a second action of the exterior derivative, one recovers the well-known formula

$$\mathrm{d} \circ \mathrm{d}f = 0 \longleftrightarrow \mathbf{rot}\,\mathbf{grad} = 0 \,. \qquad (3.17d)$$

Similarly, if the exterior derivative acts on $\mathrm{d}\overset{1}{\omega}_{\boldsymbol{a}}$ one finds

$$\mathrm{d} \circ \mathrm{d}\overset{1}{\omega}_{\boldsymbol{a}} = 0 \longleftrightarrow \mathbf{div}\,\mathbf{rot} = 0 \,. \qquad (3.17e)$$

The result (3.17d) is an equation with three components because $\mathrm{d} \circ \mathrm{d}f$ is a two-form and because the dimension of the space of two-forms is 3, $\dim \Lambda^2(\mathbb{R}^3) = 3$. In contrast, the result (3.17e) has only one component because the space of three-forms on $\mathbb{R}^3$ is one-dimensional.

3.3.4 Null Curves and Standard Forms on $\mathbb{R}^n$

In adiabatic processes the system goes through equilibrium states along curves γ on M_Σ for which the integral (3.2b) vanishes. This holds not only *globally* for given initial and final points of γ but also *locally* along arcs $\Delta\gamma$ of the curve. In coordinates of a chart an integral of this kind is

$$\int_{\Delta\gamma} \alpha = \int_t^{t+\Delta t} \mathrm{d}t \left[\sum_{i=1}^{n} a_i\,(x(t))\, \dot{x}^i(t) \right] ,$$

where $\dot{x}$ is the vector tangent to the curve in the point x. The right-hand side of this equation contains (in square brackets) the action of the one-form α on the tangent vector field $\dot{\gamma}$ of the curve γ, expressed in local coordinates and at the point

$x = \varphi(p)$, $p \in M$. These integrals can be zero if and only if the action $\alpha(\dot{\gamma})$ gives zero at every point on the curve γ. For instance, in the second part of the Example 3.2 the formula $\omega(\dot{\boldsymbol{\gamma}}) = 0$ would mean that the force field $\boldsymbol{K}$ is perpendicular to the velocity at every point of the trajectory.

This example motivates two further definitions which are useful and important for the theory of heat:

Definition 3.6 (Null Space and Null Curve of a One-Form)

(i) Let α be a smooth one-form on the manifold M, p a point of M and T_pM the tangent space in p. The subspace of all those tangent vectors $w \in T_pM$ for which $\alpha(w) = \sum a_i w_p^i = 0$, is called the *null space of the one-form* α *in the point* p. The null space is a vector space, its dimension is $(n-1)$.

(ii) A curve

$$\gamma \ : \ \mathbb{R}_t \longrightarrow M \ : \ t \longmapsto \gamma(t)$$

defined on M is called *null curve of the one-form* α*,* if for all values of t its velocity field $\dot{\gamma}(t)$ is contained in the null space of α.

The following theorem is tailored perfectly to the description of adiabatic processes in thermodynamics.

Theorem 3.1 On One-Forms on $\mathbb{R}^n$ (Carathéodory) *Let* α *be a one-form on* $M = \mathbb{R}^n$ *with the following property: In every neighborhood of any point* $p \in M$ *there are points* q *which cannot be linked to* p *by a null curve. With this assumption there are functions* f *and* g *such that the one-form can be represented locally by*

$$\alpha = f \, \mathrm{d}g \, . \tag{3.18}$$

Instead of a formal proof which would be simple but somewhat lengthy, we prefer to exhibit the plausibility of this result by means of some examples.

If a one-form can be written as $\alpha = f \mathrm{d}g$ and if f is a constant then $\mathrm{d}\alpha = \text{constant} \cdot \mathrm{d}^2 g = 0$. In this case α is a *closed* form. Therefore, by Poincaré's lemma, it can be written locally as the differential $\alpha = \mathrm{d}h$ of a smooth function h. Note that on a Euclidean space $M = \mathbb{R}^n$ this holds not only locally but also globally.

If the function f is not constant then $\mathrm{d}\alpha$ is not equal to zero, $\mathrm{d}\alpha = \mathrm{d}f \wedge \mathrm{d}g \neq 0$. However, the exterior product of α and $\mathrm{d}\alpha$ is zero,

$$\alpha \wedge \mathrm{d}\alpha = f \,\mathrm{d}g \wedge \left(\mathrm{d}f \wedge \mathrm{d}g + f \,\mathrm{d}^2 g\right) = -f \,\mathrm{d}g \wedge \mathrm{d}g \wedge \mathrm{d}f = 0 \, ,$$

This follows from the antisymmetry of the wedge product. Thus, one-forms of the kind of (3.18) have the property that either $\mathrm{d}\alpha = 0$ or $\alpha \wedge \mathrm{d}\alpha = 0$. In either case there are points in a neighborhood of p which cannot be linked to p by a null curve. This is seen as follows:

(a) If $\mathrm{d}\alpha = 0$ and therefore $\alpha = \mathrm{d}h$, every path integral from p to q is given by

$$\int_{\Delta\gamma} \alpha = h(q) - h(p) \; .$$

Though this vanishes if q lies on a surface $h(p) = \text{const.}$ there are always points in every neighborhood of p, for which $h(q) \neq h(p)$ and, hence, for which the integral is not zero.

(b) In case only $\alpha \wedge \mathrm{d}\alpha = 0$ holds true, that is, if α has the form $\alpha = f\,\mathrm{d}g$, then a curve γ is null curve of α if and only if it is null curve of the one-form $\mathrm{d}g = \alpha/f$. Indeed, the definition of a null curve holds also for arbitrarily small arcs of curve, that is, holds point-wise,

$$\int_{\Delta\gamma} \alpha = \int_{\Delta\gamma} f\,\mathrm{d}g = 0 \Longleftrightarrow \int_{\Delta\gamma} \mathrm{d}g = \int_{\Delta\gamma} \frac{1}{f}\alpha = 0 \; .$$

As there are always points for which $\int_{\Delta\gamma} \mathrm{d}g$ is different from zero, see e.g. case (a), this holds also for $\int_{\Delta\gamma} \alpha$.

Thus, it remains to show:

(c) If α fulfills neither $\mathrm{d}\alpha = 0$ nor $\alpha \wedge \mathrm{d}\alpha = 0$ and, hence, is not of the form $f\,\mathrm{d}g$, then *every* point p can be joined to any other point q by a null curve. This is shown by means of the following construction. Without loss of generality we may choose the points p and q to have the coordinates $p = (0, 0, 0)^T$ and $q = (a, b, c)^T$. It is then sufficient to find an example for a path that joins p to q for which $\int \alpha = 0$. It turns out that this is always possible independently of the values of a, b and c (see Exercise 3.6).

This construction is particularly simple if one chooses the coordinates such that in case (a) α takes the form $\alpha = \mathrm{d}x^3$, while in case (b) it takes the form $\alpha = x^1\,\mathrm{d}x^2$. Both forms are generic in the sense that they describe the general case.

In $\mathbb{R}^3$ a one-form α which obeys neither $\mathrm{d}\alpha = 0$ nor $\alpha \wedge \mathrm{d}\alpha = 0$ can be written generically as $\alpha = x^1\,\mathrm{d}x^2 + \mathrm{d}x^3$. Indeed, one verifies that

$$\alpha \wedge \mathrm{d}\alpha = \mathrm{d}x^3 \wedge \mathrm{d}x^1 \wedge \mathrm{d}x^2 = \mathrm{d}x^1 \wedge \mathrm{d}x^2 \wedge \mathrm{d}x^3 \neq 0 \; .$$

This is sufficient for the case of $\mathbb{R}^3$ because in this dimension there are no higher forms than $\alpha \wedge \mathrm{d}\alpha$ (why is that so?). For Euclidean spaces $\mathbb{R}^n$ whose dimension is higher than 3, $n > 3$, one proceeds in an analogous way: Beyond the class (c) for which $\alpha \wedge \mathrm{d}\alpha \neq 0$ but $\mathrm{d}\alpha \wedge \mathrm{d}\alpha = 0$ holds true, one will ask for

(d) the one-forms for which

$$\mathrm{d}\alpha \wedge \mathrm{d}\alpha \neq 0 \,, \quad \text{but} \quad \alpha \wedge \mathrm{d}\alpha \wedge \mathrm{d}\alpha = 0 \,.$$

If it turns out that this is not possible one asks for

(e) those one-forms for which

$$\alpha \wedge \mathrm{d}\alpha \wedge \mathrm{d}\alpha \neq 0 \,, \quad \text{but} \quad \mathrm{d}\alpha \wedge \mathrm{d}\alpha \wedge \mathrm{d}\alpha = 0 \,.$$

This quest is continued until one reaches

$$\alpha \wedge \underbrace{\mathrm{d}\alpha \wedge \cdots \wedge \mathrm{d}\alpha}_{(n-1)/2} \quad \text{in } \textit{odd} \text{ dimension,}$$

$$\underbrace{\mathrm{d}\alpha \wedge \cdots \wedge \mathrm{d}\alpha}_{n/2} \quad \text{in } \textit{even} \text{ dimension.}$$

Higher forms than these exterior products do not exist. In all of these cases, by suitable choice of coordinates, one obtains generic expressions for the one-form α in terms of coordinates x^i and base one-forms $\mathrm{d}x^k$. For instance, taking the example of the class (d), one could study the one-form $\alpha = x^1\,\mathrm{d}x^2 + x^3\,\mathrm{d}x^4$, without loss of generality. Then, although $\mathrm{d}\alpha = \mathrm{d}x^1 \wedge \mathrm{d}x^2 + \mathrm{d}x^3 \wedge \mathrm{d}x^4$ and hence $\mathrm{d}\alpha \wedge \mathrm{d}\alpha = 2\,\mathrm{d}x^1 \wedge \mathrm{d}x^2 \wedge \mathrm{d}x^3 \wedge \mathrm{d}x^4 \neq 0$, the exterior product $\alpha \wedge \mathrm{d}\alpha \wedge \mathrm{d}\alpha$ vanishes also for $n > 5$.

In case of class (e), by analogy, one can choose the generic form $\alpha = x^1\,\mathrm{d}x^2 + x^3\,\mathrm{d}x^4 + \mathrm{d}x^5$, by a suitable choice of coordinates. These examples show how to proceed if the dimension n is still higher.

One then shows that with p and q being two arbitrary points in $\mathbb{R}^n$, there are always paths linking one to the other which are null curves of any such one-form. None of them fulfills the assumption in Theorem 3.1. Having verified in this way that for all one-forms that do not belong to either class (a) or class (b), any two points can be linked by a null curve, the theorem is proven.

In Exercise 3.7 the reader is invited to check this for $\mathbb{R}^6$. On the basis of the second of these examples one sees that this proof can be generalized to $\mathbb{R}^n$ without any difficulty.

3.4 The One-Forms of Thermodynamics

In this section we take up once more, at a deeper level, essential aspects of the thermodynamics of equilibrium states in a formulation that is more concise and, we hope, more transparent than the traditional presentation in the first two chapters. Also, the laws of thermodynamics as well as their implications are described in a more concise framework.

3.4.1 One-Forms of Heat and of Work

We proceed as above by representing the amount of heat which is delivered or absorbed, by a one-form α over the manifold M_Σ of equilibrium states of a given system. Note however that this description is still incomplete. In describing thermodynamic processes it is essential to state in which way heat is exchanged. This may be done by keeping the volume V fixed, or the pressure p or any other subsidiary condition. Whatever these conditions are, the amount of heat absorbed or delivered along a path γ on the manifold M_Σ of the system is calculated from the integral

$$Q(\gamma) = \int_\gamma \alpha \tag{3.19}$$

This leads to a basic definition:

Definition 3.7 An *adiabatically reversible process* is a curve on M_Σ which is null curve of α.

Note that also here we deal with a local definition, the definition holding pointwise along the curve γ.

In a similar way the one-form describing work delivered or invested, must be analyzed in terms of the set of variables it depends on and in terms of the conditions imposed on the remaining variables. In general, it will have the form

$$\omega = \sum_{i=1}^{n} \xi_i \, \mathrm{d}x^i \, . \tag{3.20}$$

The pairs consisting each of one intensive and one extensive variable, might be, for example,

$$\left(\xi_1 = -p, x^1 = V\right) \, , \qquad \left(\xi_2 = \mu_C, x^2 = N\right) \, . \tag{3.21}$$

As before p denotes the pressure, V the volume, μ_C the chemical potential and N the number of particles.

In general, neither the one-form of heat nor the one-form of work are closed, $\mathrm{d}\alpha \neq 0$ and $\mathrm{d}\omega \neq 0$. When the exterior derivative $\mathrm{d}\omega$ of a one-form ω is not zero, this means that ω cannot be written as the differential of a smooth function, $\omega \neq \mathrm{d}f$. In this case also the integral over a closed path does not vanish,

$$\omega \neq \mathrm{d}f \Longleftrightarrow \oint \omega \neq 0 \, .$$

The two one-forms α and ω are related by the *first law*. This law says that

$$\alpha + \omega = \mathrm{d}E \quad \text{and hence} \quad \mathrm{d}\,(\alpha + \omega) = \mathrm{d}^2 E = 0\;. \tag{3.22}$$

The change in energy is given by the amount of heat which is delivered or absorbed, and by the amount of work which is invested in the system or taken from it. If the change of energy vanishes then heat and work compensate accordingly.

The *second law* in turn, states that in every neighborhood of an equilibrium state X of the system Σ there exist other such states which cannot be joined to X by an adiabatically-reversible curve. This being an empirical law it follows from Theorem 3.1 that the one-form for heat can always be written as

$$\alpha = f\,\mathrm{d}g\;, \tag{3.23}$$

where f and g are smooth functions on M_Σ.

3.4.2 More on Temperature

The properties that temperature should have in the light of empirical experience were described earlier in Sect. 1.2 and in the Definition 1.2. We also formulated the so-called zeroth law of thermodynamics which says that systems that are in equilibrium with each other, have the same temperature.

Even though the result (3.23) rests on empirical evidence as well, it reaches far deeper: it rests on the second law of thermodynamics and it makes use of the Theorem 3.1 on one-forms over Euclidean spaces. In what follows we show that the expected properties of temperature follow from the general representation (3.23) and from the analysis described above.

It is instructive to start from an imagined experiment (a Gedankenexperiment): Given two initially independent systems Σ_1 and Σ_2, each in its individual equilibrium state X_1 and X_2, respectively. The symbol X stands for the thermodynamical variables which are coordinates on the manifolds M_{Σ_1} and M_{Σ_2}, respectively. Their energies are $E_1(X_1)$ and $E_2(X_2)$. When these two systems make contact, the energies and the one-forms of work are added,

$$\begin{aligned} E(X_1, X_2) &= E_1(X_1) + E_2(X_2)\;, \\ \omega(X_1, X_2) &= \omega_1(X_1) + \omega_2(X_2)\;. \end{aligned} \tag{3.24a}$$

As we will show further down, after a while the total system will reach a state of equilibrium in which the individual temperatures will tend to a common value. The equilibrium states of the combined system are states on the submanifold of $M_{\Sigma_1} \times M_{\Sigma_2}$ on which the temperatures of the subsystems are equal, $T_1 = T_2$.

Additivity as in (3.24a) also holds for the one-forms of heat $\alpha = \alpha_1 + \alpha_2$. Therefore, given the general result (3.23) for the one-form of heat, $\alpha = f\,\mathrm{d}g$,

$\alpha_1 = f_1 \, \mathrm{d}g_1, \alpha_2 = f_2 \, \mathrm{d}g_2$ one obtains

$$f \, \mathrm{d}g = f_1 \, \mathrm{d}g_1 + f_2 \, \mathrm{d}g_2 \; . \tag{3.24b}$$

As it is always possible to change the temperature of an isolated system without exchange of heat, one concludes that α_1 and $\mathrm{d}T_1$, as well as α_2 and $\mathrm{d}T_2$, are linearly independent. This is equivalent to the assertion that $\mathrm{d}g_i$ and $\mathrm{d}T_i$, $i = 1, 2$, are linearly independent. Without loss of generality one can order the thermodynamical variables such that T_i, g_i are the first two coordinates in a set $(T_i, g_i, Y_i, \ldots)$, ($i = 1$ or 2). The combined system is described by a set of variables $(T_1, T_2, g_1, g_2, Y_1, \ldots)$, or, if the temperatures have adjusted to each other, a set $(T, g_1, g_2, Y_1, \ldots)$. Using these coordinates (3.24b) tells us that $\mathrm{d}g$ is a linear combination of $\mathrm{d}g_1$ and $\mathrm{d}g_2$, i.e.—with regard to the functions proper—that g is a differentiable function of g_1 and of g_2,

$$g = G(g_1, g_2) \; .$$

Taking into account that the one-form of heat $\alpha = f \, \mathrm{d}g$ vanishes nowhere, the same result also applies to the function f. Therefore, (3.24b) can be divided by f,

$$\mathrm{d}g = \frac{f_1}{f} \mathrm{d}g_1 + \frac{f_2}{f} \mathrm{d}g_2 \; . \tag{3.24c}$$

From this one concludes the functional dependencies to be as follows

$$\frac{f_i}{f} = h_i(g_1, g_2) \quad \text{with} \quad h_i = \frac{\partial G(g_1, g_2)}{\partial g_i} \; , \; i = 1, 2 \; , \text{i.e.} \; \frac{f_1}{f_2} = \frac{h_1}{h_2} \; ,$$

and eventually

$$\ln f_1 - \ln f_2 = \ln \left(\frac{h_1}{h_2} \right) \; . \tag{3.25a}$$

The right-hand side of (3.25a) depends only on g_1 and g_2. Differentiating this equation by the temperature T its right-hand side gives zero while its left-hand side yields:

$$\frac{\partial \ln f_1}{\partial T} = \frac{\partial \ln f_2}{\partial T} \; . \tag{3.25b}$$

Clearly, the left-hand side is expected to be a function of the variables $(T, f_1, Y_1, \ldots)$, the right-hand side a function of the variables $(T, f_2, Y_2, \ldots)$. However, by the equality (3.25b) the two sides can depend only on T and they must be the same function of temperature T. As a conclusion there is a universal function $\tau(T)$ such that

$$\tau(T) = \frac{\partial \ln f}{\partial T} \,. \tag{3.25c}$$

Empirically one knows that this function vanishes nowhere. The idea then is to replace the variable T by another variable $T^{(\text{abs})} = T^{(\text{abs})}(T)$ which is chosen in such a way that

$$\frac{\partial T^{(\text{abs})}}{\partial T} \equiv \frac{\mathrm{d}T^{(\text{abs})}}{\mathrm{d}T} = \tau(T)\, T^{(\text{abs})} \,, \tag{3.26a}$$

where τ is the same function as in (3.25c). Indeed, one has

$$\frac{\partial \ln f}{\partial T^{(\text{abs})}} = \frac{1}{T^{(\text{abs})}} = \frac{\partial \ln T^{(\text{abs})}}{\partial T^{(\text{abs})}} \,. \tag{3.26b}$$

Equation (3.26a) has the general solution

$$T^{(\text{abs})} = c \exp\left\{ \int_{T_0}^{T} \mathrm{d}T'\ \tau(T') \right\} \equiv c\, \mathrm{e}^{F(T)}$$

$$\text{with} \quad F(T) = \int_{T_0}^{T} \mathrm{d}T'\ \tau(T') \,.$$

Thus, the differential equation (3.26a) fixes the temperature $T^{(\text{abs})}(T)$ up to a scale factor c. If this factor is chosen to be positive then $T^{(\text{abs})}$ is positive for all values of T. From (3.26b) one concludes that $\ln f = \ln T^{(\text{abs})} + \ln \varphi$ where the function φ cannot depend on $T^{(\text{abs})}$. By (3.25b) and by its universality one concludes in a similar way that

$$\ln f_1 = \ln T^{(\text{abs})} + \ln \varphi_1 \quad \text{and} \quad \ln f_2 = \ln T^{(\text{abs})} + \ln \varphi_2$$

where the functions φ_1 and φ_2 do not depend on $T^{(\text{abs})}$. Starting from (3.25a) one realizes that f_1 cannot depend on g_2, and, likewise f_2 cannot depend on g_1. Hence, φ_i depends only on g_i, but not on the other of the two functions. Therefore, one obtains

$$f = T^{(\text{abs})}\varphi \,, \quad f_i = T^{(\text{abs})}\varphi_i \,, \quad i = 1, 2 \,,$$

for every system. Thus, the one-form of heat has the general expression

$$\alpha = T\varphi(g)\, \mathrm{d}g \,, \tag{3.27}$$

and we know, in addition, that the function φ is strictly different from zero. Choosing now $\mathrm{d}S = \varphi\, \mathrm{d}g$—as a side remark, the notation S suggests the entropy—, one sees that S is an indefinite integral over φ and, hence, is fixed up to an additive constant.

On the basis of these arguments and considerations one draws the following conclusions: There exists a universal absolute temperature $T^{(\mathrm{abs})}$ which is defined up to a scale factor. Any specific choice for the scale for this temperature fixes the entropy S up to an additive constant. The one-form of heat is then given by

$$\alpha = T^{(\mathrm{abs})}\,\mathrm{d}S\,. \tag{3.28}$$

It has the structure (2.55c) given in the second law.

3.5 Systems Depending on Two Variables Only

This section deals with thermodynamical systems whose equilibrium states depend only on temperature T and one further variable X. As a rule this second variable will be the volume V or the pressure p. Our aim is to express the one-form of heat in terms of the base one-forms $\mathrm{d}T$ and $\mathrm{d}X$, as well as to relate it to equations of state for the system under consideration.

We start from the following observation:

Remark One should note that heat and temperature are independent notions. Knowing the temperature of a body does not imply knowledge of the total amount of heat that it contains. Indeed, adding heat to a system (or extracting heat from it) raises (or lowers) its temperature, but a certain amount of heat is used to change the volume, or the pressure, respectively. This part of the heat content is called *latent heat*.

If the variables are chosen to be the temperature T and the volume $X = V$ the one-form of heat reads

$$\alpha = \Lambda_V\,\mathrm{d}V + c_V\,\mathrm{d}T\,. \tag{3.29}$$

The base one-forms $\mathrm{d}V$ and $\mathrm{d}T$ being linearly independent, T and V may indeed serve as independent variables. The term $c_V\,\mathrm{d}T$ describes the specific heat at constant volume while the term $\Lambda_V\,\mathrm{d}V$ is the *latent* heat with respect to the volume i.e. that part of the heat which is related to a change of volume of the system.

If besides the temperature the pressure $X = p$ is the second independent variable, the one-form of heat is given by

$$\alpha = \Lambda_p\,\mathrm{d}p + c_p\,\mathrm{d}T\,. \tag{3.30}$$

In this case the term $c_p\,\mathrm{d}T$ is the specific heat at constant pressure, the first term $\Lambda_p\,\mathrm{d}p$ describes the *latent* heat with respect to pressure. This is the amount of heat which is needed for raising the pressure, or which is gained by lowering the pressure.

As the manifold of states M_Σ is two-dimensional, calculations with exterior forms become particularly simple. The space of two-forms has dimension 1. Therefore, any two smooth two-forms are proportional to each other:

$$\text{For } \omega_1, \omega_2 \in \Lambda^2(M_\Sigma) \quad \text{one has} \quad \omega_1 = f\omega_2$$

where $f \in \Lambda^0(M_\Sigma)$ is a smooth function. Provided ω_2 does not vanish one can divide by this form, thus obtaining a function $\omega_1/\omega_2 = f$. Consider as an example the two-forms $\alpha \wedge \mathrm{d}p$ and $\alpha \wedge \mathrm{d}V$. Their ratio must be a function,

$$\frac{\alpha \wedge \mathrm{d}p}{\alpha \wedge \mathrm{d}V} = f\ .$$

This ratio has a simple thermodynamic interpretation. Let $x \in M_\Sigma$ be a point on the two-dimensional manifold (i.e. a state of the system). Let $a, b \in T_xM_\Sigma$ be two linearly independent tangent vectors in x, the first of which is chosen to be an adiabatic passing through x. Then $\alpha(a) = 0$ but $\alpha(b) \neq 0$, so that one calculates

$$\begin{aligned} f(x) &= \frac{(\alpha \wedge \mathrm{d}p)(a,b)}{(\alpha \wedge \mathrm{d}V)(a,b)} = \frac{-\alpha(b)\,\mathrm{d}p(a)}{-\alpha(b)\,\mathrm{d}V(a)} \\ &= \frac{\mathrm{d}p(a)}{\mathrm{d}V(a)} \equiv \left(\frac{\mathrm{d}p}{\mathrm{d}V}\right)^{\text{(adiabatic)}}\ . \end{aligned} \tag{3.31a}$$

Choose next $u \in T_xM_\Sigma$ a vector tangent to an isothermal passing through x and take $v \in T_xM_\Sigma$ to be another tangent vector linearly independent of u. Calculate then in the same way as above the function

$$g(x) = \frac{(\mathrm{d}T \wedge \mathrm{d}p)(u,v)}{(\mathrm{d}T \wedge \mathrm{d}V)(u,v)} = \frac{\mathrm{d}p(u)}{\mathrm{d}V(u)} = \left(\frac{\mathrm{d}p}{\mathrm{d}V}\right)^{\text{(isothermal)}}\ . \tag{3.31b}$$

Taking the wedge product of α, (3.29), and of $\mathrm{d}V$, one obtains $\alpha \wedge \mathrm{d}V = c_V\,\mathrm{d}T \wedge \mathrm{d}V$. In the same way one concludes from (3.30) that $\alpha \wedge \mathrm{d}p = c_p\,\mathrm{d}T \wedge \mathrm{d}p$. Using (3.31a) and (3.31b) one obtains the relation

$$\left(\frac{\mathrm{d}p}{\mathrm{d}V}\right)^{\text{(adiabatic)}} = \gamma \left(\frac{\mathrm{d}p}{\mathrm{d}V}\right)^{\text{(isothermal)}} \qquad \text{with} \quad \gamma = \frac{c_p}{c_V}\ . \tag{3.31c}$$

The factor γ is the ratio of the specific heat at constant pressure and of the specific heat at constant volume, respectively. In the case of the ideal gas this parameter has the value $\gamma^{\text{ideal gas}} = 5/3$, see (2.25a).

The first two laws yield the following relations

$$\mathrm{d}E = \alpha - p\,\mathrm{d}V \quad (1^{\text{st}}\ \text{law})\,, \quad \alpha = T\,\mathrm{d}S \quad (2^{\text{nd}}\ \text{law}). \tag{3.32}$$

As $\mathrm{d}^2E = 0$ one concludes

$$\mathrm{d}T \wedge \mathrm{d}S = \mathrm{d}p \wedge \mathrm{d}V\ , \tag{3.33}$$

an equation that will be used repeatedly below.

Before doing so it is instructive to return for a while to the ideal gas. In the case of the ideal gas the law of Boyle-Mariotte implies that *isothermals* are contour lines of the function

$$t(p, V) := pV \tag{3.34a}$$

with $t(p, V) = kT$. From this and from (3.31c) one shows that the *adiabatics* are the contour lines of the function

$$a(p, V) := pV^{\gamma}\ . \tag{3.34b}$$

This is shown as follows: Moving along isothermals the relation $pV =$ const. yields the equation $V\,\mathrm{d}p + p\,\mathrm{d}V = 0$ and from this $\mathrm{d}p/\,\mathrm{d}V = -p/V$. In turn, along adiabatics (3.31c) yields $\mathrm{d}p/\,\mathrm{d}V = -\gamma\,p/V$. From this one concludes

$$V\,\mathrm{d}p + \gamma p\,\mathrm{d}V = 0 \quad \text{or} \quad V^{\gamma}\,\mathrm{d}p + \gamma V^{\gamma-1}p\,\mathrm{d}V = 0$$

and hence $pV^{\gamma} =$ const.

The curves $t(p, V) =$ const. are isothermals in the (p, V)-plane. The function t and the temperature T have the same contour lines, their derivatives vanish nowhere. Therefore T is a function of t, $T = T(t)$, and $T'(t) \equiv \mathrm{d}T/\,\mathrm{d}t$ is nowhere zero. A similar argument applies to the function a and the entropy variable S, so that the latter can be expressed in terms of a, $S = S(a)$. This allows to calculate the following wedge product:

$$\mathrm{d}T \wedge \mathrm{d}S = T'(t)S'(a)\,\mathrm{d}t \wedge \mathrm{d}a\ ,$$

which, by (3.33), is equal to $\mathrm{d}p \wedge \mathrm{d}V$. One first calculates $\mathrm{d}t \wedge \mathrm{d}a$ for the example of the ideal gas,

$$\begin{aligned} \mathrm{d}t \wedge \mathrm{d}a &= (p\,\mathrm{d}V + V\,\mathrm{d}p) \wedge \left(p\gamma V^{\gamma-1}\,\mathrm{d}V + V^{\gamma}\,\mathrm{d}p\right) \\ &= (\gamma-1)pV^{\gamma}\,\mathrm{d}p \wedge \mathrm{d}V = (\gamma-1)a(p,V)\,\mathrm{d}p \wedge \mathrm{d}V \,. \end{aligned}$$

It follows from these equations that

$$\frac{\mathrm{d}p \wedge \mathrm{d}V}{\mathrm{d}t \wedge \mathrm{d}a} = \frac{1}{(\gamma-1)a(p,V)} \,. = T'(t)S'(a)$$

Obviously, this equation is invariant under the simultaneous replacements $T' \mapsto cT'$ and $S' \mapsto (1/c)S'$ with c a positive real number. Therefore, without loss of generality, one can scale the variables such that $T' = 1$ is obtained. If this is done, one has

$$S'(a) = \frac{1}{(\gamma-1)a(p,V)}$$

and hence

$$T(t) = t + T_0 \,, \quad S(a) = \frac{1}{\gamma-1}\ln a + S_0 \,. \tag{3.35}$$

As was to be expected, the entropy is determined up to an additive constant term. In contrast, the constant T_0 can be determined and also the energy can be calculated. This is done as follows: Starting from the system of equations

$$\begin{aligned} \mathrm{d}t &= p\,\mathrm{d}V + V\,\mathrm{d}p \,, \\ \mathrm{d}a &= p\gamma V^{\gamma-1}\,\mathrm{d}V + V^{\gamma}\,\mathrm{d}p \end{aligned}$$

using (3.34a) and (3.34b) which yield the relation $V^{\gamma-1} = a/t$, one concludes

$$p\,\mathrm{d}V = \frac{\mathrm{d}a}{(\gamma-1)V^{\gamma-1}} - \frac{\mathrm{d}t}{\gamma-1} \,.$$

With these intermediate results and making use of the first law, one obtains

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V = T_0\frac{1}{\gamma-1}\,\mathrm{d}\,(\ln a) + \frac{dt}{\gamma-1} \,. \tag{3.36}$$

If one now considers adiabatic expansion of the (ideal) gas, the temperature does not change, by (2.32), and also the energy remains unchanged, i.e. $\mathrm{d}E = 0$. This conclusion is compatible with the result (3.36) only if

$$T_0 = 0\,. \tag{3.37}$$

Using this result, (3.36) can be integrated. One obtains

$$E = \frac{1}{\gamma - 1} t \tag{3.38}$$

(This holds up to an additive constant which, however, is irrelevant here.). If, as before, all quantities are defined referring to 1 mol, then $E = (3/2)RT$, according to (2.25b), $t = RT$, where T is the temperature measured in Kelvin.

It is instructive to derive the relation between the specific heats of the ideal gas also in this framework. Inserting the one-form of heat (3.30) into the first law (3.32), one obtains

$$\mathrm{d}E \wedge \mathrm{d}p = \alpha \wedge \mathrm{d}p - p\,\mathrm{d}V \wedge \mathrm{d}p = c_p\,\mathrm{d}T \wedge \mathrm{d}p - p\,\mathrm{d}V \wedge \mathrm{d}p$$

and from this the formula

$$c_p = \frac{(\mathrm{d}E + p\,\mathrm{d}V) \wedge \mathrm{d}p}{\mathrm{d}T \wedge \mathrm{d}p} = \left.\frac{\mathrm{d}E}{\mathrm{d}T}\right|_p + p\left.\frac{\mathrm{d}V}{\mathrm{d}T}\right|_p\,.$$

From $\mathrm{d}E/\mathrm{d}T|_p = R/(\gamma - 1)$ and from $\mathrm{d}V/\mathrm{d}T|_p = R/p$ follows the relation (2.25a),

$$c_p = c_V + R\,.$$

The example of the ideal gas above gives a hint at how to proceed in the case of *real* gases. As before, the isothermals are the contour lines of the function $t(p, V)$, (3.34a), $t(p, V) = \text{const}$. However, this function is no longer equal to pV. The ratio $\gamma = c_p/c_V$ whose value was $5/3$ for the ideal gas, is no longer a constant. Equation (3.31c) is now used to determine the adiabatics. In a next step, one determines the functions $T'(t)$ and $S'(a)$, from which follow the entropy S and, eventually, the energy E using the relation $\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V$.

Remark Consider as an example the enthalpy $H = pV + E$, cf. Definition 2.1. From the first law (3.32) one has $\mathrm{d}H = \alpha + V\,\mathrm{d}p$. Thus, for constant pressure $\mathrm{d}H$ is the amount of heat which is transmitted to or from the system. It is useful to represent the behaviour of real gases in the form of diagrams in the (H, p)-plane, that is to say, with enthalpy along the abscissa and pressure along the ordinate. Diagrams of this type are called *Mollier-diagrams* (after R. Mollier, 1863–1935, professor in Dresden). In this plane one draws the contour lines $S = \text{const.}$, $V = \text{const.}$ and $T = \text{const.}$ If two of these are given, the diagram may be used to determine the functions p, V, H, T and S, as well as the energy from $E = H - pV$.

3.6 *An Analogy from Mechanics

Instead of the enthalpy one may as well consider the *free enthalpy*, Definition 2.2,

$$G = -TS + E + pV \,. \tag{3.39a}$$

Dividing this definition by RT it reads

$$\hat{G} \equiv \frac{G}{RT} = -\hat{S} + \beta E + \nu V \,, \tag{3.39b}$$

where we introduced the abbreviations

$$\hat{S} \equiv \frac{S}{R} \,, \quad \beta = \frac{1}{RT} \quad \text{and} \quad \nu = \beta p \,. \tag{3.39c}$$

The product (RT) having the physical dimension of energy it is seen that the quantities $\hat{G}$ and $\hat{S}$ are dimensionless. Using the first law and the second law (3.32) one obtains the relation $\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V$, or, after division by RT,

$$\mathrm{d}\hat{S} = \beta\,\mathrm{d}E + \nu\,\mathrm{d}V \,, \tag{3.40a}$$

and, hence, the relation

$$\mathrm{d}\hat{G} = E\,\mathrm{d}\beta + V\,\mathrm{d}\nu \,. \tag{3.40b}$$

Consider a four-dimensional Euclidean space $\mathbb{R}^4$, with the choice of coordinates (β, ν, E, V). On this space define the two-form

$$\Omega := \mathrm{d}\beta \wedge \mathrm{d}E + \mathrm{d}\nu \wedge \mathrm{d}V \,. \tag{3.41a}$$

Then, on the whole space $\mathbb{R}^4$ one has

$$\Omega = \mathrm{d}\,(\beta\,\mathrm{d}E + \nu\,\mathrm{d}V) \quad \text{and} \quad \Omega = -\mathrm{d}\,(E\,\mathrm{d}\beta + V\,\mathrm{d}\nu) \,. \tag{3.41b}$$

Note, however, that with (3.40a) or (3.40b) the two-form Ω vanishes. Therefore, the system evolves on a submanifold $\mathcal{L} \subset \mathbb{R}^4$ of $\mathbb{R}^4$ on which Ω is equal to zero. A similar situation is well-known from mechanics where it is called a *Lagrange manifold* [see Marsden and Ratiu (1994)]. We consider a canonical system with one degree of freedom and describe this system by means of two different sets (q, p) and (Q, P) of canonically conjugate variables. On the direct product $\mathbb{R}^4 \simeq T^*\mathbb{R} \times T^*\mathbb{R}$ of its phase space $T^*\mathbb{R}$ with itself we define the two-form

$$\Omega^{(\mathrm{M})} := \mathrm{d}q \wedge \mathrm{d}p - \mathrm{d}Q \wedge \mathrm{d}P \,. \tag{3.42}$$

A two-dimensional submanifold $\mathcal{L}$ of this four-dimensional space is called *Lagrange manifold* if the two-form $\Omega^{(\mathrm{M})}$, restricted to $\mathcal{L}$, vanishes.

In order to better understand this analogy consider a somewhat more general framework. Let M_1 and M_2 be two symplectic manifolds of dimension 2. These manifolds are characterized by the data (M_1, ω_1) and (M_2, ω_2), respectively, with ω_1 and ω_2 nondegenerate closed two-forms. Consider the diffeomorphism

$$\varphi \ : \ M_1 \longrightarrow M_2 \ .$$

Its graph is denoted $\Gamma(\varphi) \subset M_1 \times M_2$, the inclusion in $M_1 \times M_2$ is

$$i_\varphi \ : \ \Gamma(\varphi) \longrightarrow M_1 \times M_2 \ .$$

With π_i denoting the projection of the product manifold $M_1 \times M_2$ onto M_i, define the two-form

$$\Omega^{(\mathrm{M})} := \pi_1^* \omega_1 - \pi_2^* \omega_2 \tag{3.43}$$

where, as usual, π_i^* is the pull-back of the projection. The composition of the two mappings $\pi_1 \circ i_\varphi$ yields the projection from the product manifold $M_1 \times M_2$ onto M_1, provided it is restricted to the graph $\Gamma(\varphi)$. Furthermore, on $\Gamma(\varphi)$ one has $\pi_2 \circ i_\varphi = \varphi \circ \pi_1$. Therefore one has

$$i_\varphi^* \Omega^{(\mathrm{M})} = \left(\pi_1|_{\Gamma(\varphi)}\right)^* \left(\omega_1 - \varphi^* \omega_2\right) \ .$$

The mapping $(\pi_1|_{\Gamma(\varphi)})^*$ is injective. Therefore $i_\varphi^* \Omega^{(\mathrm{M})} = 0$ holds if and only if φ is a symplectic mapping. In this case $\Gamma(\varphi)$ is a submanifold of $M_1 \times M_2$ on which the symplectic form Ω is defined.

One may go one step further in the analysis of the canonical transformation considered above. If there is a one-form θ such that $\Omega^{(\mathrm{M})} = -\mathrm{d}\theta$ holds true, then locally there exists a function $S : \Gamma(\varphi) \to \mathbb{R}$ on $\Gamma(\varphi)$ such that $i_\varphi^* \theta = \mathrm{d}S$. The function S is a generating function for the canonical transformation φ.

These matters which are familiar in canonical mechanics can be translated directly to the thermodynamics of two-dimensional systems discussed in Sect. 3.5. The role of the pairs of coordinates (q, p) and (Q, P) is taken over by the pairs (ν, β) and (E, V), respectively. Alternatively, one may choose (β, V) or (ν, E) as the local coordinates, provided the differentials of any of these pairs are linearly independent. Note that this corresponds to the four possible choices in defining generating functions for canonical transformations in Hamiltonian mechanics. Suppose a submanifold $\mathcal{L} \subset M_1 \times M_2$ of the direct product of the manifold M_1, described by (ν, β), and of M_2, described by (E, V), is a Lagrange manifold. Then, restricting to $\mathcal{L}$ one has

$$\mathrm{d}\left(\beta \, \mathrm{d}E + \nu \, \mathrm{d}V\right) = 0 \ . \tag{3.44a}$$

There exists a function $\hat{S}$ defined on $\mathcal{L}$ such that

$$\mathrm{d}\hat{S} = \beta\,\mathrm{d}E + \nu\,\mathrm{d}V\ . \tag{3.44b}$$

With respect to the second pair of coordinates and for the restriction to $\mathcal{L}$, one has in exactly the same way,

$$\mathrm{d}\left(-E\,\mathrm{d}\beta - V\,\mathrm{d}\nu\right) = 0\ . \tag{3.45a}$$

Locally there exists a function $\hat{G}$ defined on $\mathcal{L}$, for which

$$\mathrm{d}\hat{G} = E\,\mathrm{d}\beta + V\,\mathrm{d}\nu\ . \tag{3.45b}$$

In Fig. 3.3 a manifold is sketched (center of the figure) together with the two equivalent ways of describing it.

The first and the second law of thermodynamics imply the following assertion:

Theorem *The manifold of equilibrium states of a two-dimensional thermodynamic system is a Lagrange submanifold of the four-dimensional space described by the coordinates* (β, ν, E, V).

If instead one takes E and V as the local coordinates, one has

$$\mathrm{d}\hat{S} = \frac{\partial\hat{S}}{\partial E}\mathrm{d}E + \frac{\partial\hat{S}}{\partial V}\mathrm{d}V$$

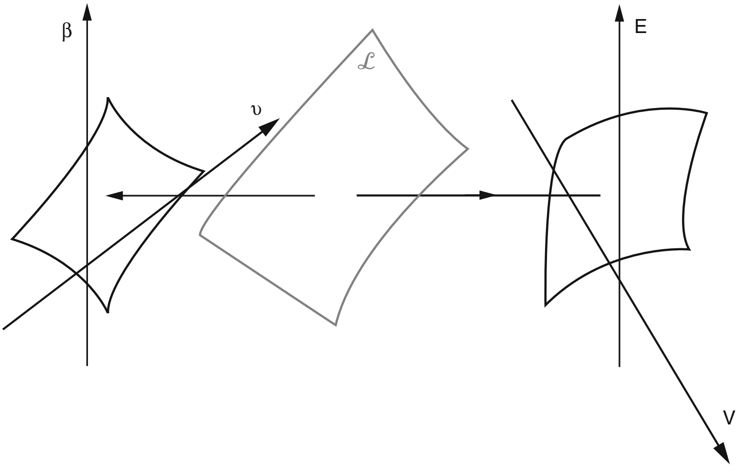


Fig. 3.3 A Lagrange manifold $\mathcal{L}$ which is a submanifold of the direct product of two two-dimensional manifolds M_1 and M_2, $\mathcal{L} \subset M_1 \times M_2$, is described in two different ways

and therefore

$$\beta = \frac{\partial \hat{S}}{\partial E} \quad \text{or} \quad \frac{1}{T} = \frac{\partial S}{\partial E} \,, \tag{3.46a}$$

$$\nu = \frac{\partial \hat{S}}{\partial V} \quad \text{or} \quad \frac{p}{T} = \frac{\partial S}{\partial V} \,. \tag{3.46b}$$

The first of these equations is known from (1.26), while the second is known from Definition 1.8.

If one uses the variables β and V as an alternative and the two-form

$$\Omega = -\mathrm{d}\left(E\,\mathrm{d}\beta - \nu\,\mathrm{d}V\right) \ ,$$

then on the Lagrange manifold one obtains

$$E\,\mathrm{d}\beta - \nu\,\mathrm{d}V \equiv -\mathrm{d}\hat{F} \,,$$

where $\hat{F}$ stands for the function

$$\hat{F} = -\beta E + \hat{S} \,. \tag{3.47}$$

This is verified by calculating

$$\mathrm{d}\hat{F} = -E\,\mathrm{d}\beta - \beta\,\mathrm{d}E + \mathrm{d}\hat{S} = -E\,\mathrm{d}\beta + \nu\,\mathrm{d}V \,.$$

Here, use was made of the two laws of thermodynamics (3.32) which yield the relation

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}E + p\,\mathrm{d}V \,.$$

The function $Z = \hat{F}$ is called *Massieu function.* The function $\hat{F}$, upon multiplication with $(-RT)$, is identical with the free energy (1.42a).

Probabilities, States, Statistics

4

4.1 Introduction

In this chapter we clarify some important notions which are relevant in a statistical theory of heat: The definitions of *probability measure,* and of *thermodynamic states* are illustrated, successively, by the classical Maxwell-Boltzmann statistics, by Fermi-Dirac statistics and by Bose-Einstein statistics. We discuss observables and their eigenvalue spectrum as well as entropy and we calculate these quantities for some examples. The chapter closes with a comparison of statistical descriptions of classical and quantum gases.

4.2 The Notion of State in Statistical Mechanics

In the preceding chapters we described thermodynamic systems mostly by *global* state variables such as pressure, temperature, entropy and others. These were quantities which are averages of properties the system has at small scales. To quote an example, let us return to Chap. 1 where we defined the microcanonical example as the set of all microstates which belong to a given macrostate with energy E, particle number N and volume V, cf. Definition 1.5. Statistical mechanics digs deeper because it identifies the microscopic states and provides them with specific probabilities. For example, one divides the phase space of an N-particle system into cells of size $\omega_0 = h^3$ and one studies the probabilities of different assignments of the N particles to these cells, for various macroscopic states.

A somewhat more abstract formulation is the following: Given a space M, (viz. in the example, the set of cells in phase space) which we assume to be finite, for the sake of simplicity. On this space define a set $\mathcal{A}$ of subsets as well as a *measure* μ with the property that $\mu(A)$ is a positive semi-definite number, for all $A \in \mathcal{A}$, i.e. $\mu(A) \in \mathbb{R}_+$. The set $\mathcal{A}$ of subsets is assumed to be closed with respect to countable

F. Scheck, *Statistical Theory of Heat*, Graduate Texts in Physics,
DOI 10.1007/978-3-319-40049-5_4

union, intersection and complement. A few examples will be helpful in illustrating these matters:

Example 4.1 Let M be a *countable* set and $\mathcal{A}$ the set of *all* subsets of M. In particular, the individual points $m \in M$ are subsets $\{m\}$ of M and, therefore, are contained in $\mathcal{A}$. The measure μ has the value $\mu(\{m\})$ at the point $m \in M$. A subset $A \in \mathcal{A}$ composed of such points yields the value

$$\mu(A) = \sum_{m \in A} \mu(\{m\}) \; . \tag{4.1}$$

Now, if f is a function on the space M which describes some physical quantity, its integral over M is given by

$$\int \mu\, f = \sum_{m \in M} \mu(\{m\}) f(m) \; . \tag{4.2}$$

It is equal to the sum of the values of the function at the points m, multiplied by the weights $\mu(m)$.

In the example of the integers $M = \mathbb{Z}$, the measure is

$$\mu(M) = \sum_{m=-\infty}^{+\infty} \mu(\{m\}) \; . \tag{4.3a}$$

If M is the set of the integers, including zero, $M = \mathbb{N}_0$, one has

$$\mu(M) = \sum_{m=0}^{\infty} \mu\left(\{m\}\right) \; . \tag{4.3b}$$

Of course, nothing is said about convergence of these sums. However, even in case the sum does not converge, the integral $\int \mu\, f$ may exist. One says that the function f is integrable if this series converges absolutely.

Another example is the real axis, $M = \mathbb{R}$. In this case $\mathcal{A}$ is assumed to contain all intervals $[a, b]$, and the measure is taken to be $\mu([a, b]) = b - a$. This is a Lebesgue measure. If f is piecewise continuous and if it decreases sufficiently fast at infinity, then

$$\int \mu\, f = \int_{-\infty}^{+\infty} \mathrm{d}x\, f(x)$$

is the familiar integral over the real axis.

In the statistical theory of heat one needs a *normalized* measure so that it may serve as a probability measure. It is defined as follows:

Definition 4.1 (Probability Measure) A normalized measure on the set M is called a *probability measure*, if $\mu(M) = 1$, i.e. when evaluated over all of M it yields certainty.

From the point of view of statistical mechanics a thermodynamical system is a space M of the kind described above, endowed with a measure μ. In this context the function μ can be interpreted as a measure for our knowledge about the system.

Example 4.2 Let M be a *finite* space and $\mathcal{A} = \{m\}$ the set of all subspaces. If

$$\mu(\{m\}) = 1 \quad \text{for all} \quad m \in M \, ,$$

then all states are equally probable. This measure is not normalized.

Example 4.3 Let $M = \mathbb{R}$ and let $\mathcal{A}$ be the set of all sets admitting a Lebesgue measure, i.e. $\mu([a,b]) = b - a$. In this example the a priori probabilities are proportional to the length of the intervals. The function μ as such cannot be a probability measure because $\mu(\mathbb{R})$ is infinite. However, if an integrable, positive-definite function ϱ is given for which $\int_{-\infty}^{+\infty} \mathrm{d}x \varrho(x) = 1$, then this defines a probability measure on the real axis $\mathbb{R}$. One has

$$W([a,b]) = \int_a^b \mathrm{d}x \varrho(x) \, .$$

If there is a measure μ on M (which possibly is not normalized) and if ϱ an integrable, positive-definite function on M, one can construct a new measure $\varrho\mu$ for every such function. If, in addition, one normalizes this function to 1, one obtains a new probability measure.

This example suggests a further definition, viz.

Definition 4.2 (States in Statistical Mechanics) Given a measure space $(M, \mathcal{A}, \mu)$ and a positive semi-definite function ϱ on M, $\varrho \geq 0$, for which the condition

$$\int \mu\varrho = 1 \tag{4.4}$$

is fulfilled. The function ϱ describes a state in the sense of statistical mechanics.

Example 4.4 The set of all states is assumed to be $M = \mathbb{N} = \{1, 2, \ldots\}$, the measure being

$$\mu(\{k\}) = \frac{1}{k!} \, , \tag{4.5a}$$

(which is to say that the function ϱ is identically 1). This example can be illustrated as follows. We are given n "boxes" and N particles, the particles being distributed over the boxes such that there are k_1 of them in box number 1, k_2 of them in box number 2, … and k_n particles in box number n. At first we assume the particles to be *distinguishable.* As is well known the number of permutations of N particles is $N!$. However, if one accounts for their distribution over n boxes, permutations *within* a box must not be counted. This means that $N!$ is to be divided by $k_i!$, $i = 1, 2, \ldots, n$. Therefore the number of possibilities is

$$Z(N, n) = \frac{N!}{k_1!k_2!\cdots k_n!} \ . \tag{4.5b}$$

Even if one knows neither the number of particles N nor the number of states n, the probability to find k_i particles in the box number i must be proportional to $1/k_i!$. The relative a priori probability is

$$\mu\left(\{k\}\right) = \frac{1}{k!} \quad \text{(classical, distinguishable particles)} \ . \tag{4.5c}$$

In the form of (4.5c) this measure is not normalized.

Example 4.5 (Fermions) A special case of Example 4.2 which from the point of view of physics is especially important, is the following: The states are occupied by particles obeying *Fermi-Dirac statistics.* The space M consists of only two points and the measure μ has the same value on each of these points.

$$M = \{0, 1\} \ , \quad \mu(\{0\}) = \mu(\{1\}) = 1 \ . \tag{4.6a}$$

One may visualize M by boxes which can contain at most one particle. Boxes of this kind can be pure quantum states which are assigned to *one* fermion or to *none.*
As another variant of this example one may define the model as follows:

$$\begin{aligned} &M = \mathbb{N}_0 \ , \\ &\mu(\{0\}) = \mu(\{1\}) = 1 \ , \mu(\{k\}) = 0 \quad \text{for all} \quad k \geq 2 \ . \end{aligned} \tag{4.6b}$$

Among the possible occupation numbers of single particle states, $n \in \mathbb{N}_0$, only zero and one will occur. An arbitrarily chosen state is either empty, or contains at most one particle.

Example 4.6 (Bosons) The states of the countable set in Example 4.4 are occupied by particles which obey *Bose-Einstein statistics*:

$$M = \mathbb{N} = \{1, 2, \ldots\} \ , \quad \mu(\{k\}) = 1 \quad \text{for all} \quad k \ . \tag{4.7}$$

In contrast to the model of Example 4.4, the $k_i!$ permutations of the k_i particles in box number is i, must not be distinguished nor should they be counted. The relative probabilities for having k_i particles in "i" are all equal.
Note that a different interpretation of this example could be that there is only one box which may contain arbitrarily many particles. The a priori probability is the same for all particles.

Example 4.7 (Spin States) Suppose N particles are given about which no more is known than that each one of them is in either of two spin states, $\uparrow$ or $\downarrow$. In many physical situations only the difference $N(\uparrow) - N(\downarrow)$ of all particles with spin "up" and all particles with spin "down" matters. If N is *even,* $N = 2p$, and if this difference is equal to $2q$, $N(\uparrow) - N(\downarrow) = 2q$, then $N(\uparrow) = N/2 + q = p + q$ and $N(\downarrow) = N/2 - q = p - q$. In this case the set M can be restricted to what really matters, that is to the subset $M = \{-N, -N + 2, \dots, N - 2, N\}$. The number of possibilities of realizing this configuration, is

$$\binom{2p}{p+q} = \frac{(2p)!}{(p+q)!(p-q)!} = \binom{2p}{p-q} . \tag{4.8a}$$

For fixed p this function takes its largest value at $q = 0$. Therefore, the relative probability of the actual configuration is given by

$$\mu(\{2q\}) = \binom{2p}{p+q}\binom{2p}{p}^{-1} = \frac{(p!)^2}{(p+q)!(p-q)!} . \tag{4.8b}$$

For the example $N = 4$ we have $q = 0, 1$ or 2 and

$$\mu(\{0\}) = 1 , \quad \mu(\{2\}) = \frac{2}{3} \quad \text{and} \quad \mu(\{4\}) = \frac{1}{6} .$$

Whenever N is very large as compared to 1 as well as to q, $N \gg 1$ and $N \gg q$, the factorials in (4.8b) can be estimated by means of Stirling's formula for the asymptotics of the Gamma function. It is well known that for $x \gg 1$

$$\begin{aligned} x! = \Gamma(x+1) &\simeq \sqrt{2\pi}\, \mathrm{e}^{(x+1/2)\ln(x+1)-x-1} \\ &\simeq \sqrt{2\pi}\, \mathrm{e}^{(x+1/2)\ln x - x} = \sqrt{(2\pi x)} x^x \mathrm{e}^{-x} , \quad (x \gg 1) . \end{aligned}$$

This yields the following estimate,

$$\frac{(p!)^2}{(p+q)!(p-q)!} \simeq \frac{p}{\sqrt{p^2-q^2}} \frac{p^{2p}}{(p+q)^{p+q}(p-q)^{p-q}}$$

$$
\begin{aligned}
&= \frac{p}{\sqrt{p^2 - q^2}} \exp\{2p \ln p\} \\
&\cdot \exp\{-p\,[\ln(p+q) + \ln(p-q)] - q\,[\ln(p+q) - \ln(p-q)]\} \\
&\simeq \mathrm{e}^{-q^2/p} \,. \qquad (4.8\mathrm{c})
\end{aligned}
$$

Here use was made of the approximations

$$
[\ln(p+q) + \ln(p-q)] \simeq 2\ln p + \mathcal{O}\left(\frac{q^2}{p^2}\right)\,, \quad [\ln(p+q) - \ln(p-q)] \simeq \frac{q}{p}\,,
$$

and $p^2 \gg q^2$ was assumed.

Example 4.8 The preceding example can be modified as follows. With N again denoting the particle number, let

$$
M = \mathbb{Z}\,, \quad \mu(\{m\}) = \mathrm{e}^{-m^2/(2N)}\,. \qquad (4.9)
$$

This is a Gauss measure for the discrete case. The function $\mu(\{m\})$ has its maximum at $m = 0$. The larger the particle number N, the more pronounced is this maximum. Using the abbreviation $x_m := m/\sqrt{N}$, one has

$$
\mu(\{a \le x_m \le b\}) = \sum_{[a,b]} \mathrm{e}^{-x_m^2/2}\,. \qquad (4.10\mathrm{a})
$$

Divide this integral by $\sqrt{2\pi N}$ and let N go to infinity. In this limit the right-hand side of (4.10a) tends to

$$
I = \frac{1}{\sqrt{2\pi}} \int_a^b \mathrm{d}x\ \mathrm{e}^{-x^2/2}\,. \qquad (4.10\mathrm{b})
$$

This is easily verified by means of the formulae

$$
\int_a^b \mathrm{d}x\ \mathrm{e}^{-x^2/2} \simeq \sum \mathrm{e}^{-x_k^2/2}(x_{k+1} - x_k) = \frac{1}{\sqrt{N}} \sum \mathrm{e}^{-x^2/2}\,.
$$

As a result one obtains the normalized *Gauss measure*

$$
\mu([a,b]) = \frac{1}{\sqrt{2\pi}} \int_a^b \mathrm{d}x\ \mathrm{e}^{-x^2/2}\,, \qquad (4.11)
$$

which holds on the whole real axis $M = \mathbb{R}$.

4.3 Observables and Their Expectation Values

Observables are functions on the set M of possible states and take values on the real axis,

$$\mathcal{O} : M \longrightarrow \mathbb{R} \, .$$

Clearly their inverse $\mathcal{O}^{-1}([a,b])$ on an arbitrary interval $[a,b]$ of the real axis, belongs to the set $\mathcal{A}$ of all subsets of M. If $\mathcal{O}$ describes an observable and if ϱ is a state, then for every interval $[a,b] \in \mathbb{R}$ one considers the subset $A(\mathcal{O}) \equiv \mathcal{O}^{-1}([a,b])$ of M, and the integral

$$W_F([a,b];\varrho) := \int_{A(\mathcal{O})} \varrho\mu \; , \tag{4.12}$$

where μ is the measure, cf. Definition 4.2, (4.4). The integral (4.12) can be analyzed in two ways: With the assumption that $\varrho\mu$ describes the distribution of probabilities on the set M, the integral W is the probability for a point of M to lie in the subset $A(\mathcal{O}) = \mathcal{O}^{-1}([a,b])$ of M. Alternatively: the integral (4.12) is the probability for the observable $\mathcal{O}$ to take values in the interval $[a,b]$.

The observable $\mathcal{O}$ and the state ϱ, taken together, yield a probability distribution on the real axis which assigns to every interval $[a,b] \in \mathbb{R}$ the probability for the observable $\mathcal{O}$ to take values in this interval. This leads to the following

Definition 4.3 (Expectation Value of an Observable $\mathcal{O}$ in the State ϱ) The expectation value of the observable $\mathcal{O}$ is given by the integral over the whole set M

$$\langle \mathcal{O} \rangle_\varrho = \int_M \varrho\mu \; \mathcal{O} \; , \tag{4.13}$$

where μ denotes the normalized measure and ϱ denotes the state.

Example 4.9 (Phase Space of a Classical Particle) Let $M = \mathbb{R}^6$ be the phase space of a particle in classical mechanics. We describe this space by means of coordinates $(q^1, q^2, q^3, p_1, p_2, p_3)$ for position and momentum. In this example one has

$$M = \mathbb{R}^6 \; , \quad \text{with} \quad \mu = \mathrm{d}q^1\,\mathrm{d}q^2\,\mathrm{d}q^3\,\mathrm{d}p_1\,\mathrm{d}p_2\,\mathrm{d}p_3 \; . \tag{4.14a}$$

This measure is called the *Liouville measure.* The state ϱ is assumed to be a positive-definite function on $\mathbb{R}^6$ which is normalized to 1. The expectation value (4.13) is given by the integral

$$\langle \mathcal{O} \rangle_\varrho = \int_{\mathbb{R}^6} \varrho \; \mathrm{d}q^1\,\mathrm{d}q^2\,\mathrm{d}q^3\,\mathrm{d}p_1\,\mathrm{d}p_2\,\mathrm{d}p_3 \; \mathcal{O}(\boldsymbol{q},\boldsymbol{p}) \; . \tag{4.14b}$$

As an example we choose the Hamiltonian function $\mathcal{O} \equiv H(\boldsymbol{q},\boldsymbol{p})$

$$H(\boldsymbol{q},\boldsymbol{p}) = \frac{1}{2m}\left(p_1^2 + p_2^2 + p_3^2\right) + U\left(q^1, q^2, q^3\right) \ , \tag{4.14c}$$

where U denotes the potential energy. A particle which moves in a box with volume V but is not constrained any further, is described by the potential

$$U \equiv 0 \quad \text{for all} \quad \boldsymbol{q} \in V \ , \ U \equiv \infty \quad \text{for} \quad \boldsymbol{q} \in \partial V \ ,$$

that is to say, the potential vanishes inside the box, it rises to infinity on its walls. The expectation value (4.14b) is reduced to the interior of the box V in position space and it is equal to

$$\langle H \rangle_\varrho = \int_{V\times\mathbb{R}^3} \varrho(\boldsymbol{q},\boldsymbol{p})\,\mathrm{d}^3\boldsymbol{q}\,\mathrm{d}^3\boldsymbol{p}\,\frac{\boldsymbol{p}^2}{2m} \, .$$

If inside the volume V the state ϱ does not depend on the position coordinates $\boldsymbol{q}$ there remains

$$\langle H \rangle_\varrho = V \int_{\mathbb{R}^3} \varrho(\boldsymbol{p})\,\mathrm{d}^3 p\,\frac{\boldsymbol{p}^2}{2m} \, .$$

As an example we consider Maxwell's velocity distribution of Example 1.7, (1.53a),

$$\varrho(\boldsymbol{q},\boldsymbol{p}) = \frac{1}{V}\left(\frac{\beta}{2m\pi}\right)^{3/2} \mathrm{e}^{-\beta \boldsymbol{p}^2/(2m)} \ , \ \boldsymbol{q} \in V \ , \ \beta = \frac{1}{kT} \, . \tag{4.15a}$$

Making use of the calculations in (1.53b) and (1.53c) one verifies that the state (4.15a) is normalized correctly,

$$\int_{V\times\mathbb{R}^3} \varrho\mu = 1 \tag{4.15b}$$

and then calculates the expectation value

$$\langle H \rangle_\varrho = \left(\frac{\beta}{2m\pi}\right)^{3/2} \int_{\mathbb{R}^3} \mathrm{d}^3 p\,\frac{\boldsymbol{p}^2}{2m}\,\mathrm{e}^{-\beta \boldsymbol{p}^2/(2m)} = \frac{3}{2\beta} \, . \tag{4.15c}$$

Both calculations, (4.15b) and (4.15c), are checked by means of the integral formulae

$$\int_0^\infty x^2\,\mathrm{d}x\ \mathrm{e}^{-x^2} = \frac{\sqrt{\pi}}{4} \ , \quad \int_0^\infty x^4\,\mathrm{d}x\ \mathrm{e}^{-x^2} = \frac{3\sqrt{\pi}}{8}$$

and using the substitution $p = x\sqrt{2m/\beta}$ as follows:

$$\begin{aligned}
I_1 &:= \int \mathrm{d}^3\boldsymbol{p}\ \mathrm{e}^{-\beta\boldsymbol{p}^2/(2m)} = 4\pi \int_0^\infty p^2\,\mathrm{d}p\ \mathrm{e}^{-\beta p^2/(2m)} \\
&= 4\pi\left(\frac{2m}{\beta}\right)^{3/2} \int_0^\infty x^2\,\mathrm{d}x\ \mathrm{e}^{-x^2} = \left(\frac{2m\pi}{\beta}\right)^{3/2} , \\
I_2 &:= \int \mathrm{d}^3\boldsymbol{p}\ \boldsymbol{p}^2\,\mathrm{e}^{-\beta\boldsymbol{p}^2/(2m)} \\
&= 4\pi\left(\frac{2m}{\beta}\right)^{5/2} \frac{1}{2m}\int_0^\infty x^2\,\mathrm{d}x\, x^2\,\mathrm{e}^{-x^2} = \frac{3(2m\pi)^{3/2}}{2\beta^{5/2}} .
\end{aligned}$$

The result (4.15c) is the energy of the state ϱ, $E(\varrho) = \langle H\rangle_\varrho$, and, therefore, is a function on the space of states.

The notion of a state ϱ as well as the expression

$$E(\varrho) = \langle H\rangle_\varrho \tag{4.16}$$

for the energy of the state ϱ, by now, are well-defined. However, the question remains of how to describe the equilibrium states of the system. In Example 4.9 one would consider the function $\exp\{-\beta H\}$ with $\beta = 1/(kT)$. A glance at (4.15a) shows that the expression

$$\frac{1}{V}\left(\frac{\beta}{2m\pi}\right)^{3/2} \mathrm{e}^{-\beta H} \equiv \frac{1}{Z}\,\mathrm{e}^{-\beta H} \tag{4.17}$$

can indeed be interpreted as a *state*. Remaining for a while within the example, we define

$$Z := \int_{\mathbb{R}^6} \mathrm{d}^3q\ \mathrm{d}^3p\ \mathrm{e}^{-\beta H} \quad \text{and} \quad W := \ln Z . \tag{4.18a}$$

The derivative of W by the variable β yields the energy,

$$\begin{aligned}
\frac{\partial W}{\partial\beta} &= \frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\int_{\mathbb{R}^6} \mathrm{d}^3q\ \mathrm{d}^3p\ H\,\frac{1}{Z}\,\mathrm{e}^{-\beta H} \\
&= -\int_{\mathbb{R}^6} \mu\ H\,\varrho = -\langle H\rangle_\varrho \equiv -E(\varrho) .
\end{aligned} \tag{4.18b}$$

One sees also that in the model that we consider here, one has

$$\frac{\partial W}{\partial V}\,\mathrm{d}V = -\beta\omega ,$$

where ω is the one-form of work (see Exercise 4.6). Using $\omega = -p\,\mathrm{d}V$ this becomes

$$\frac{\partial W}{\partial V} = \beta p \equiv \nu \tag{4.18c}$$

[see the definition (3.39c)]. Comparing formulae (4.18b) and (4.18c) with the derivatives of the function $\hat{F}$ as defined in (3.47), by β and by V, respectively,

$$\frac{\partial \hat{F}}{\partial \beta} = -E\,, \quad \frac{\partial \hat{F}}{\partial V} = \nu\,,$$

shows that $W = \hat{F}$ is the *Massieu function* as defined in Sect. 3.6.

4.4 Partition Function and Entropy

The examples and calculations of the preceding section lead rather naturally to the following definition.

Definition 4.4 (Partition Function) Given a system $(M, \mathcal{A}, \mu)$ which is described by the Hamiltonian function H on M. The integral

$$Z := \int_M \mu\ \mathrm{e}^{-\beta H} \tag{4.19}$$

is called the *partition function* of the system.

Assume a system of the kind described above is in a state ϱ. How does one calculate its entropy $S(\varrho)$ from the given data?

Like in some of the previous cases it is useful to first study the situation in a simple model. For that purpose assume that M is a space of finite dimension $M = \{m_1, m_2, \ldots, m_k\}$. The state ϱ is defined through the knowledge of the probabilities

$$w_i = \varrho(\{m_1\})\,, \quad i = 1, 2, \ldots, k\,,$$

where w_i is the probability for an "event" in m_i. (For example, a particle located in "box" number "i" or the like). The entropy, in the sense of statistical mechanics, of a distribution described by ϱ is given by (1.12) of Definition 1.6, viz.

$$\sigma(\varrho) = -\sum_{i=1}^{k} w_i \ln w_i\ .$$

All rules and results obtained in Sect. 1.4 apply to this function.

By generalizing this example one obtains a definition of entropy:

Definition 4.5 (Entropy Function) In a system defined by the triple $(M, \mathcal{A}, \mu)$ and for a state the ϱ of this system the *entropy function* is defined by the integral

$$S(\varrho) = -k \int_M \mu \; \varrho \ln \varrho \; . \tag{4.20}$$

Here k is Boltzmann's constant (1.23).

The study of equilibrium states of a thermodynamical system or, more generally, a system of statistical mechanics, can be formulated in a rather general framework. Suppose we are given a system Σ as well as a set of (real) observables

$$(F_1, F_2, \ldots, F_n) \equiv \boldsymbol{F} \; , \quad \boldsymbol{F} \, : \, M \longrightarrow V \; . \tag{4.21a}$$

The observables are defined on M. The notation suggests to collect them in a vector-like quantity $\boldsymbol{F}$ which maps M onto a real vector space V with dimension n. Using this notation we calculate the expectation value

$$\langle \boldsymbol{F} \rangle_\varrho = \int_M \mu \; \varrho \boldsymbol{F} \; . \tag{4.21b}$$

Equilibrium states are characterized by the property of maximal entropy. Therefore, the problem gives rise to the question: What is the state ϱ in which the function $\langle \boldsymbol{F} \rangle_\varrho$ has a fixed value and whose entropy is the largest?

Denote by V^* the dual vector space of V and let $\boldsymbol{u}$ be an element of V^*. One takes the scalar product $\boldsymbol{u} \cdot \boldsymbol{F}$ of $\boldsymbol{u}$ and $\boldsymbol{F}$ and one defines the quantity

$$Z(\boldsymbol{u}) := \int_M \mu \; \mathrm{e}^{-\boldsymbol{u} \cdot \boldsymbol{F}} \; , \quad (\boldsymbol{F} : M \to V \; , \; \boldsymbol{u} \in V^*) \; . \tag{4.22}$$

As long as $Z(\boldsymbol{u})$ stays finite the function

$$\varrho_{\boldsymbol{u}} := \frac{1}{Z(\boldsymbol{u})} \mathrm{e}^{-\boldsymbol{u} \cdot \boldsymbol{F}} \tag{4.23}$$

is positive-definite and is normalized to 1,

$$\int_M \mu \; \frac{1}{Z(\boldsymbol{u})} \mathrm{e}^{-\boldsymbol{u} \cdot \boldsymbol{F}} = 1 \; .$$

Therefore, $\varrho_{\boldsymbol{u}}$ is a *state* on M. By the formula (4.20) its entropy is

$$\begin{aligned} S(\varrho_{\boldsymbol{u}}) &= -k \int \mu \, \frac{1}{Z(\boldsymbol{u})} \mathrm{e}^{-\boldsymbol{u}\cdot\boldsymbol{F}} \left(-\ln Z(\boldsymbol{u}) - \boldsymbol{u}\cdot\boldsymbol{F}\right) \\ &= k \left(\ln Z(\boldsymbol{u}) + \boldsymbol{u}\cdot \langle \boldsymbol{F}\rangle_{\varrho_{\boldsymbol{u}}}\right) \, . \end{aligned} \tag{4.24}$$

As a particularly simple example containing only one observable, take $\boldsymbol{F}$ to be the Hamiltonian function, $\boldsymbol{F} = H$. The set M is the phase space, the measure is $\mu = \mathrm{d}^3 q \, \mathrm{d}^3 p$. In this example we have $\hat{S} = S/k = Z + \beta E$, in close analogy to formula (3.47). We recall that the latter was verified by making use of the first and the second law of thermodynamics.

The following theorem applies to the entropy:

Theorem 4.1 (State of Maximal Entropy) *Assume* $\boldsymbol{u} \in V^*$ *to be chosen such that* $Z(\boldsymbol{u})$, (4.22), *is finite. With* $\varrho_{\boldsymbol{u}}$ *as defined in* (4.23) *above, let*

$$S(\varrho_{\boldsymbol{u}}) = k \left(\ln Z(\boldsymbol{u}) + \boldsymbol{u}\cdot \langle \boldsymbol{F}\rangle_{\varrho_{\boldsymbol{u}}}\right) \, . \tag{4.25a}$$

Furthermore, let ϱ *be another state of the system in which the observables* $\boldsymbol{F}$ *have the same values, i.e.*

$$\int \mu \, \varrho \boldsymbol{F} = \langle \boldsymbol{F}\rangle_{\varrho_{\boldsymbol{u}}} \, . \tag{4.25b}$$

Then one has

$$S(\varrho) \le S(\varrho_{\boldsymbol{u}}) \, ; \tag{4.25c}$$

The "smaller"-sign holds if ϱ *and* $\varrho_{\boldsymbol{u}}$ *differ on a set with positive* μ*-measure.*

Proof In a first step one shows that for all states ϱ and all elements $m \in M$ the following inequality holds true:

$$-\varrho(m) \ln \varrho(m) + \varrho(m) \ln \varrho_{\boldsymbol{u}}(m) \le \varrho_{\boldsymbol{u}}(m) - \varrho(m) \, .$$

If $\varrho(m)$ vanishes this is obvious. If $\varrho(m) > 0$ then

$$\begin{aligned} &- \varrho(m) \left[\ln \varrho(m) - \ln \varrho_{\boldsymbol{u}}(m)\right] = -\varrho(m) \ln \left(\frac{\varrho(m)}{\varrho_{\boldsymbol{u}}(m)}\right) \\ &\le \varrho(m) \left[\frac{\varrho_{\boldsymbol{u}}(m)}{\varrho(m)} - 1\right] = \varrho_{\boldsymbol{u}}(m) - \varrho(m) \, . \end{aligned}$$

In passing from the first to the second line we made use of the inequality (1.15) $-\ln x/x \le 1/x - 1$ proved in Sect. 1.4.

Integrating over M with the measure μ the right-hand side of the inequality gives zero, hence

$$-\int_M \mu\ \varrho \ln \varrho + \int_M \mu\ \varrho \ln \varrho_{\boldsymbol{u}} \le \int_M \mu\ \varrho_{\boldsymbol{u}} - \int_M \mu\ \varrho = 1 - 1 = 0\ .$$

As a consequence we obtain, quite generally,

$$-\int_M \mu\ \varrho \ln \varrho \le -\int_M \mu\ \varrho \ln \varrho_{\boldsymbol{u}}\ . \tag{4.26a}$$

This is the inequality (4.25c) as verified by the following calculation: From (4.23) one has

$$\ln \varrho_{\boldsymbol{u}} = -\ln Z(\boldsymbol{u}) - \boldsymbol{u} \cdot \boldsymbol{F}\ ,$$

and, upon multiplication with $\mu\varrho$ and integrating over M,

$$\begin{aligned}-\int_M \mu\ \varrho \ln \varrho_{\boldsymbol{u}} &= \ln Z(\boldsymbol{u}) + \int_M \mu\ \varrho \boldsymbol{u}\ \cdot \boldsymbol{F} \\ &= \ln Z(\boldsymbol{u}) + \boldsymbol{u} \cdot \langle \boldsymbol{F} \rangle_{\varrho_{\boldsymbol{u}}} = \frac{1}{k} S(\varrho_{\boldsymbol{u}})\ .\end{aligned}$$

In much the same way one calculates

$$-\int_M \mu\ \varrho \ln \varrho = \frac{1}{k} S(\varrho)\ .$$

Inserting these integrals there follows indeed

$$S(\varrho) \le S(\varrho_{\boldsymbol{u}})\ . \tag{4.26b}$$

Finally, one shows that $S(\varrho)$ is strictly *smaller* than $S(\varrho_{\boldsymbol{u}})$, $S(\varrho) < S(\varrho_{\boldsymbol{u}})$ if $\varrho(m)$ is different from $\varrho_{\boldsymbol{u}}$ for a set with positive measure (with respect to μ).

The result of this theorem is incorporated in a definition:

Definition 4.6 (Equilibrium State) Let $\boldsymbol{F}$ be an observable on the space $(M, \mathcal{A}, \mu)$. If for some $\boldsymbol{u} \in V^*$ the integral $Z(\boldsymbol{u}) = \int_M \mu\ \exp\{-\boldsymbol{u} \cdot \boldsymbol{F}\}$ is finite then

$$\varrho_{\boldsymbol{u}} = \frac{1}{Z(\boldsymbol{u})} \mathrm{e}^{-\boldsymbol{u} \cdot \boldsymbol{F}} \tag{4.27}$$

is said to be an *equilibrium state* with respect to the observable $\boldsymbol{F}$.

The results obtained in Theorem 4.1 and the Definition 4.6 are illustrated and amplified by some examples:

Example 4.10 (Grand Canonical Ensemble) The grand canonical ensemble, Definition 2.3, is described by the partition function (2.10). Therefore, in this case one has

$$\boldsymbol{u} = (\beta, -\beta\mu_C)^T\,, \quad \boldsymbol{F} = (H, N)^T\,, \quad \mu = \mathrm{d}^{3N}q\,\mathrm{d}^{3N}p\,, \tag{4.28a}$$

where $\beta = 1/kT$ and where μ_C denotes the chemical potential. The state which has maximal entropy for fixed values of H and N is given by

$$\varrho_{\boldsymbol{u}} = \frac{1}{Z(\boldsymbol{u})} \exp\{-\beta(H(q,p) - \mu_C N)\}\,, \tag{4.28b}$$

the normalization factor is calculated from the integral over phase space

$$Z(\boldsymbol{u}) = \int_{\mathbb{P}} \mathrm{d}^{3N}q\,\mathrm{d}^{3N}p\; \exp\{-\beta(H(q,p) - \mu_C N)\}\,. \tag{4.28c}$$

It is instructive to note that the *extensive* quantities H (energy) and N (particle number) take values in the vector space V while the *intensive* quantities β (replacing the temperature) and μ_C (chemical potential) take values in the dual vector space V^*.

Example 4.11 (Maxwell-Boltzmann Distribution) This example takes up Example 4.2 where we had chosen

$$M = \{m_1, m_2, \dots, m_k\}\,, \quad \mu(m_i) = 1 \tag{4.29a}$$

for all i. In the present case we take the vector space V to be one-dimensional, $V = \mathbb{R}$. Also, we assume a series of energies,

$$F(m_i) = \varepsilon_i\,, \quad \text{with} \quad \varepsilon_1 \le \varepsilon_2 \le \dots \le \varepsilon_k\,. \tag{4.29b}$$

The dual vector space of V is $V^* = \mathbb{R}$. For

$$\beta \in V^* \quad \text{let} \quad Z(\beta) = \sum_{j=1}^{k} \mathrm{e}^{-\beta\varepsilon_j}\,, \quad \left(\beta = \frac{1}{kT}\right)\,. \tag{4.29c}$$

For a given value of β the equilibrium state reads

$$\varrho_\beta(m_i) = \frac{\mathrm{e}^{-\beta\varepsilon_i}}{\sum_{j=1}^{k} \mathrm{e}^{-\beta\varepsilon_j}}\,, \tag{4.29d}$$

it describes a *Maxwell-Boltzmann distribution.* Making use of this formula one calculates the expectation value

$$\langle F\rangle_{\varrho_\beta} = \frac{1}{Z(\beta)}\sum_{j=1}^{k}\varepsilon_j \mathrm{e}^{-\beta\varepsilon_j} = -\frac{\partial}{\partial\beta}\ln Z(\beta)\ . \tag{4.29e}$$

The calculation of the negative derivative of this expectation value yields an interesting result:

$$\begin{aligned} -\frac{\partial\langle F\rangle_{\varrho_\beta}}{\partial\beta} &= \frac{\sum\varepsilon_j^2\,\mathrm{e}^{-\beta\varepsilon_j}}{\sum\mathrm{e}^{-\beta\varepsilon_j}} - \frac{\left(\sum\varepsilon_j\mathrm{e}^{-\beta\varepsilon_j}\right)^2}{\left(\sum\mathrm{e}^{-\beta\varepsilon_j}\right)^2} \\ &= \int\mu\ \varrho_\beta F^2 - \left(\int\mu\ \varrho_\beta F\right)^2 = \int\mu\ \varrho_\beta\left(F-\langle F\rangle_{\varrho_\beta}\right)^2\ . \end{aligned}$$

Excluding the exceptional case in which all energies are equal, i.e. excluding the choice $\varepsilon_1 = \varepsilon_2 = \ldots = \varepsilon_k$, this expression is always larger than zero. Therefore, the expectation value $\langle F\rangle_{\varrho_\beta}$ is a strictly monotonous, decreasing function of β, or, equivalently, a strictly monotonous, *increasing* function of temperature T. Furthermore, one has

$$\lim_{\beta\to 0}\langle F\rangle_{\varrho_\beta} = \frac{1}{k}\left(\varepsilon_1+\varepsilon_2+\ldots+\varepsilon_k\right) \equiv \bar{\varepsilon}\ , \qquad \lim_{\beta\to+\infty}\langle F\rangle_{\varrho_\beta} = \varepsilon_1\ .$$

This implies that by suitable choice of β (or the temperature) the expectation value $\langle F\rangle_{\varrho_\beta}$ can take any value between ε_1 and $\bar{\varepsilon}$. The choice of β or of T is unique.

Example 4.12 (Normal Distribution) Here we return to Example 4.3 with $M=\mathbb{R}$, $\mu([a,b]) = b-a$ and with $\mathcal{A}$ being the set of all Lebesgue measurable subsets. We choose x and its square x^2 as our observables,

$$\boldsymbol{F}\ :\ M=\mathbb{R}\to\mathbb{R}^2\ :\ x\mapsto(x,x^2)\ . \tag{4.30a}$$

With $\boldsymbol{u} = (u_1,u_2)^T$ and with the restriction $u_2>0$ one has

$$Z(\boldsymbol{u}) = \int_{-\infty}^{+\infty}\mathrm{d}x\ \mathrm{e}^{-u_1x-u_2x^2} = \sqrt{\frac{\pi}{u_2}}\,\mathrm{e}^{u_1^2/(4u_2)}\ .$$

Thus, the state with the largest entropy is

$$\varrho_{\boldsymbol{u}} = \frac{1}{Z(\boldsymbol{u})}\mathrm{e}^{-u_1x-u_2x^2} = \frac{1}{Z(\boldsymbol{u})}\mathrm{e}^{u_1^2/(4u_2)}\,\mathrm{e}^{-u_2[x+u_1/(2u_2)]^2}\ . \tag{4.30b}$$

This function is usually written in the form

$$\varrho_{m,\sigma}(x) = \frac{1}{\sigma\sqrt{2\pi}} \mathrm{e}^{-(x-m)^2/(2\sigma^2)} , \tag{4.31}$$

where m is the *mean value* of x and σ^2 denotes the *variance*. Indeed, with the definition $z := (x-m)//\sigma\sqrt{2}$ one finds

$$\langle x\rangle = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{+\infty} \mathrm{d}x\, x \mathrm{e}^{-(x-m)^2/(2\sigma^2)} = \frac{1}{\sqrt{\pi}} m \int_{-\infty}^{+\infty} \mathrm{d}z\ \mathrm{e}^{-z^2} = m ,$$

$$\langle x^2\rangle = \frac{1}{\sqrt{\pi}} \left\{ 2\sigma^2 \int_{-\infty}^{+\infty} \mathrm{d}z\, z^2 \mathrm{e}^{-z^2} + m^2 \int_{-\infty}^{+\infty} \mathrm{d}z\ \mathrm{e}^{-z^2} \right\} = \sigma^2 + m^2 ,$$

so that $\langle x^2\rangle - \langle x\rangle^2 = \sigma^2$, as expected.

The normal distribution (4.31) *for the random variable x, with given mean value m and variance σ, has maximal entropy.*

We conclude this example by an explicit calculation of the entropy. Without loss of generality one can choose the origin of the real axis such that m in (4.31) is zero. In the example studied above this means that $u_1 = 0$, $u_2 = 1/(2\sigma^2)$ and $Z(\boldsymbol{u}) = \sqrt{2\pi}\sigma$. The entropy follows either from

$$\begin{aligned}\frac{1}{k} S &= Z + \boldsymbol{u} \cdot \langle \boldsymbol{F}\rangle_{\varrho_{\boldsymbol{u}}} = \ln Z + \boldsymbol{u} \cdot \langle \boldsymbol{F}\rangle_{\varrho_{\boldsymbol{u}}} \\ &= \tfrac{1}{2} \ln 2\pi + \ln\sigma + \frac{1}{2\sigma^2} \langle x^2\rangle_{\varrho_{\boldsymbol{u}}} = \tfrac{1}{2} \ln 2\pi + \ln\sigma + \frac{1}{2} ,\end{aligned} \tag{4.32a}$$

or from the integral

$$\begin{aligned}\frac{1}{k} S &= -\int_{-\infty}^{+\infty} \mathrm{d}x\ \varrho_{\boldsymbol{u}} \ln \varrho_{\boldsymbol{u}} \\ &= \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{+\infty} \mathrm{d}x\ \mathrm{e}^{-x^2/(2\sigma^2)} \left\{ \frac{x^2}{(2\sigma^2)} + \ln\sigma + \tfrac{1}{2} \ln 2\pi \right\} \\ &= \tfrac{1}{2} + \ln\sigma + \tfrac{1}{2} \ln 2\pi .\end{aligned} \tag{4.32b}$$

If σ tends to zero, the entropy S goes to minus infinity. Question: what is the interpretation of this result?

Example 4.13 (Poisson Distribution) This example builds on Example 4.4. In detail, let

$$M = \mathbb{N} , \quad \mu(\{k\}) = \frac{1}{k!} \quad \text{and} \quad F(k) = k . \tag{4.33}$$

Choosing $\boldsymbol{u}$ to be a one-dimensional real variable β one has

$$Z(\beta) = \sum_{k=1}^{\infty} \frac{1}{k!} \mathrm{e}^{-\beta k} = \exp\{\mathrm{e}^{-\beta}\} \,. \tag{4.34a}$$

It is helpful to set $\mathrm{e}^{-\beta} =: \lambda$ so that $Z(\beta) = \mathrm{e}^{\lambda}$. Then the state with maximal entropy is

$$\varrho_\beta(k) = \frac{1}{Z(\beta)} \mathrm{e}^{-\beta k} \equiv \mathrm{e}^{-\lambda} \lambda^k \,. \tag{4.34b}$$

The probability to find the state k in a measurement is given by

$$w(k) = \mathrm{e}^{-\lambda} \frac{\lambda^k}{k!} \,. \tag{4.35}$$

This distribution is called a *Poisson distribution*, it is illustrated by Fig. 4.1. The calculation of the variable F gives the result

$$\langle F \rangle_{\varrho_\beta} = -\frac{\partial}{\partial \beta} \ln Z(\beta) = -\frac{\partial}{\partial \beta} \mathrm{e}^{-\beta} = \mathrm{e}^{-\beta} = \lambda \,.$$

This is a measure for the number of particles in "box" number k.

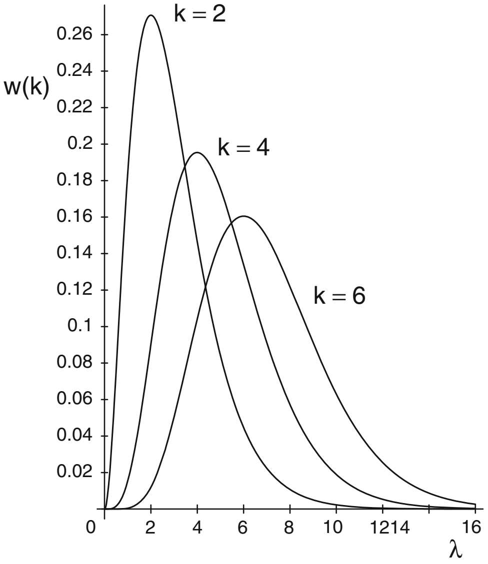


Fig. 4.1 The Poisson distribution (4.35) as a function of λ, for $k = 2$, $k = 4$ and $k = 6$

Summarizing the results obtained so far and the experience gained from the examples that we studied above, one realizes that the entropy function takes various, rather different forms. Accordingly this means that entropy allows for various different interpretations. Specifically we found the following interpretations of the entropy:

(i) The *thermodynamic entropy:* This is the entropy contained in the one-form of heat,

$$\alpha = T\,\mathrm{d}S \tag{4.36a}$$

that was the topic of Theorem 2.3, of Theorem 3.1 and of (3.28). Seen in a somewhat more general framework it contributes to Gibb's fundamental form

$$\mathrm{d}E = T\,\mathrm{d}S + \sum \xi_\alpha\,\mathrm{d}X^\alpha\ , \tag{4.36b}$$

which contains, beside the one-form of heat, the analogous one-forms for work and other contributions.

(ii) The entropy function in *statistical mechanics* contains the logarithm of the number of states characterizing the system,

$$S = k \ln \Omega(E, X^1, X^2, \ldots, X^n)\ , \tag{4.37}$$

cf. Sect. 1.4 (see also Sect. 2.4 and the equations in that section).

(iii) The form of the entropy function

$$S = -k \sum w_i \ln w_i\ , \tag{4.38}$$

in reality, refers to *information theoretic entropy* whose interpretation can be either one of the following two:

(a) The set $\{w_i\}$ describes an ensemble of admissible states. The quantity w_j yields the relative frequency of occurrence of an arbitrary state "j" in this ensemble;

(b) Alternatively, the numbers $\{w_i\}$ can be understood in terms of measure of ignorance about any particular system, w_j being the probability to find this system in the state "j".

One shows that the first of these alternatives is equivalent to (4.37). In case of a canonical ensemble one has $\langle E\rangle = \sum w_i E_i$ and, therefore,

$$\begin{aligned}\mathrm{d}\langle E\rangle &= \sum_i \mathrm{d}w_i E_i + \sum_i w_i\,\mathrm{d}E_i\\ &= \sum_i \mathrm{d}w_i E_i + \sum_\alpha \xi_\alpha\,\mathrm{d}X^\alpha \quad \text{with} \quad \xi_\alpha = \sum_i w_i \frac{\partial E_i}{\partial X^\alpha}\ .\end{aligned}$$

From (4.38) and using $\sum_i \mathrm{d}w_i = 0$ one obtains

$$\frac{1}{k}\,\mathrm{d}S = -\sum_i \mathrm{d}w_i \ln w_i - \sum_i \mathrm{d}w_i = -\sum_i \mathrm{d}w_i \ln w_i \ .$$

Inserting now $w_i = \mathrm{e}^{-\beta E_i}/Z$ one has

$$\frac{1}{k}\,\mathrm{d}S = \sum_i \mathrm{d}w_i\,(\ln Z + \beta E_i) = \beta \sum_i \mathrm{d}w_i E_i \ .$$

Finally, inserting this into the expression for $\mathrm{d}\langle E\rangle$ one obtains

$$\mathrm{d}\langle E\rangle = \frac{1}{\beta k}\,\mathrm{d}S + \sum_\alpha \xi_\alpha\,\mathrm{d}X^\alpha = T\,\mathrm{d}S + \sum_\alpha \xi_\alpha\,\mathrm{d}X^\alpha \ . \tag{4.39}$$

This is precisely Gibbs' fundamental form (1.34b).

4.5 Classical Gases and Quantum Gases

Given N independent particles which either are distinguishable objects, to be described by classical mechanics, or, if they are all of the same kind, are indistinguishable and obey the laws of quantum mechanics. In the latter case the objects can be thought of as elementary particles carrying either half-integral spin, in which case they are fermions, or integer spin in which case they are bosons. For the sake of simplicity, we assume that the energy levels that these particles can occupy, belong to a discrete spectrum. In what follows they will be denoted by ε_i while the occupation number of the energy level "i" will be denoted by n_i. One has

$$\sum_{i=1}^{k} n_i = N \ , \quad \sum_{i=1}^{k} n_i\varepsilon_i = E \equiv \langle E\rangle \ . \tag{4.40}$$

In a grand-canonical ensemble, cf. Definition 2.3 and Example 4.10, the state (4.28b) is equal to

$$\varrho_{\boldsymbol{u}} = \frac{1}{Z}\,\mathrm{e}^{-\beta\sum_i n_i(\varepsilon_i-\mu_C)} = \frac{1}{Z}\prod_i \mathrm{e}^{-\beta n_i(\varepsilon_i-\mu_C)} \ . \tag{4.41}$$

Consider an individual state whose energy is ε_i. The distribution over occupation numbers n is

$$w_i(n) = \frac{1}{Z_i}\,\mathrm{e}^{-\beta n(\varepsilon_i-\mu_C)}\mu(\{n\}) \tag{4.42a}$$

$$\text{with} \quad Z_i = \sum_{n=0}^{\infty} \mathrm{e}^{-\beta n(\varepsilon_i - \mu_C)} \mu(\{n\}) \, . \tag{4.42b}$$

This is a starting point for various special cases as follows:

(i) Like in Example 4.4 choose $M = \mathbb{N}$ and the measure (4.5a), $\mu(\{n\}) = 1/n!$. Then one has

$$Z_i = \exp\left\{\mathrm{e}^{-\beta(\varepsilon_i - \mu_C)}\right\} \equiv \exp\left\{\mathrm{e}^{-u_1 \varepsilon_i - u_2}\right\} \, , \quad \text{with} \tag{4.43a}$$

$$u_1 = \beta \, , \quad u_2 = -\beta \mu_C \, , \tag{4.43b}$$

the expectation value of the total energy E becomes

$$\langle E \rangle_i = -\frac{\partial}{\partial u_1} \ln Z_i = \varepsilon_i \mathrm{e}^{-\beta(\varepsilon_i - \mu_C)} \, . \tag{4.43c}$$

This is again of the type of a Maxwell-Boltzmann distribution (4.29d).

(ii) In analogy to Example 4.5 one chooses

$$\begin{aligned} &\mu(\{0\}) = 1 = \mu(\{1\}) \, , \\ &\mu(\{n\}) = 0 \quad \text{for all} \quad n \geq 2 \, . \end{aligned} \tag{4.44a}$$

The partition function and the energy are given by, respectively,

$$Z_i = 1 + \mathrm{e}^{-\beta(\varepsilon_i - \mu_C)} \equiv 1 + \mathrm{e}^{-u_1 \varepsilon_i - u_2} \, , \tag{4.44b}$$

$$\langle E \rangle_i = -\frac{\partial}{\partial u_1} \ln Z_i = \frac{\varepsilon_i \mathrm{e}^{-\beta(\varepsilon_i - \mu_C)}}{1 + \mathrm{e}^{-\beta(\varepsilon_i - \mu_C)}} \, . \tag{4.44c}$$

This formula corresponds to *Fermi-Dirac statistics.*

(iii) The analogous distribution for bosons is obtained, using the abbreviation $z := \mathrm{e}^{-\beta(\varepsilon_i - \mu_C)}$, by assuming

$$M = \mathbb{N} \, , \quad \mu(\{n\}) = 1 \quad \text{for all} \quad n \, , \tag{4.45a}$$

$$\begin{aligned} Z_i &= \sum_{n=0}^{\infty} \mathrm{e}^{-\beta n(\varepsilon_i - \mu_C)} \equiv 1 + z + z^2 + z^3 + \cdots = \frac{1}{1 - z} \\ &= \frac{1}{1 - \mathrm{e}^{-\beta(\varepsilon_i - \mu_C)}} \equiv \frac{1}{1 - \mathrm{e}^{-u_1 \varepsilon_i - u_2}} \, , \end{aligned} \tag{4.45b}$$

$$\langle E \rangle_i = -\frac{\partial}{\partial u_1} \ln Z_i = \frac{\varepsilon_i \mathrm{e}^{-\beta(\varepsilon_i - \mu_C)}}{1 - \mathrm{e}^{-\beta(\varepsilon_i - \mu_C)}} \, . \tag{4.45c}$$

This distribution corresponds to *Bose-Einstein statistics.*

Table 4.1 Probabilities for distinguishable and indistinguishable particles, respectively

Statistics	Probability
Maxwell-Boltzmann	$w(n_i) = \mathrm{e}^{-v} v^{n_i}/n_i!$
Fermi-Dirac	$w(n_i = 0) = 1/(1+v)$
	$w(n_i = 1) = v/(1+v)$
	$w(n_i \geq 2) = 0$
Bose-Einstein	$w(n_i) = (1-v)v^{n_i}$

We summarize these three cases in Table 4.1: For fixed energy ε_i define

$$v := \mathrm{e}^{-\beta(\varepsilon_i - \mu_C)} . \tag{4.46}$$

The results for the probabilities (4.42a) are listed in the table:

One confirms that in all three cases the sum rule $\sum_0^\infty w(n_i) = 1$ is fulfilled.

In order to illustrate the differences in the three types of statistics one takes the ratios $\langle E\rangle_i/\varepsilon_i$ of the expectation value of the energy in the state "i" and the energy ε_i from (4.43c), (4.44c) and (4.45c), respectively. With the abbreviation $t := \beta(\varepsilon_i - \mu_C)$ these ratios are

$$\frac{\langle E\rangle_i}{\varepsilon_i} = \mathrm{e}^{-t} \quad \text{(Maxwell-Boltzmann)}, \tag{4.47a}$$

$$\frac{\langle E\rangle_i}{\varepsilon_i} = \frac{1}{\mathrm{e}^t + 1} \quad \text{(Fermi-Dirac)}, \tag{4.47b}$$

$$\frac{\langle E\rangle_i}{\varepsilon_i} = \frac{1}{\mathrm{e}^t - 1} \quad \text{(Bose-Einstein)}. \tag{4.47c}$$

The three distributions are plotted in Fig. 4.2 in terms of the variable t. As the variable t increases to large values as compared to 1, the differences between the three statistics eventually disappear. Note that the limit $t \to \infty$ means to dilute the gas more and more so that any differences in the effect of statistics tend to disappear. In the opposite case, when t tends to zero, marked differences between the three classes become more and more pronounced.

Example 4.14 (Mean Occupation Number and Entropy) As an example we calculate the mean occupation number $\langle n\rangle_i$ of the level with energy ε_i. Defining

$$\alpha_i := -\beta\,(\varepsilon_i - \mu_C) , \tag{4.48a}$$

(4.42b) reads

$$Z_i = \sum_k \mathrm{e}^{\alpha_i n_k} \mu(\{n_k\}) , \tag{4.48b}$$

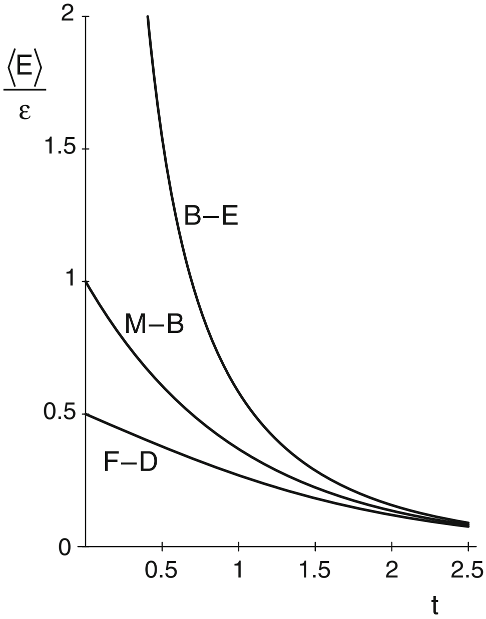


Fig. 4.2 Classical Maxwell-Boltzmann distribution (4.47a) in comparison to the Fermi-Dirac distribution (4.47b) and the Bose-Einstein distribution (4.47c), respectively

the mean occupation number is

$$\langle n\rangle_i = \frac{1}{Z_i}\sum_k n_k\, \mathrm{e}^{\alpha_i n_k}\mu(\{n_k\}) = \frac{\partial Z_i/\partial\alpha_i}{Z_i} = \frac{\partial}{\partial\alpha_i}\ln Z_i\ . \tag{4.48c}$$

In a similar manner the variance of this quantity can be computed. It is

$$\begin{aligned}\sigma_i^2(n) = \langle n^2\rangle_i - (\langle n\rangle_i)^2 &= \frac{1}{Z_i}\left\{\frac{\partial^2 Z_i}{\partial\alpha_i^2} - \frac{1}{Z_i}\left(\frac{\partial Z_i}{\partial\alpha_i}\right)^2\right\}\\ &= \frac{\partial^2}{\partial\alpha_i^2}\ln Z_i\ . \end{aligned}\tag{4.48d}$$

When dealing with identical fermions the right statistics is Fermi-Dirac statistics. From (4.44a) one has

$$Z_i = 1 + \mathrm{e}^{\alpha_i}\ ,$$

from which one obtains the mean particle number and the corresponding variance, respectively:

$$\langle n\rangle_i = \frac{\partial}{\partial\alpha_i}\ln\left(1+\mathrm{e}^{\alpha_i}\right) = \frac{\mathrm{e}^{\alpha_i}}{1+\mathrm{e}^{\alpha_i}} = \frac{1}{\mathrm{e}^{-\alpha_i}+1}\ , \tag{4.49a}$$

$$\begin{aligned}\sigma_i^2(n) &= \frac{\partial^2}{\partial\alpha_i^2}\ln\left(1+\mathrm{e}^{\alpha_i}\right) = \frac{\partial}{\partial\alpha_i}\frac{\mathrm{e}^{\alpha_i}}{1+\mathrm{e}^{\alpha_i}}\\ &= \frac{\mathrm{e}^{\alpha_i}}{1+\mathrm{e}^{\alpha_i}} - \frac{\mathrm{e}^{2\alpha_i}}{\left(1+\mathrm{e}^{\alpha_i}\right)^2} = \langle n\rangle_i\left(1-\langle n\rangle_i\right)\ .\end{aligned} \tag{4.49b}$$

In dealing with bosons one has from (4.45b)

$$Z_i = \frac{1}{1-\mathrm{e}^{\alpha_i}}\ ,$$

the mean particle number and the variance are, respectively,

$$\langle n\rangle_i = -\frac{\partial}{\partial\alpha_i}\ln\left(1-\mathrm{e}^{\alpha_i}\right) = \frac{\mathrm{e}^{\alpha_i}}{1-\mathrm{e}^{\alpha_i}} = \frac{1}{\mathrm{e}^{-\alpha_i}-1}\ , \tag{4.50a}$$

$$\sigma_i^2(n) = -\frac{\partial^2}{\partial\alpha_i^2}\ln\left(1-\mathrm{e}^{\alpha_i}\right) = \frac{\partial}{\partial\alpha_i}\frac{\mathrm{e}^{\alpha_i}}{1-\mathrm{e}^{\alpha_i}} = \langle n\rangle_i\left(1+\langle n\rangle_i\right)\ . \tag{4.50b}$$

Note, by looking at (4.48a), that the expression for $\langle n\rangle_i$ is positive only if the energy of the lowest state is larger than the chemical potential, $\varepsilon_0 > \mu_C$.
We conclude this example by a calculation of the entropy both for fermions and for bosons.

(i) In the case of *Fermi-Dirac statistics* the entropy of any of the states "i" is calculated very easily. Using

$$w(0) = \frac{1}{1+\mathrm{e}^{\alpha_i}} = 1-\langle n\rangle_i\ , \quad w(1) = \frac{\mathrm{e}^{\alpha_i}}{1+\mathrm{e}^{\alpha_i}} = \langle n\rangle_i$$

and $w(n) = 0$ for $n \geq 2$, the entropy is seen to be

$$\begin{aligned}S^{\text{F-D}}(i) &= -k\sum_{n=0}^{\infty} w(n)\ln w(n)\\ &= -k\left\{\left(1-\langle n\rangle_i\right)\ln\left(1-\langle n\rangle_i\right) + \langle n\rangle_i\ln\langle n\rangle_i\right\}\ .\end{aligned} \tag{4.51}$$

(ii) In the case of *Bose-Einstein statistics* the calculation is slightly more intricate. In this case one has with

$$w(n) = \frac{1}{Z_i}\,\mathrm{e}^{\alpha_i n} = (1-\mathrm{e}^{\alpha_i})\,\mathrm{e}^{\alpha_i n}\ :$$

$$\begin{aligned}\sum_{n=0}^{\infty} w(n)\ln w(n) &= \sum_{n=0}^{\infty}\mathrm{e}^{\alpha_i n}\,(1-\mathrm{e}^{\alpha_i})\,[\alpha_i n + \ln(1-\mathrm{e}^{\alpha_i})]\\ &= \sum_{n=0}^{\infty}\alpha_i n\,\mathrm{e}^{\alpha_i n}\,(1-\mathrm{e}^{\alpha_i}) + \ln(1-\mathrm{e}^{\alpha_i})\ . \end{aligned}\tag{4.52a}$$

Here use was made of $\sum_{n=0}^{\infty}\mathrm{e}^{\alpha_i n} = 1/(1-\mathrm{e}^{\alpha_i})$. The first term of (4.52a) can be rewritten as follows

$$\begin{aligned}&\sum_{n=0}^{\infty}\alpha_i n\,\mathrm{e}^{\alpha_i n}\,(1-\mathrm{e}^{\alpha_i})\\ &= \alpha_i\left\{\frac{\partial}{\partial\alpha_i}\left(\sum_{n=0}^{\infty}\mathrm{e}^{\alpha_i n}(1-\mathrm{e}^{\alpha_i})\right) - \sum_{n=0}^{\infty}\mathrm{e}^{\alpha_i n}\frac{\partial}{\partial\alpha_i}(1-\mathrm{e}^{\alpha_i})\right\}\\ &= \alpha_i\left\{\frac{\partial}{\partial\alpha_i}1 + \frac{\mathrm{e}^{\alpha_i}}{1-\mathrm{e}^{\alpha_i}}\right\} = \frac{\alpha_i\,\mathrm{e}^{\alpha_i}}{1-\mathrm{e}^{\alpha_i}}\ .\end{aligned}$$

Insertion in (4.52a) yields

$$\begin{aligned}\sum_{n=0}^{\infty} w(n)\ln w(n) &= \frac{\alpha_i\,\mathrm{e}^{\alpha_i}}{1-\mathrm{e}^{\alpha_i}} + \ln(1-\mathrm{e}^{\alpha_i})\\ &= \langle n\rangle_i\ln\langle n\rangle_i - (1+\langle n\rangle_i)\ln(1+\langle n\rangle_i)\ .\end{aligned}\tag{4.52b}$$

Thus, the entropy of the state "*i*" is given by

$$S^{\text{B-E}}(i) = -k\left\{\langle n\rangle_i\ln\langle n\rangle_i - (1+\langle n\rangle_i)\ln(1+\langle n\rangle_i)\right\}\ .\tag{4.53}$$

The results for the fermionic and the bosonic cases with energy levels $\varepsilon_0 \le \varepsilon_1 \le \varepsilon_2\cdots$, can be combined in formulae that are valid for both, fermions and bosons if one applies the rule: the upper sign holds for fermions, the lower sign for bosons. The partition function is seen to be

$$Z = \prod Z_i\ ,\quad \ln Z = \sum_i \ln Z_i = \pm\sum_i \ln(1\pm\mathrm{e}^{\alpha_i})\ .\tag{4.54}$$

The total particle number and the energy are, respectively,

$$N = \sum_i \langle n \rangle_i = \sum_i \frac{\mathrm{e}^{\alpha_i}}{1 \pm \mathrm{e}^{\alpha_i}} , \tag{4.55}$$

$$E = \sum_i \langle n \rangle_i \varepsilon_i = \sum_i \frac{\varepsilon_i \mathrm{e}^{\alpha_i}}{1 \pm \mathrm{e}^{\alpha_i}} . \tag{4.56}$$

Finally, one finds for the entropy

$$\begin{aligned} S &= k \{\ln Z + \beta (E - \mu_C N)\} \\ &= k \sum_i \{\pm \ln (1 \pm \mathrm{e}^{\alpha_i}) + \beta \langle n \rangle_i (\varepsilon_i - \mu_C)\} \\ &= k \sum_i \{\pm \ln (1 \pm \mathrm{e}^{\alpha_i}) - \alpha_i \langle n \rangle_i\} \\ &= -k \sum_i \{\langle n \rangle_i \ln \langle n \rangle_i \pm (1 \mp \langle n \rangle_i) \ln (1 \mp \langle n \rangle_i)\} . \end{aligned} \tag{4.57}$$

This concludes the example.

4.6 Statistics, Quantum and Non-quantum

In this section we elaborate similarities and specific differences between *classical statistics* and *quantum statistics*. To simplify matters we assume again that the space M is a finite, discrete set and that the measure μ has the same value in every point of M.

4.6.1 The Case of Classical Mechanics

In the framework of *classical* physics a state is described by a positive semi-definite function ϱ, cf. Definition 4.2, whose values $\varrho(1)$, $\varrho(2)$, ... in the points of M are given. Anticipating the comparison with quantum statistics it is useful to write the state in the form of a diagonal matrix,

$$\varrho = \operatorname{diag}(\varrho(1), \varrho(2), \ldots) . \tag{4.58}$$

Furthermore, an observable of the kind of (4.21a) which has more than one component, is written as a vector-like diagonal matrix. Its expectation value in the state (4.58), formally, is the trace of the product of two diagonal matrices,

$$\boldsymbol{F} = \operatorname{diag}\left(\boldsymbol{F}(1), \boldsymbol{F}(2), \ldots\right) \ , \tag{4.59a}$$

$$\langle \boldsymbol{F} \rangle_{\varrho} = \operatorname{tr}\left(\boldsymbol{F} \cdot \varrho\right) \ . \tag{4.59b}$$

The partition function in (4.19) is seen to be the trace of a diagonal matrix as well,

$$Z(\beta) = \operatorname{tr}\left(\mathrm{e}^{-\beta \mathcal{E}}\right) \quad \text{with} \quad \mathcal{E} = \operatorname{diag}\left(\varepsilon_1, \varepsilon_2, \ldots\right) \ . \tag{4.60}$$

Finally, equilibrium states can be written in the same form, too,

$$\varrho_\beta = \frac{1}{Z(\beta)} \operatorname{diag}\left(\mathrm{e}^{-\beta\varepsilon_1}, \mathrm{e}^{-\beta\varepsilon_2}, \ldots\right) \equiv \frac{1}{Z(\beta)} \mathrm{e}^{-\beta \mathcal{E}} \ , \tag{4.61}$$

i.e., in our example, as diagonal matrices in the space M.

4.6.2 Quantum Statistics

In classical, non-quantum, physics the observables are real functions and may be written as the entries of diagonal matrices, for example like in (4.59a). Quantum theory replaces these classical observables by *self-adjoint operators* $\mathcal{O}$. These operators may still depend on position and momentum variables but act on elements of a Hilbert space $\mathcal{H}$. For the convenience of the reader we summarize the most important notions of quantum mechanics.

The Hilbert space is endowed with a scalar product (f, g), $f, g \in \mathcal{H}$ which is linear in the second argument but antilinear in the first argument, i.e. with c a complex number, $c \in \mathbb{C}$, one has $(f, cg) = c(f, g)$ but $(cf, g) = c^*(f, g)$. To specify an operator one must know its domain of definition $\mathcal{D}$, so that, more correctly, one should define the pair $(\mathcal{O}, \mathcal{D})$, with $\mathcal{D} \subset \mathcal{H}$. If an operator $(\mathcal{O}, \mathcal{D})$ is given whose domain of definition is dense in $\mathcal{H}$ and if g is an arbitrary element in $\mathcal{D}$, the operator adjoint to $\mathcal{O}$ is defined via the scalar product $(\cdot, \cdot)$

$$(f, \mathcal{O}g) = \left(\mathcal{O}^\dagger f, g\right) \ .$$

The set of all $f \in \mathcal{H}$ for which there exists a function $f' \in \mathcal{H}$ such that $(f, \mathcal{O}g) = (f', g)$ for all $g \in \mathcal{D}$, is the domain of definition $\mathcal{D}^\dagger$ of the adjoint operator. Indeed, for every $f \in \mathcal{D}^\dagger$ one then has $\mathcal{O}^\dagger f = f'$.

A *self-adjoint* operator coincides with its adjoint, i.e. one has $\mathcal{D}^\dagger = \mathcal{D}$ and $\mathcal{O}f = \mathcal{O}^\dagger f$ for all $f \in \mathcal{D}$. Scalar products then have the properties

$$(g, \mathcal{O}f) = (\mathcal{O}g, f) = (f, \mathcal{O}g)^* \quad \text{for all} \quad f, g \in \mathcal{D} \ , \tag{4.62a}$$

$$(f, \mathcal{O}f) \quad \text{is real for all} \quad f \in \mathcal{D} \ . \tag{4.62b}$$

The eigenvalues of a self-adjoint operator are real. Two eigenfunctions f_1 and f_2 which pertain to two different eigenvalues λ_1 and λ_2, respectively, are orthogonal,

$$\mathcal{O}\varphi_1 = \lambda_1\varphi_1 \ , \ \mathcal{O}\varphi_2 = \lambda_2\varphi_2 \ , \ \lambda_1 \neq \lambda_2 \implies (\varphi_1, \varphi_2) = 0 \ . \tag{4.62c}$$

If all eigenvalues of $\mathcal{O}$ are positive semi-definite, then

$$(f, \mathcal{O}f) \geq 0 \quad \text{for all} \quad f \in \mathcal{H} \ . \tag{4.62d}$$

An operator with this property is said to be *positive semi-definite* and one writes symbolically $\mathcal{O} \geq 0$.

Among the self-adjoint operators the *projection operators* are particularly important from the point of view of physics. Formally, a *projection operator* P_λ maps every element of Hilbert space to the subspace $\mathcal{H}_\lambda$ which belongs to the eigenvalue λ of a self-adjoint operator $\mathcal{O}$. It can be written as follows,

$$P_\lambda f = \sum_{i=1}^{K} \varphi_{\lambda,i}(\varphi_{\lambda,i}, f) \quad \text{for all} \quad f \in \mathcal{H} \ . \tag{4.63a}$$

Here, K is the dimension of $\mathcal{H}_\lambda$ and, hence, is equal to the degree of degeneracy of the eigenvalue λ, the functions $\varphi_{\lambda,i}$ are eigenfunctions of $\mathcal{O}$ pertaining to the eigenvalue λ. Projection operators are self-adjoint and idempotent, i.e.

$$P_\lambda^\dagger = P_\lambda \ , \qquad P_\lambda P_\lambda = P_\lambda \ . \tag{4.63b}$$

Their eigenvalue spectrum is $\{0, 1\}$. In their interpretation in terms of physics they describe "Yes/No" experiments: They give the answer to the question whether in a measurement of the observable $\mathcal{O}$ in the state f one will find the eigenvalue λ, by "yes" for the eigenvalue 1, or by "no" if the eigenvalue is 0. Asking the same question twice gives the same answer as when one asks only once.

Projection operators are useful tools in the construction of quantum states. A *state* of a quantum system is represented by a *statistical operator* W or, equivalently, by a *density matrix* ϱ. The density matrix is nothing but a matrix representation, in the sense of representation theory of quantum mechanics, of the abstractly defined statistical operator. The statistical operator W is a convex linear combination of projection operators, i.e. a linear combination with real, nonnegative coefficients whose sum is 1. Thus, the operator W is self-adjoint, positive semi-definite and normalized to 1,

$$W = W^\dagger \ , \quad W \geq 0 \ , \quad \text{tr}(W) = 1 \ , \tag{4.64a}$$

$$W = \sum_i w_i P_i \quad \text{with} \quad 0 \leq w_i \leq 1 \ , \ \sum_i w_i = 1 \ . \tag{4.64b}$$

The actual values of the real coefficients w_i depend on how the state was prepared. The notation of (4.64b) presupposes that the preparation of the state is defined by the eigenvalues of an observable and by the (eigen-)subspaces to which they belong. Details of these matters can be found, e.g., in "Quantum Physics", Sect. 3.5. While the formulae of (4.64a) hold generally, those of (4.64b) reflect a specific representation.

For the sake of simplicity, we stay with the representation of the statistical operator W as a density *matrix*. A quantum state then is described by a density matrix ϱ which has the same properties (4.64a) as W, i.e.

$$\varrho = \varrho^\dagger \,, \quad \varrho \geq 0 \,, \quad \mathrm{tr}(\varrho) = 1 \,. \tag{4.65}$$

Furthermore, one knows that ϱ describes a *pure* state, i.e. a state allowing for full interferences without restrictions, if the condition $\mathrm{tr}(\varrho^2) = \mathrm{tr}(\varrho) = 1$ is fulfilled. In this case one has $\sum_i w_i^2 = \sum_i w_i = 1$. By the normalization condition this is only possible if one of the weights is different from zero and, hence, equal to 1, while all others are zero. If, instead, one finds $\mathrm{tr}(\varrho^2) < \mathrm{tr}(\varrho) = 1$, the quantum state is a *mixed* state. In this case at least two weights w_j and w_k must be different from zero and, hence, must be smaller than 1. The capacity of interfering, typical for quantum mechanics, is restricted to the subspaces $\mathcal{H}_i \subset \mathcal{H}$ of Hilbert space which are the target spaces of the projection operators P_i. Interferences between *different* subspaces are no longer possible and the ensuing situation becomes somewhat more like in classical statistical mechanics.

The expectation value of an observable $\mathcal{O}$ which is defined on Hilbert space, in the state ϱ, is given by the trace of the product $\mathcal{O}\varrho$ of the operator and the density matrix,

$$\langle \mathcal{O} \rangle_\varrho = \mathrm{tr}\left(\mathcal{O}\varrho\right) \,. \tag{4.66}$$

One is now well prepared for writing down the following equations.

Let $\boldsymbol{F} = (F_1, F_2, \dots, F_k)^T$ be a set of observables whose commutators are all equal to zero,

$$\left[F_i, F_j\right] = 0 \quad \text{for all} \quad i, j \in (1, 2, \dots, k) \,.$$

Let $\boldsymbol{\beta} = (\beta_1, \beta_2, \dots, \beta_k)^T$ be a set of real numbers. Using the abbreviation $\boldsymbol{\beta} \cdot \boldsymbol{F} = \sum_{i=1}^k \beta_i F_i$ the expression

$$Z(\boldsymbol{\beta}) = \mathrm{tr}\left(\mathrm{e}^{-\boldsymbol{\beta}\cdot\boldsymbol{F}}\right) \tag{4.67}$$

(continued)

defines the partition function for a system whose equilibrium state is described by

$$\varrho_{\boldsymbol{\beta}} = \frac{1}{Z(\boldsymbol{\beta})} \mathrm{e}^{-\boldsymbol{\beta}\cdot\boldsymbol{F}} . \tag{4.68}$$

The expectation value of the observable $\mathcal{O}$ is equal to

$$\langle\mathcal{O}\rangle_{\varrho_{\beta}} = \frac{1}{Z(\boldsymbol{\beta})} \operatorname{tr}\left(\mathcal{O}\,\mathrm{e}^{-\boldsymbol{\beta}\cdot\boldsymbol{F}}\right) . \tag{4.69}$$

These equations are the basic equations of quantum statistical mechanics.

Remarks

(i) Projection operators which project onto subsets of M, can also be introduced in the framework of *classical* statistical physics. This is particularly instructive in the comparison with quantum theory. Like in Sect. 4.2 let $\mathcal{A} = \{A_i\}$ be a set of subsets of M. One defines functions f_i on M which act as follows:

$$f_i(p) = 1 \quad \text{for all} \quad p \in A_i \, , \tag{4.70a}$$

$$f_i(q) = 0 \quad \text{for all} \quad q \in A_j \quad \text{with} \quad j \neq i \, . \tag{4.70b}$$

Obviously f_i tells no more than the answer to the question whether an arbitrary point of M belongs to the subset A_i. Therefore, like in (4.63b), one has $f_i f_i = f_i$. The product of two functions $f_i f_j$ is also a "Yes/No"-observable which tells whether or not a point lies in the intersection of A_i and A_j,

$$f_i f_j = f_{A_i \cap A_j} \, , \quad \text{or}$$

$$f_i(q) f_j(q) = 1 \Longleftrightarrow \left\{ f_i(q) = 1 \textit{ and } f_j(q) = 1 \right\} ,$$

i.e. whether $q \in A_i \cap A_j$ is true. Conversely if A_i and A_j do not intersect, then

$$A_i \cap A_j = \emptyset \Longleftrightarrow f_i f_j = 0 \quad \text{and} \quad f_i + f_j = f_{A_i \cup A_j} \, .$$

These classical projection operators obey the distribution law

$$f_{\mathcal{A}_1}\left(f_{\mathcal{A}_2} + f_{\mathcal{A}_3}\right) = f_{\mathcal{A}_1} f_{\mathcal{A}_2} + f_{\mathcal{A}_1} f_{\mathcal{A}_3} \, . \tag{4.71a}$$

This is equivalent to the relation

$$\mathcal{A}_1 \cap (\mathcal{A}_2 \cup \mathcal{A}_3) = (\mathcal{A}_1 \cap \mathcal{A}_2) \cup (\mathcal{A}_1 \cap \mathcal{A}_3) \tag{4.71b}$$

for the sets proper. The statement "a point lies in $\mathcal{A}_1$ *and* in $\mathcal{A}_2$ *or* $\mathcal{A}_3$" is equivalent with the statement "this point lies in $\mathcal{A}_1$ *and* in $\mathcal{A}_2$, *or* it lies in $\mathcal{A}_1$ *and* $\mathcal{A}_3$".

(ii) In *quantum theory* matters are different: Denote by $P_{\mathcal{H}_i}$ the projection operators which project onto the pairwise orthogonal subspaces $\mathcal{H}_i$ which belong to the degenerate eigenvalues λ_i of a self-adjoint operator. Any such operator $P_{\mathcal{H}_i}$ describes the (orthogonal) projection onto the subspace $\mathcal{H}_i$ and responds by the eigenvalue 1 when acting on this subspace, i.e. one has for all $i \neq j$

$$P_{\mathcal{H}_i} P_{\mathcal{H}_j} = 0 \Longleftrightarrow \mathcal{H}_i \cap \mathcal{H}_j = \{0\} .$$

If $P_{\mathcal{H}_i} P_{\mathcal{H}_j} = 0$ then this holds also for the product in the other order $P_{\mathcal{H}_j} P_{\mathcal{H}_i} = 0$. Their sum is also a "Yes/No"-observable since we have

$$\left(P_{\mathcal{H}_i} + P_{\mathcal{H}_j}\right)^2 = P_{\mathcal{H}_i} + P_{\mathcal{H}_j} . \tag{4.72a}$$

It describes the projection onto the direct sum $\mathcal{H}_i \oplus \mathcal{H}_j$ of the two subspaces:

$$\text{If} \quad P_{\mathcal{H}_j} P_{\mathcal{H}_i} = 0 \quad \text{then} \quad P_{\mathcal{H}_i} + P_{\mathcal{H}_j} = P_{\mathcal{H}_i \oplus \mathcal{H}_j} . \tag{4.72b}$$

In contrast to the *classical* case the *product* of two projection operators, in general, is not an observable. Indeed, in general, the product $P_{\mathcal{H}_i} P_{\mathcal{H}_j}$ is not equal to $P_{\mathcal{H}_j} P_{\mathcal{H}_i}$ and, therefore, is not self-adjoint. The distributive law analogous to the classical relation (4.71b)

$$\mathcal{H}_i \cap \left(\mathcal{H}_j \oplus \mathcal{H}_k\right) \overset{?}{=} \left(\mathcal{H}_i \cap \mathcal{H}_j\right) \oplus (\mathcal{H}_i \cap \mathcal{H}_k) \tag{4.73}$$

does not hold, except for special cases.

4.6.3 Planck's Radiation Law

The discovery of the quantum nature of light was of utmost importance for the early development of quantum theory. Bose-Einstein statistics applied to photons gave at once the correct description of the radiation spectrum of a so-called "black body". A black body is a cavity with volume V which contains no matter inside and which is heated up in a controlled manner. One measures the spectral distribution of the electromagnetic radiation emitted by this body. In the framework of statistical mechanics one deals with a gas of free massless photons which, therefore, obey Bose-Einstein statistics. From a thermodynamic point of view the system, in principle, is a grand-canonical ensemble because the temperature T, the volume V and a chemical potential μ_C are given. The total number of photons is not conserved, in contradistinction to a gas consisting of massive bosons. As photons have no rest mass and, therefore, as their energy can be arbitrarily small, it is possible any time to create or annihilate photons on the inner boundaries of the cavity. For this reason it is not meaningful to introduce a chemical potential at all. Without prejudice one may set $\mu_C = 0$. For fixed energy and fixed volume the system will always tune itself to a state of equilibrium.

With the assumption $\mu_C = 0$ the partition function for the radiation of the black body will be the one of the canonical ensemble. The formulae (4.45b) and (4.45c) of Sect. 4.5 can be applied to the case where the energy of the photons take continuous values. The photon gas in coordinate space is confined to the volume V of the black body. We divide again the phase space volume in elementary cells of size h^3. With this choice the momentum space is divided into cells with volume $\Delta = h^3/V$. In Exercise 4.7 the reader is invited to show that the sum over the states "i" is replaced by an integral, according to the rule

$$\sum_i \longrightarrow \sum_{m_s} \frac{V}{h^3} \iiint \mathrm{d}^3 p \tag{4.74}$$

where $h = 2\pi\hbar$ is the (original) Planck constant and $|\boldsymbol{p}|c = E = \hbar\omega$.

Since the photon is strictly massless it does not carry a spin of the conventional kind, with its $(2s + 1)$ orientations in space. Instead, it carries a *helicity* $|\lambda| = 1$ which has only *two* possible orientations, that is to say $\lambda = \pm 1$. As nothing in our purely statistical reasoning depends on λ, the sum over m_s in (4.74) is replaced by a factor 2. For the integration over all momenta one uses spherical polar coordinates,

$$\mathrm{d}^3 p = |\boldsymbol{p}|^2 \mathrm{d}|\boldsymbol{p}| \, \mathrm{d}\Omega_{\boldsymbol{p}} = (\hbar/c)^3 \, \omega^2 \mathrm{d}\omega \, \mathrm{d}\Omega_{\boldsymbol{p}} \; .$$

Finally, if the integrand is isotropic, i.e. if it does not single out any direction, the integral over the angular variables $\int \mathrm{d}\Omega_{|\boldsymbol{p}|}$ is replaced by the factor (4π). With (4.45c) and with $\mu_C = 0$ one has

$$\langle E \rangle_i = \frac{\varepsilon_i}{\mathrm{e}^{\beta\varepsilon_i} - 1} \; .$$

The total energy is obtained from a continuum version of (4.56), together with (4.48a)

$$E = V \frac{8\pi}{(2\pi c)^3} \int_0^\infty \omega^2 \mathrm{d}\omega \, \frac{\hbar\omega}{\mathrm{e}^{\hbar\omega/(kT)} - 1} \tag{4.75a}$$

$$= \frac{4\sigma}{3c} V T^4 \quad \text{with} \quad \sigma = \frac{\pi^2 k^4}{60\hbar^3 c^2} \; . \tag{4.75b}$$

Here the definition $x = \hbar/(kT)\omega$ was introduced and use was made of the integral formula

$$\int_0^\infty \mathrm{d}x \, \frac{x^{2n-1}}{\mathrm{e}^x - 1} = \frac{(2\pi)^{2n}}{4n} |B_{2n}|$$

where B_m are the Bernoulli numbers. In our case we need only $B_4 = 1/30$. The formula (4.75b) is called *Stefan-Boltzmann law*. The constant σ has the numerical value

$$\sigma = 5.6704 \times 10^{-8}\,\mathrm{Wm}^{-2}\mathrm{K}^{-4} \,. \tag{4.75c}$$

In a similar way one calculates the total number of photons by integration over all momenta. One obtains

$$\begin{aligned} N &= V\frac{8\pi}{h^3} \int_0^\infty |\boldsymbol{p}|^2 \,\mathrm{d}|\boldsymbol{p}| \, \frac{1}{\mathrm{e}^{\beta c|\boldsymbol{p}|-1}} \\ &= V\frac{8\pi\hbar^3}{h^3c^3} \int_0^\infty \omega^2 \,\mathrm{d}\omega \, \frac{1}{\mathrm{e}^{\hbar\omega/(kT)} - 1} \\ &= V\frac{2(kT)^3}{\pi^2(\hbar c)^3}\zeta(3) \,. \end{aligned} \tag{4.76}$$

In this expression use was made of the integral formula

$$\int_0^\infty x^2 \,\mathrm{d}x \, \frac{1}{\mathrm{e}^x - 1} = \Gamma(3)\zeta(3) = 2\zeta(3) \,,$$

where

$$\zeta(n) = \sum_{k=1}^\infty \frac{1}{k^n} \quad \text{with} \quad n = 2, 3, \ldots$$

is Riemann's Zeta function.

Planck's radiation formula proper is obtained from (4.55) by replacing α_i by $-\beta\varepsilon = -\beta\hbar\omega$ as defined in (4.48a). The mean occupation number of the state with energy $\hbar\omega$ is

$$\langle n \rangle_{(\omega,T)} = \frac{1}{\mathrm{e}^{\hbar\omega/(kT)-1}} \,. \tag{4.77a}$$

Some small interval $\mathrm{d}\omega$ about the value ω makes a contribution to the total energy that can be read off (4.75a),

$$\begin{aligned} &V\frac{8\pi}{(2\pi c)^3}\hbar\omega\langle n\rangle_{(\omega,T)}\,\omega^2\,\mathrm{d}\omega \\ &= V\mathrm{d}\omega\;\frac{\hbar}{\pi^2c^3}\frac{\omega^3}{\mathrm{e}^{\hbar\omega/(kT)-1}} \equiv V\mathrm{d}\omega\;\varrho(\omega,T)\;. \end{aligned} \tag{4.77b}$$

This formula defines a function

$$\varrho(\omega,T) = \frac{\hbar}{\pi^2c^3}\frac{\omega^3}{\mathrm{e}^{\hbar\omega/(kT)}-1} \tag{4.77c}$$

which describes the spectral energy density of the black body radiation. This is what is called *Planck's radiation formula* of the black body. In Fig. 4.3 we show the function

$$\begin{aligned} &v(x) := \frac{\varrho(\omega,T)}{\varrho_0}\frac{x^3}{\mathrm{e}^{(T_0/T)x}-1} \\ &\text{with}\quad \varrho_0 = \frac{\hbar}{\pi^2}\left(\frac{kT_0}{\hbar c}\right)^3 \quad\text{and}\quad x = \frac{\hbar}{kT_0}\,\omega \end{aligned}$$

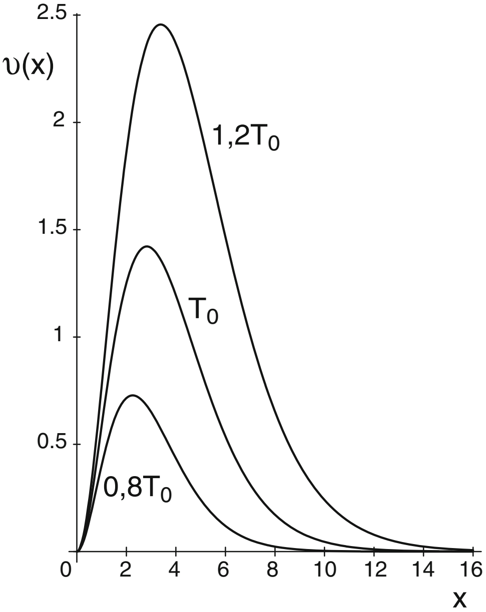


Fig. 4.3 Spectral distribution of the radiation of a black body for three different temperatures (Planck's radiation formula): $T = T_0$ (*middle curve*), $T = 0.8T_0$ (*lower curve*), $T = 1.2T_0$ (*upper curve*). For more details see text

for three values of the temperature, $T = 0.8\ T_0$, $T = T_0$ and $T = 1.2\ T_0$, where T_0 is an arbitrary reference temperature.

Remarks

(i) The maximum of the function shown in Fig. 4.3 is obtained by solving the equation

$$3(\mathrm{e}^u - 1) = u\mathrm{e}^u \quad \text{with} \quad u = \frac{\hbar\omega}{kT} \ .$$

It is located at $u \simeq 2.82$. As a function of temperature this maximum moves linearly with temperature according to the relation

$$\hbar\omega_{\max} \simeq 2.82\ (kT)\ . \tag{4.78}$$

This is known as *Wien's displacement law.*

(ii) The constant σ in (4.75b) is proportional to k^4/h^3, while (4.78) may be used to determine the ratio k/h. In this way one obtains both Planck's constant h and the Boltzmann constant k. Finally, using the relation $R = kL$ for the ideal gas, on sees that one may obtain Loschmidt's number L from entirely macroscopic measurements,

$$L = 6.022 \times 10^{23}. \tag{4.79}$$

(iii) For large temperatures one has $\hbar\omega \ll kT$. Then, with $\mathrm{e}^{\hbar\omega/(kT)-1} \simeq \hbar\omega/(kT)$ the distribution (4.77c) can be approximated by

$$\varrho(\omega, T) \simeq \frac{\omega^2 kT}{\pi^2 c^3}\ . \tag{4.80a}$$

This formula no longer contains Planck's constant. Indeed, this law which is called the *Rayleigh-Jeans radiation law*, was obtained in the framework of a classical theory, before the advent of quantum mechanics.

(iv) In turn, for small temperatures one has $\hbar\omega \gg kT$, the denominator of the formula (4.77c) for the spectral distribution can be replaced by the exponential, neglecting the constant term 1. One then obtains

$$\varrho(\omega, T) \simeq \frac{\hbar\omega^3}{\pi^2 c^3}\,\mathrm{e}^{-\hbar\omega/(kT)}\ . \tag{4.80b}$$

This approximation is called *Wien's radiation law.* Like the Rayleigh-Jeans law, it was already known before the development of the quantum hypothesis for the photon.

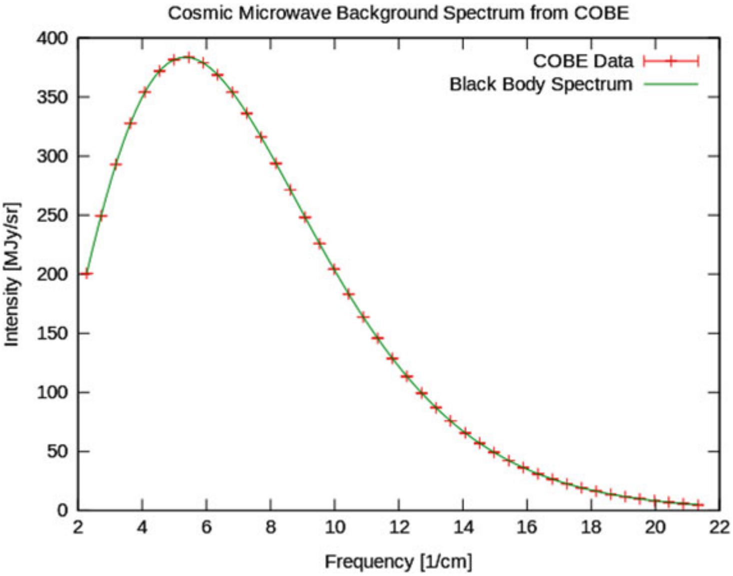


Fig. 4.4 The cosmic microwave spectrum which is measured by the COBE and WMAP collaborations, is a perfect black-body spectrum corresponding to temperature $T \simeq 2.725\,\mathrm{K}$

Example 4.15 (The Cosmic Microwave Background) The *cosmic microwave background* (CMB) discovered in 1965 by Arno A. Penzias and Robert W. Wilson is of central importance for modern cosmology. In particular, it provides an impressive example for black body radiation. Its spectrum as obtained from the COBE data, represents the most accurate measurement of Planck's formula (4.77c). This spectrum is shown in Fig. 4.4, plotting the intensity versus the inverse wave length, and comparing to the calculated Planck spectrum.

According to the standard model of cosmology this radiation is a remnant of a dramatic and very singular past of our universe—the so-called *big bang cosmology*. The CMB radiation is found to be homogeneous and isotropic to a very high degree. It corresponds to a temperature of $T = (2.72548 \pm 0.00057)\,\mathrm{K}$. The big bang cosmology describes the genesis of the background radiation schematically as follows.

The initial phase of formation of the universe in this model took about 10^6 years. During that phase matter and radiation were in thermal equilibrium. While the universe expanded the temperature decreased from some 10^{11} K to about $T_\mathrm{c} = 3000\,\mathrm{K}$ which is the temperature at which matter and radiation decoupled. After the formation of atoms, stars and galaxies, light no longer interacted substantially with matter. The remnant radiation had the frequency spectrum of the Planck formula (4.77c) corresponding to the temperature T_c. Due to the expansion of the universe from an initial radius R_c to the actual radius R, the photons of this background radiation reach us with augmented wave lengths as if they came from sources receding from us with a velocity proportional to their distance from us. This is the Doppler effect. Furthermore, the number of photons with initial frequency ν_{c} has remained constant but these photons now fill a volume which is expanded by the factor $(R/R_{\mathrm{c}})^3$ where R is a radius characterizing the size of the universe at present.

The two effects, the apparent shift of frequencies due to the Doppler effect

$$\nu = \nu_{\mathrm{c}} \frac{R_{\mathrm{c}}}{R} \tag{4.81}$$

and the distribution of the same number of photons over a volume magnified by a factor $(R/R_{\mathrm{c}})^3$, imply that the distribution (4.77b) at present (now expressed in terms of frequency ν, $\omega = 2\pi\nu$) is again a Planck distribution given by

$$\frac{\varrho(\nu, T)\,\mathrm{d}\nu}{h\nu} = \left(\frac{R}{R_{\mathrm{c}}}\right)^3 \frac{\varrho(\nu_{\mathrm{c}}, T_{\mathrm{c}})\,\mathrm{d}\nu_{\mathrm{c}}}{h\nu_{\mathrm{c}}} \quad \text{with} \quad T = \frac{T_{\mathrm{c}} R_{\mathrm{c}}}{R}\,. \tag{4.82}$$

Indeed, from (4.78) the maximum of the distribution shown in Fig. 4.4 is situated approximately at

$$\frac{\nu_{max}}{c} = 2.82 \frac{kT}{2\pi\hbar c} \simeq 5.341\,\mathrm{cm}^{-1}\,,$$

equivalent to the quoted temperature. The temperature of this cosmic afterglow is an important input in cosmological models.

Mixed Phases, Phase Transitions, Stability of Matter

5

5.1 Introduction

Phase mixtures and phase transitions are two major themes of thermodynamics. A third one, related to the former, is the stability of macroscopic matter around us. Mixed phases can be analyzed and illustrated in a nice geometric way. Phase transitions are dealt with from the point of view of classical thermodynamics as well as in the framework of models of statistical mechanics. A good introduction to phase transitions is provided by the *Ising model* which we discuss in its simplest version. Finally, the conditions for macroscopic matter to be stable against implosion or explosion can be explored by means of simple estimates of the energy of ground states, for positive temperatures, and by some thermodynamics. The solution of this important problem of physics of which we give a heuristic discussion, rests on classical many body dynamics, quantum mechanics and thermodynamics.

5.2 Phase Transitions

Like in other areas of thermodynamics and statistical mechanics the problems dealt with in this chapter make frequent use of the theory of convex functions and their Legendre transforms. Likewise, in the discussion of the stability of matter one makes use of Theorem 5.1 which relates superadditivity (or subadditivity) of a function, its property of being concave (or convex) and its extensivity. For this reason the chapter begins with a discussion of some mathematical notions and recalls some propositions before turning to a discussion of phase transitions proper.

F. Scheck, *Statistical Theory of Heat*, Graduate Texts in Physics,
DOI 10.1007/978-3-319-40049-5_5

5.2.1 Convex Functions and Legendre Transformation

For what follows it is useful to collect some mathematical definitions, propositions and theorems to which we refer in a physical context below.

Definition 5.1 (Simplex) Let $x_0, x_1, \ldots, x_k$ be a set of points in $\mathbb{R}^n$ such that the differences $(x_1 - x_0)$, $(x_2 - x_0)$, ..., $(x_k - x_0)$ are linearly independent. The set of convex combinations of $x_0, x_1, \ldots, x_k$ defines a *k-simplex*.

For the convenience of the reader we recall the meaning of the term convex combination:

Definition 5.2 (Convex Combination) A point $x \in \mathbb{R}^n$ is said to be a *convex combination* of the points $x_1, x_2, \ldots, x_m$ in $\mathbb{R}^n$ if it can be represented in the form

$$x = \sum_{i=1}^{m} t_i x_i \quad \text{with} \quad t_i \geq 0 \quad \text{and} \quad \sum_{i=1}^{n} t_i = 1 \; . \tag{5.1}$$

In Fig. 5.1 we show three examples of simplices, a 1-simplex, a 2-simplex and a 3-simplex. For example, a 1-simplex consists of the set $(1-t)x_0 + tx_1$ with $0 \leq t \leq 1$, that is, of the points of the segment of the straight line which links the points x_0 and x_1.

For a 2-simplex the condition (5.1) reads

$$x = t_0 x_0 + t_1 x_1 + t_2 x_2 \quad \text{with} \quad 0 \leq t_i \leq 1 \; , \; t_0 + t_1 + t_2 = 1 \; .$$

These are the points which lie inside the triangle spanned by x_0, x_1 and x_2 or on its boundary.

A 3-simplex is defined by the conditions

$$x = t_0 x_0 + t_1 x_1 + t_2 x_2 + t_3 x_3 \; , \; t_0 + t_1 + t_2 + t_3 = 1 \; ,$$

with $t_i \in [0, 1]$. These are the points lying in the interior or on the boundary surfaces of the tetrahedron defined by x_0, x_1, x_2 and x_3 .

Simplices are special cases of *convex bodies*. These are defined as follows:

Definition 5.3 (Convex Body) A body K embedded in $\mathbb{R}^n$ is said to be convex if the segment of straight line linking two arbitrary points $p \in K$ and $q \in K$ is contained entirely in K.

An example of a convex body in $\mathbb{R}^3$ is sketched in Fig. 5.2.

As a rule, thermodynamic potentials of systems in equilibrium are described by means of three variables. Examples are the entropy as a function of the energy, the volume and the particle number, $S = S(E, V, N)$, or the energy, $E = E(S, V, N)$, as a

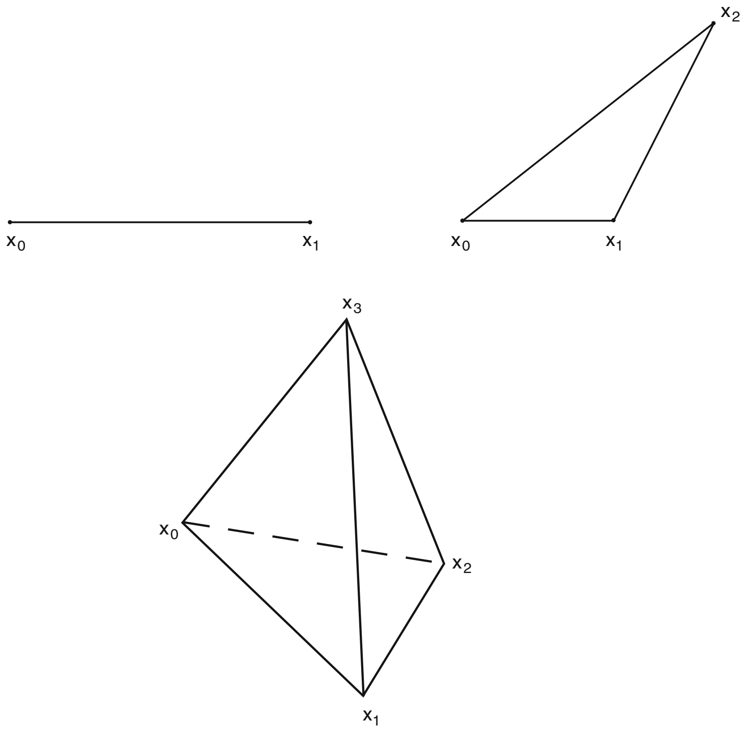


Fig. 5.1 Examples of simplices: a 1-simplex, a 2-simplex and a 3-simplex

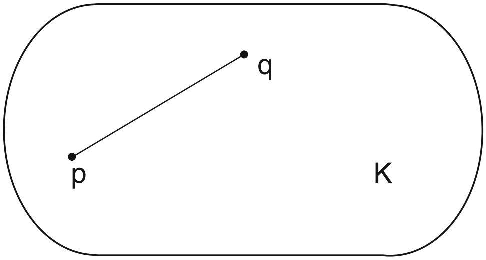


Fig. 5.2 Example for a convex body embedded in $\mathbb{R}^3$

function of the entropy, the volume and the particle number. If one of these variables is held fixed, e.g. the particle number, the potential depends on two variables only. Thus, in the first example the entropy becomes $S(E, V)$. In many cases we denote the set of variables, (E, V, N) or (E, V), by a single symbolic variable X which then has several components.

The following definition which is related to Theorem 2.5, is relevant here and below:

Definition 5.4 (Convex (Concave) Function) A function $S(u, v)$ is called *convex* if the set of points $(u, v, Z) \in \mathbb{R}^3$, for which $S(u, v) \leq Z$ holds true, forms a convex body, i.e. if with $X_a \equiv (u_a, v_a)$, $X_b \equiv (u_b, v_b)$ and for all $0 \leq t \leq 1$,

$$S\left(tX_b + (1-t)X_a\right) \leq tS(X_b) + (1-t)S(X_a)\ . \tag{5.2}$$

This criterion is akin to the one-dimensional case of (1.46).

The function is *concave* if the set of points $(u, v, Z) \in \mathbb{R}^3$ for which $S(u, v) \geq Z$ span a convex body. In this case one has, for all t with $0 \leq t \leq 1$,

$$S\left(tX_b + (1-t)X_a\right) \geq tS(X_b) + (1-t)S(X_a)\ . \tag{5.3}$$

For the sake of simplicity we give this definition for the case of two variables. Its generalization to more than two variables should be obvious. Already at this point one can draw some elementary conclusions. Let F be a convex function and let K^+ be the set of all points which lie *above* the graph of F. By virtue of the Definition 5.3 K^+ is a convex body. (In case F is concave one considers the set of all points K^- below the graph. This is a convex body, too.) Points on the boundary of the body are particularly interesting. Indeed, a point on the boundary is either an extremal point or an interior point of a segment of straight line as sketched in Fig. 5.3.

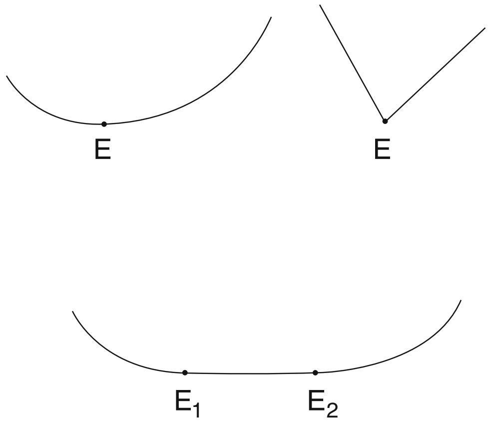


Fig. 5.3 Boundaries of convex bodies in dimension 2. A point on the boundary is either an extreme point or an inner point on a section of straight line. An example would be a point somewhere between E_1 and E_2

The following theorem concerns convex functions[1]:

Theorem 5.1 *Given a continuous real function $f(X)$ for which $f(0) = 0$. This function is assumed to have two out of three properties :*

(a) With μ a real positive number it fulfills

$$f(\mu X) = \mu f(X) \,, \tag{5.4a}$$

i.e. the function f is extensive, or homogeneous of degree 1.

(b) The function f is superadditive, i.e. obeys the inequality

$$f(X_2 + X_1) \geq f(X_2) + f(X_1) \,. \tag{5.4b}$$

(c) For $0 \leq t \leq 1$ one has

$$f\left(tX_2 + (1-t)X_1\right) \geq tf(X_2) + (1-t)f(X_1) \,, \tag{5.4c}$$

i.e. the function f is concave.

Any two of these properties imply the third one.

Proof Among the three cases that must be considered, two are easy to prove.

i) From (5.4a) and (5.4b) follows (5.4c): In order to show this, one substitutes $tX_2 = Y_2$ and $(1-t)X_1 = Y_1$. With (5.4b) one has

$$f(Y_2 + Y_1) \geq f(Y_2) + f(Y_1) \,.$$

Using the property (5.4a) the right-hand side is equal to

$$f(Y_2) + f(Y_1) = tf(X_2) + (1-t)F(X_1) \,,$$

therefore one obtains the property (5.4c).

ii) From (5.4a) and (5.4c) one deduces (5.4b): This is obvious if one writes (5.4c) for $t = 1/2$,

$$f\left(\tfrac{1}{2}X_2 + \tfrac{1}{2}X_1\right) \geq \tfrac{1}{2}f(X_2) + \tfrac{1}{2}f(X_1)$$

and if one notes that by (5.4a) the left-hand side is equal to $\frac{1}{2}f(X_2 + X_1)$.

---

[1] P.T. Landsberg, J. Stat. Phys. **35** (1984) 159.

iii) The third case, to prove (5.4a) from (5.4b) and (5.4c), is slightly more intricate: In a first step choose $t = 1/n$, $X_2 = Y$ and $X_1 = 0$. With the assumption $f(0) = 0$ and by (5.4c) one has:

$$f(\tfrac{1}{n}Y) \geq \tfrac{1}{n}f(Y) + \tfrac{n-1}{n}f(0) = \tfrac{1}{n}f(Y) \ . \tag{5.5a}$$

Setting $X_1 = X_2$ in (5.4b) one concludes

$$f(2X_2) \geq 2f(X_2) \quad \text{and} \quad f(nX_2) \geq nf(X_2) \ .$$

Choose now $nX_2 = Y$, thus obtaining

$$f(Y) \geq nf(\tfrac{1}{n}Y) \ . \tag{5.5b}$$

From the results (5.5a) and (5.5b) follows

$$\begin{aligned} &nf(\tfrac{1}{n}Y) \leq f(Y) \leq nf(\tfrac{1}{n}Y) \ , \\ &\text{hence} \quad f(Y) = nf(\tfrac{1}{n}Y) \quad \text{or} \quad f(nX_2) = nf(X_2) \ . \end{aligned}$$

Finally, if one replaces n by rational and then by real positive numbers, the property (5.4a) is proven. This concludes the proof of Theorem 5.1.

In the discussion of phase transitions a geometric interpretation of Legendre transformation is particularly helpful, cf. e.g. Wightman (1979). For the sake of simplicity, we consider Legendre transformation for a single variable. In this case all drawings and graphs of functions lie in a plane. Consider the unit circle in $\mathbb{R}^2$,

$$(x = \cos\alpha \ , y = \sin\alpha) \quad \text{or} \quad x^2 + y^2 = 1 \ , \tag{5.6a}$$

and a fixed point P outside the circle whose abscissa and ordinate are $z = b\cos\phi_0$ and $w = b\sin\phi_0$, respectively. The straight line

$$\cos\alpha\cos\phi_0 + \sin\alpha\sin\phi_0 = \frac{1}{b} =: a \quad \text{or} \quad xz + yw = 1 \tag{5.6b}$$

is perpendicular to the straight line passing through P and the origin, and goes through the point $P' = (a\cos\phi_0, a\sin\phi_0)$, the conjugate of P. The relationship between P and P' is called *inversion on the unit circle.* As can be read off Fig. 5.4 the tangents at the points T_1 and T_2 (points of intersection of the second straight line with the circle) go through P. In this sense the straight line (5.6b) is dual to the point (z, w).

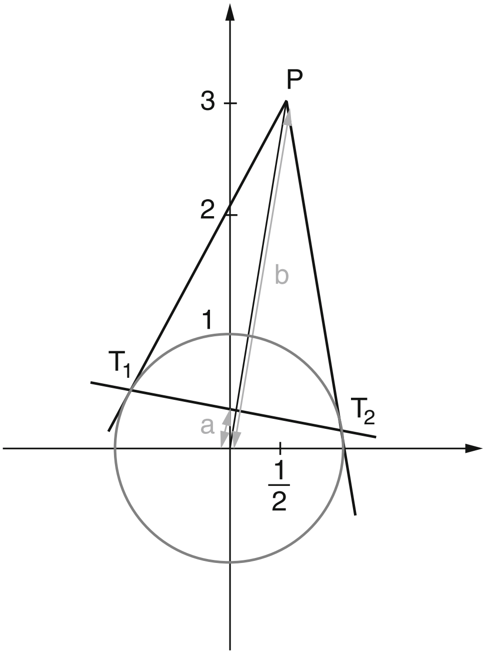


Fig. 5.4 Inversion on the unit circle: the straight line T_1T_2 is dual to the point P

From elementary geometry, or from function theory, it is known that an arbitrary projective transformation

$$x \longmapsto x' = \frac{a_1x + b_1y + c_1}{a_3x + b_3y + c_3} \,, \tag{5.7a}$$

$$y \longmapsto y' = \frac{a_2x + b_2y + c_2}{a_3x + b_3y + c_3} \,, \tag{5.7b}$$

maps the unit circle to a more general conic section

$$Ax^2 + By^2 + 2Cxy + 2Dx + 2Ey + F = 0 \,,$$

while the straight line (5.6b) dual to P, for fixed values of z and w, is mapped to another straight line

$$Axz + Byw + C(xw + yz) + D(x + z) + E(y + w) + F = 0 \,.$$

It is not necessary to discuss the general case as the following simple example shows fairly well all salient features. Choose

$$(a_1 = 1\,,\, a_2 = 0 = a_3)\,, \quad (b_1 = 0\,,\, b_2 = \tfrac{1}{\sqrt{2}} = b_3)\,,$$
$$(c_1 = 0\,,\, c_2 = -\tfrac{1}{\sqrt{2}} = -c_3)\,.$$

Expressed in terms of the coordinates (x, y) and (z, w), the replacements are

$$x \longmapsto x' = \frac{x\sqrt{2}}{y+1}\,, \quad y \longmapsto y' = \frac{y-1}{y+1}\,,$$
$$z \longmapsto z' = \frac{z\sqrt{2}}{w+1}\,, \quad w \longmapsto w' = \frac{w-1}{w+1}\,.$$

The unit circle (5.6a) and the straight line (5.6b) conjugate to P, respectively, are transformed as follows

$$x'^2 + y'^2 = 1 \longmapsto 2y - x^2 = 0\,, \tag{5.8a}$$

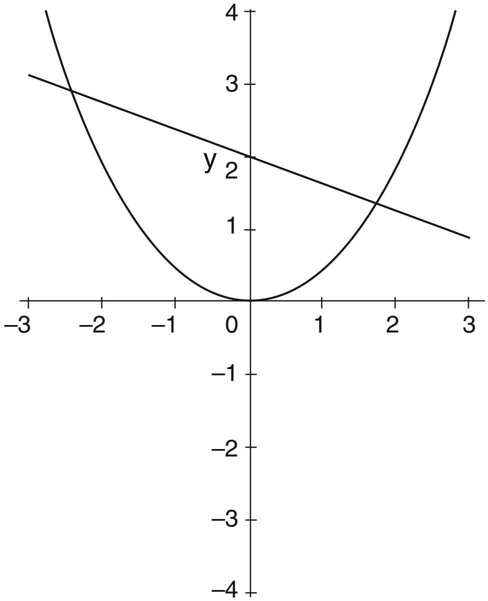
$$x'z' + y'w' = 1 \longmapsto y + w - xz = 0\,, \tag{5.8b}$$

These are the parabola and the straight line, respectively, drawn in Fig. 5.5 for the example $(z' = 0.5, w' = 3)$.

Using these tools one easily shows that the Legendre transform of a convex function is convex, too. Let $f(x)$ be a convex function, denote by $\mathcal{L}f(z) \equiv f^*(z)$ its Legendre transform, or *conjugate,* cf. (1.48),

$$f^*(z) \equiv \mathcal{L}f(z) = \sup_x \left[xz - f(x)\right]\ . \tag{5.9}$$

Fig. 5.5 Inversion on the unit circle, after a conformal transformation, yields the figure shown here



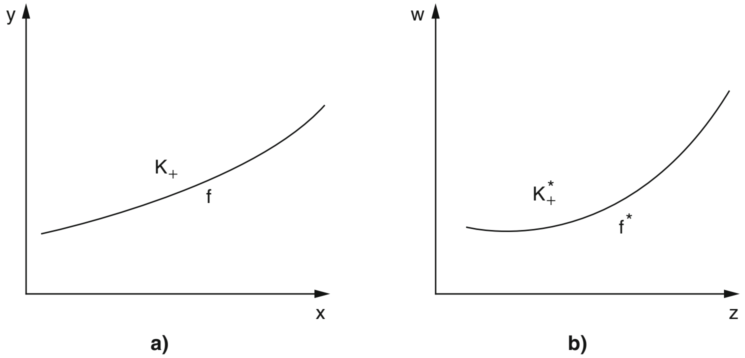


Fig. 5.6 If the function f is convex, that is, if the set of all points above f form a convex body (part (**a**) of the figure), then this holds also for its Legendre transformed function [part (**b**)]

The set K_+ of all points lying *above* the graph of the function f form a convex body. This is sketched in Fig. 5.6a. It remains to show that the set of all points which lie above the graph of the conjugate function f^* form a convex body, too, cf. Fig. 5.6b.

By analogy to (5.6b) and with regard to the straight line (5.8b), assign to each point $(x, y) \in K_+$ the transformed line in the (z, w)-plane

$$(x, y) \in K_+ \longleftrightarrow w = xz - y \ .$$

This line divides the (z, w)-plane in an upper and a lower half-plane. Keeping x fixed and letting the point (x, y) tend to f from above, as sketched in Fig. 5.7a, the upper half-plane moves upwards, cf. Fig. 5.7b. From this one concludes, one the one hand, that the intersection of the set of points (z, w), for which $w \geq xz - y$ for all $y \geq f(x)$, is the set of points of the (z, w)-plane for which $w \geq xz - f(x)$. Expressed in symbols,

$$\bigcap_{y \geq f(x)} \{(z, w) | \, w \geq xz - y\} = \{(z, w) | \, w \geq xz - f(x)\} \ . \tag{5.10a}$$

On the other hand, taking the intersection of the right-hand side of (5.10a) over all x, one obtains the space K_+^* of all points above the graph of f^*,

$$\begin{aligned} &\bigcap_{x} \{(z, w) | \, w \geq xz - f(x)\} \\ &= \left\{(z, w) | \, w \geq \sup_x [xz - f(x)]\right\} = K_+^* \ . \end{aligned} \tag{5.10b}$$

When $(x, y = f(x))$ moves along the graph of f, the graph of the conjugate function f^* is seen to be the envelope of the set of straight lines $w = xz - f(x)$. The space K_+^* is the intersection of half-spaces which obviously are convex. As it is the intersection

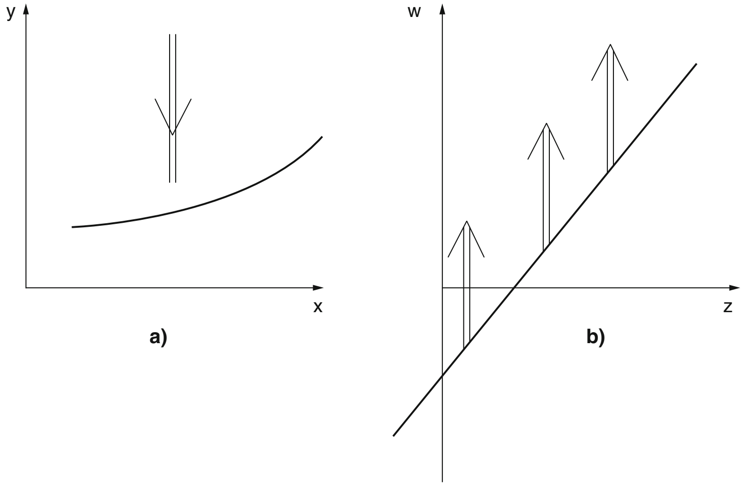


Fig. 5.7 When a point moves vertically from above towards the graph of f [part (**a**)], the half-space above the corresponding straight line moves upwards [part (**b**)]

of convex spaces, the space K_+^* is a convex body. This shows that f^* is a convex function.

The Legendre-transform of a convex function is again a convex function.

Remarks

i) We studied the case of a single variable, for simplicity. It is easy to generalize the situation as described above to two or more variables. Graphs of functions become hypersurfaces, straight lines are replaced by hyperplanes. The graph of f^* then is the envelope of the set of hyperplanes $w = xz - f(x)$.

ii) A situation where the function f comprises a straight line segment, as sketched in Fig. 5.8, is interesting. The function f is continuous but not differentiable.

Suppose the straight line segment lies between $x = x^{(0)}$ and $x = x^{(1)}$. Then

$$\left(x^{(t)}, f(x^{(t)})\right) = t(x^{(1)}, f(x^{(1)}) + (1-t)(x^{(0)}, f(x^{(0)}) \;,$$

with $0 \le t \le 1$, is the graph of the straight line segment between $x^{(0)}$ and $x^{(1)}$. The straight lines

$$w = x^{(0)}z - f(x^{(0)}) \quad (t = 0) \;,$$

$$w = x^{(1)}z - f(x^{(1)}) \quad (t = 1) \;,$$

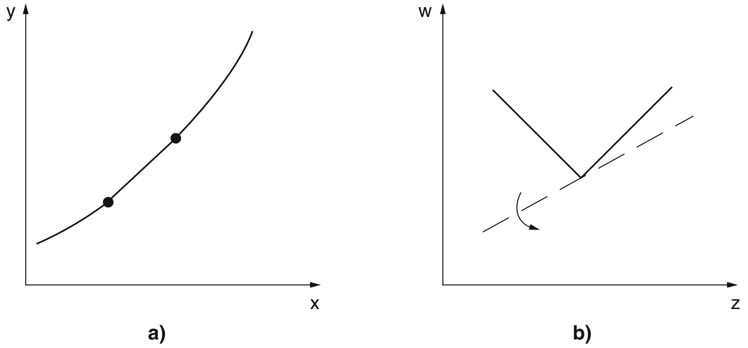


Fig. 5.8 A section of straight line in a continuous convex curve by Legendre transform is mapped into a point

combined with coefficients $(1-t)$ and t, respectively, yield a sheaf of lines

$$w = x^{(t)}z - f(x^{(t)}) \ . \tag{5.11}$$

All of these straight lines go through the point $(z, f^*(z))$ where

$$f^*(z) = \sup_x \left\{ x^{(t)}z - f(x^{(t)}) \right\} \ .$$

Thus, under Legendre transform, the straight line segment from $x^{(0)}$ to $x^{(1)}$, as a whole, is mapped to a single point. This is shown in Fig. 5.8. While $x^{(t)}$ moves from $x^{(0)}$ to $x^{(1)}$, $x^{(t)} = (1-t)x^{(0)} + tx^{(t)}$, the dual straight line (5.11) rotates about this corner.

5.2.2 Phase Mixtures and Phase Transitions

We consider a given, fixed quantity of a fluid such as water, for example. As the number of particles, though large, is constant, the manifold M_Σ of equilibrium states has dimension 2. Therefore, the system can be described

- either by the entropy S as a function of energy E and of volume V,
- or by the energy E as a function of S and V .

The ranges of these variables are

$$S_0 \le S \le +\infty \ , \quad E_0 \le E \le +\infty \ .$$

With the first of these choices, $S(E, V)$ is a *concave* function which is at least once differentiable. The partial derivatives by the energy E and by the volume V exist. Denoting the pair of two variables by $(E, V) \equiv X$ then, by (5.3) and (2.64), one has

$$S(tX_2 + (1-t)X_1) \geq tS(X_2) + (1-t)S(X_1) \tag{5.12a}$$

with $t \in [0, 1]$. From the first and the second laws of thermodynamics one has the equations

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_V > 0 \,, \quad \frac{p}{T} = \left.\frac{\partial S}{\partial V}\right|_E \,. \tag{5.12b}$$

With the second choice the function $E(S, V)$ is a single-valued, *convex* function, i.e. with $Y \equiv (S, V)$ and for $t \in [0, 1]$, using (5.2) and (1.46),

$$E(tY_2 + (1-t)Y_1) \leq tE(Y_2) + (1-t)E(Y_1) \,. \tag{5.13a}$$

The function $E(Y)$ is at least C^1 in both arguments. Its first derivatives are

$$T = \left.\frac{\partial E}{\partial S}\right|_V > 0 \,, \quad p = -\left.\frac{\partial E}{\partial V}\right|_S \,. \tag{5.13b}$$

As shown in Sect. 2.7, the homogeneity relation (2.63) holds true. Suppose the surface $Z = E(S, V)$ has a boundary which contains a straight line segment from $P_1 = (S_1, E_1, V_1)$ to $P_2 = (S_2, E_2, V_2)$. A point on this straight part has the coordinates

$$P(X) = (S, E, V) \quad \text{with} \quad X = tX_2 + (1-t)X_1 \tag{5.14}$$

with t in the interval $[0, 1]$. The physical interpretation is fairly obvious: A state $P(X)$ with $0 < t < 1$, (5.14), is a mixture of two coexisting phases P_1 and P_2. The edges P_1 and P_2 describe *pure phases.* The tangent plane at P_1 is tangent to the straight line segment P_1P_2. Therefore, all mixtures P have the same pressure and the same temperature,

$$T = \left.\frac{\partial E}{\partial S}\right|_V \,, \quad p = -\left.\frac{\partial E}{\partial V}\right|_S \,.$$

These variables span the tangent planes of the surface $E(S, V) = \text{const}$. The intersection of the surface $E = E(S, V)$ with the tangent plane T_PE is convex and compact, see Fig. 5.9. Therefore, every state P on this surface can be represented as a convex combination of pure phases.

Clearly, analogous considerations apply to the concave surface $S = S(E, V)$ and its tangent planes, cf. (5.12b).

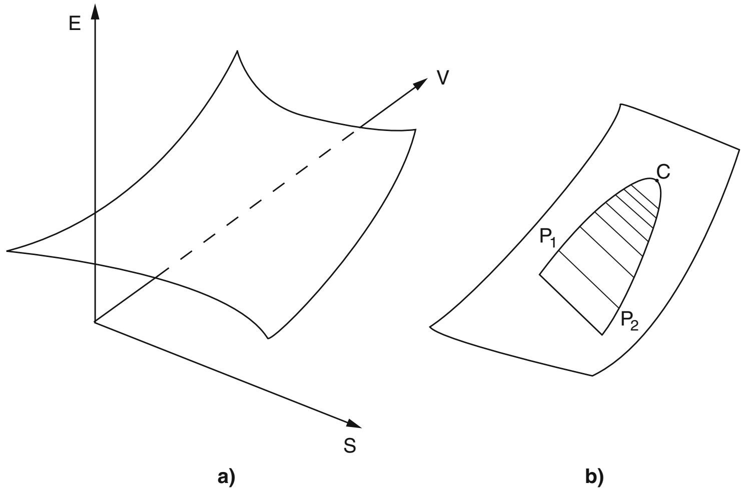


Fig. 5.9 (**a**) A surface $E = E(S, V)$. If this surface contains a flat patch then the intersection of the tangent plane in one of its boundary points with the surface is convex and compact. Any point of this section is a convex combination of pure phases. (**b**) A ruled surface for the example of a mixture of two pure phases. The extreme point C is a critical point

In the case of a mixture of *two* pure phases we obtain a 1-simplex, this is the segment of straight line P_1P_2, cf. Sect. 5.2.1. In fact, the surface is locally what is called a *ruled surface,* that is to say, it is generated by a one-parameter family of straight line segments as shown in Fig. 5.9b but no longer contains any flat patches itself. The extremal point C in Fig. 5.9b is a critical point in the terminology of thermodynamics: In every neighbourhood of this point there exist two distinct, coexisting phases of the same substance.

In all states on the ruled surface the pressure p and the temperature T depend on each other, only one of these quantities can be chosen freely within its range of definition. If the ruled surface is embedded in $\mathbb{R}^3$, then this gives rise to a curve $p(T)$ in the (p, T)-plane which characterizes the coexistence of two phases. Every straight line segment corresponds to a point on this surface.

Example 5.1 (Clausius–Clapeyron Relation) Assume $S = S(E, V)$ contains a ruled surface. The defining equations (2.8a) and (2.8b) of Sect. 2.2.3 which hold in the case of the grand canonical potential $K(T, \mu_C, V)$, give the relations for the entropy and the pressure, respectively,

$$S = -\frac{\partial K}{\partial T}\,, \quad p = -\frac{\partial K}{\partial V}$$

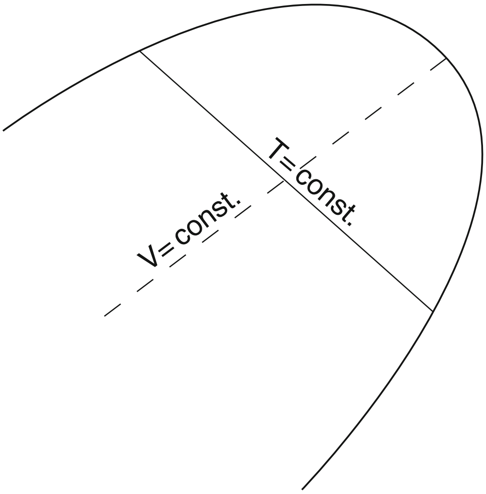


Fig. 5.10 Example of a ruled surface with curves of constant volume and of constant temperature, respectively

and from there the Maxwell relation

$$\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial p}{\partial T}\right|_V , \tag{5.15}$$

(see also Fig. 5.10). On the ruled surface one has

$$\left.\frac{\partial p}{\partial T}\right|_V = \frac{\mathrm{d}p}{\mathrm{d}T} .$$

Furthermore, the entropy S is a linear function of the energy and the volume so that one has

$$\left.\frac{\partial S}{\partial V}\right|_T = \frac{S_2 - S_1}{V_2 - V_1} .$$

Thus, the Maxwell relation (5.15) yields the Clausius–Clapeyron relation for the vapor pressure

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S_2 - S_1}{V_2 - V_1} \equiv \frac{L}{T\Delta V} \quad \text{with} \quad L = T(S_2 - S_1) . \tag{5.16}$$

It relates the derivative of the curve $p(T)$ which describes the equilibrium of phases, to the latent heat L, i.e. the amount of heat that must be furnished, or lead away, in a reversible transition from one phase to another.

An example is provided by the evaporation of a liquid. Referring all quantities to volumes v_1 and v_2 and to entropies s_1 and s_2 per particle, respectively, the volume v_2 in vapor is certainly much larger than in the liquid phase, $v_2 \gg v_1$. The vapor phase can be described, to good approximation, as an ideal gas so that one has $pv = kT$ and therefore

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{Lp}{kT^2} \, .$$

With the assumption that the latent heat, in essence, does not depend on temperature, the Clausius–Clapeyron relation can be integrated to

$$p(T) = p_0 \, \mathrm{e}^{-L/(kT)} \, .$$

The next case of special interest is the mixture of *three* pure phases. A good example is provided by water in the neighbourhood of the triple point. In the space which is spanned by the variables $\{S, E, V\}$, the convex function $E(S, V)$ has flat parts, a triangle and three ruled surfaces which are attached to the triangle. These structures are sketched in Fig. 5.11 as seen from above. The pressure p and the temperature T have constant values on the whole triangle. There is a ruled surface attached to each of the edges of the triangle, see Fig. 5.11, which correspond, respectively, to coexistence of gas and liquid, coexistence of liquid and solid phase, and of gas and solid phase. In the (T, p)-plane the image of this triangle is a single point, called *triple point.* In a projection onto the (T, p)-plane and for the example

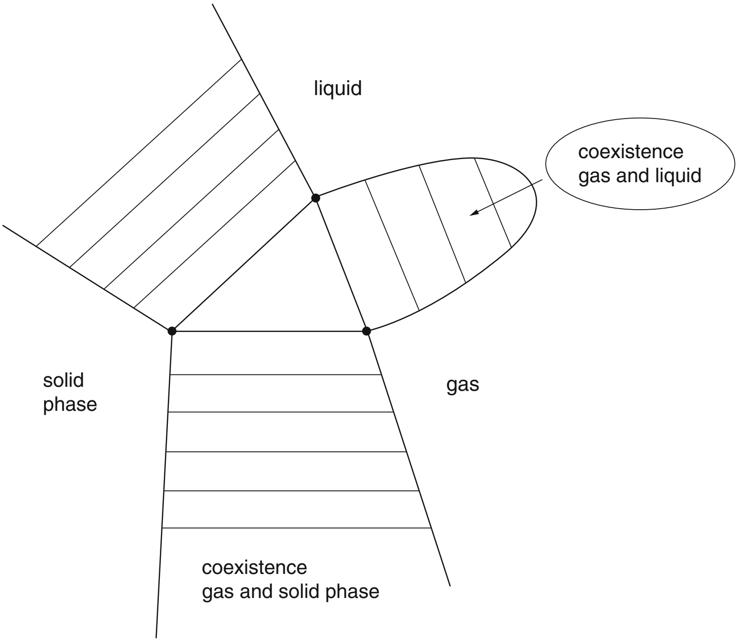
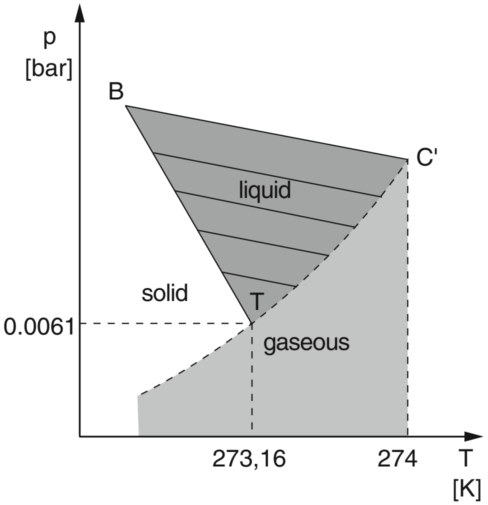


Fig. 5.11 Illustration of a mixture of three pure phases: gas, liquid and solid state, and of their domains of coexistence

Fig. 5.12 Curve of vapour pressure *TC* and three pure phases for the example of water



of water the situation looks qualitatively as sketched in Fig. 5.12. The three curves of coexistence which separate vapor, ice and liquid water start from the triple point ($T = 273.16\,\text{K}$, $p = 0.61 \times 10^{-2}\,\text{bar}$). The curve separating liquid water from the vapor phase, called the water pressure curve, terminates in C', the image of the critical point. Below this point the chemical potentials μ_C^{liquid} and μ_C^{gaseous} differ from each other, the former being defined in the domain "liquid", the latter in the domain "vapor". For temperatures above T_C, the abscissa of C', the potentials are equal. The difference between liquid water and water vapor disappears. Furthermore, one notes that

- in the one phase–domain there are *two* independent variables,
- in the two phase–domain there is *one* variable only, but
- in the three phase–domain there is no longer any variable.

Of course, instead of the convex energy function $E = E(S, V)$ one might as well discuss the concave entropy function $S = S(E, V)$ and illustrate matters by figures analogous to Figs. 5.11 and 5.12. Similarly, the generalization to systems containing more than one substance is possible.

5.2.3 Systems with Two or More Substances

We consider a mixture of n pure substances, the aim being to understand the different phases and their respective domains of coexistence. In this class of systems the energy is a convex, piecewise continuously differentiable function of the entropy S, the volume V and the numbers of particles N_1, N_2, $\ldots$,N_n of all substances contained in the mixture. Definition 1.9 and (1.35) tell us that the chemical potentials

$\mu_C^{(j)}$ are given by the derivatives by N_j, keeping all other variables fixed,

$$\mu_C^{(j)} = \left.\frac{\partial E}{\partial N_j}\right|_{\{X\}} \tag{5.17}$$

$$\text{with} \quad \{X\} = (S, V, N_1, \ldots, N_{j-1}, \widehat{N}_j, N_{j+1}, \ldots, N_n) \ .$$

By definition *pure* phases correspond to extrema of the energy or, alternatively, the entropy. The following criterion is suitable to identify coexistence of any two phases. The hypersurface $E(S, V, N_1, \ldots, N_n)$ (or $S = S(E, V, N_1, \ldots, N - N)$) contains a straight line segment whose end points are denoted by P_1 and P_2. For all points on this line segment we have

$$p_1 = p_2 \ , \quad T_1 = T_2 \ , \quad \mu_C^{(j)1} = \mu_C^{(j)2} \ (j = 1, 2, \ldots, n) \ .$$

Note that Maxwell's rule of equal surfaces can be derived in this framework:

The homogeneity relation (2.63), when written in the form $E = TS - pV + \mu_C N$, yields the differential condition

$$\mathrm{d}E = T\,\mathrm{d}S + S\,\mathrm{d}T - p\,\mathrm{d}V - V\,\mathrm{d}p + \mu_C\,\mathrm{d}N + N\,\mathrm{d}\mu_C \ . \tag{5.18a}$$

Using the first and second law, cf. (2.55c), (3.22) or (3.23), this one-form is seen to be equal to

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu_C\,\mathrm{d}N \ . \tag{5.18b}$$

Taking the difference of (5.18a) and (5.18b) one obtains the relation

$$S\,\mathrm{d}T = V\,\mathrm{d}p - N\,\mathrm{d}\mu_C = 0 \ . \tag{5.18c}$$

Take now the integral from P_1 to P_2 along an isothermal in the (V, p)-plane as sketched in Fig. 5.13,

$$0 = \int_{P_1}^{P_2} \mathrm{d}p \ V + N\left(\mu_C^{(2)} - \mu_C^{(1)}\right) \ . \tag{5.18d}$$

As the second term is equal to zero, the integral in the first term vanishes. The two surfaces enclosed by the isothermal and the straight segment P_1P_2 are equal. This is *Maxwell's rule of equal surfaces.*

The picture-based methods of the preceding paragraph, Sect. 5.2.2, used in describing phase transitions, can be generalized to mixtures of n substances. This is worked out in Wightman (1979). Given the number n of substances, the $(n + 1)$-simplex is the simplex of highest order which can be embedded in the hypersurface of energy. Such a simplex describes an $(n + 2)$-tuple point of coexisting pure phases. For example, for $n = 2$ this is a 3-simplex, i.e. a tetrahedron.

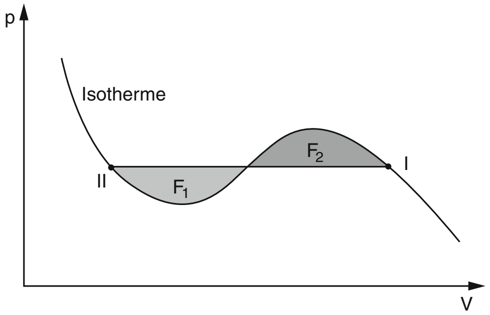


Fig. 5.13 An isothermal in the (V,p)-plane. The surfaces F_1 and F_2 which are enclosed by the straight section P_1P_2 and the curve, are equal

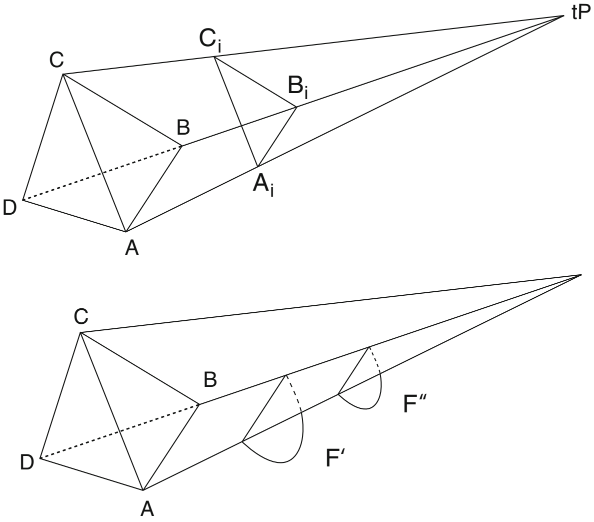


Fig. 5.14 **(a)** Illustration of the situation with four coexisting phases. The triangles in the sections represent triple points of coexisting phases; **(b)** points such as F' and F'' are critical points like in the case of water. The point *tP* is a tricritical point where all neighbouring phases are indistinguishable

It is useful to use thermodynamic variables normalized to the number of particles,

$$\varepsilon := \frac{E}{N}\,, \quad s := \frac{S}{N}\,, \quad v := \frac{V}{N}\,, \quad x_1 := \frac{N_1}{N}\,.$$

As the total number of particles is fixed, $N = N_1 + N_2$, the number N_2 of particles of the second substance no longer is a variable.

On the tetrahedron the hypersurface $\varepsilon(s,v,x_1)$ contains a flat patch. At every corner of the tetrahedron we find four coexisting phases. On any of the side faces of the tetrahedron a structure builds up which consists of triangles of decreasing size. This is sketched in Fig. 5.14. Each of these triangles represents a triple point of coexisting phases. The points F' and F'' are critical points of the kind found for water where fluid and vapor can no longer be distinguished. If the line segments A_iC_i and B_iC_i represent phases akin to those of water, the point *tP* is a tri-critical point where the adjacent phases become indistinguishable.

Further examples and a more detailed discussion can be found in a beautiful article by Wightman quoted above [Wightman, 1979]. The geometrical methods developed in Sect. 5.2.1 provide instructive illustrations for them.

5.3 Thermodynamic Potentials as Convex or Concave Functions

In this section we return to the thermodynamic potentials and the relations between them, but now making use of the mathematical tools developed in Sect. 5.2.1. This supplements and completes the results obtained in Chap. 2. For convenience we list once more the various potentials in use in thermodynamics:

$$\text{entropy } S(E,V,N_1,\ldots,N_n)\ , \tag{5.19a}$$

$$\text{energy } E(S,V,N_1,\ldots,N_n)\ , \tag{5.19b}$$

$$\text{enthalpy } H(S,p,N_1,\ldots,N_n) = pV + E\ , \tag{5.19c}$$

$$\text{free energy } F(T,V,N_1,\ldots,N_n) = E - TS\ , \tag{5.19d}$$

$$\text{free enthalpy } G(T,p,N_1\ldots,N_n) = E - TS + pV\ , \tag{5.19e}$$

grand canonical potential

$$K(T,V,\mu_1,\ldots,\mu_n) = E - TS - \sum \mu_C^{(i)} N_i\ . \tag{5.19f}$$

For the enthalpy H see Definition 2.1, for the free energy cf. Definition 1.12, for the free enthalpy cf. Definition 2.2 and for the grand canonical potential cf. Definition 2.3. Another choice could be the variable $(-p)$ as the Legendre transform of E/V. With this choice one has

$$\frac{E}{V} = \varepsilon\left(\frac{S}{V},\frac{N_i}{V}\right) \longmapsto -p = g(T,\mu_C^{(i)})\ , \quad i = 1,2,\ldots,n\ ,$$

where the negative pressure, as a thermodynamic potential, is given by

$$-p = \frac{E}{V} - T\frac{S}{V} - \sum_{i=1}^{n} \mu_C^{(i)} \frac{N_i}{V}\ . \tag{5.20}$$

We discuss a number of examples:

Example 5.2 (Enthalpy from Energy) The Legendre transform from energy E to enthalpy H is effected in the variable V (in favor of p). If the function E is differentiable one proceeds as in Sect. 1.8. The energy is a strictly convex function so that the equation

$$p = \frac{\partial(-E(S,V,N_i))}{\partial V}$$

can be solved for V. In this case the enthalpy is given by

$$H(S,p,N_i) = pV(S,p,N_i) + E\left(S, V(S,p,N_i), N_i\right) \ . \tag{5.21}$$

If the energy function, though continuous, is only piecewise differentiable, this construction is replaced by

$$\begin{aligned} H(S,p,N_i) &= \sup_V \{(-p)V - E(S,V,N_i)\} \\ &= \inf_V \{pV + E(S,V,N_i)\} \ . \end{aligned} \tag{5.22}$$

Example 5.3 (Free Energy) By Legendre transform in the variable S from the energy E one obtains the free energy F, the volume V and the particle numbers N_i being spectator variables. In the differentiable case $T = \partial E/\partial S$ provides an equation which can be solved for S. In the other case F is obtained from the condition

$$F(T,V,N_i) = \inf_S \{E(S,V,N_i) - TS\} \ , \tag{5.23}$$

by which the variable S is replaced by the temperature.

Example 5.4 (Free Enthalpy) The free enthalpy G can be obtained either from the free energy F or from the enthalpy H by Legendre transform. Going from F to G means Legendre transform from the variable V to the variable p, in the differentiable case via the formula $-p = \partial F/\partial V$, or else by means of

$$G(T,p,N_i) = \inf_V \{E(S,V,N_i) - TS + pV\} \ . \tag{5.24a}$$

If, instead, the Legendre transform is applied to H one replaces the variable S by $T = \partial H/\partial S$. If the condition of differentiability is not fulfilled the Legendre transformed potential is obtained from

$$G(T,p,N_i) = \inf_S \{H(S,p,N_i) - TS\} \ . \tag{5.24b}$$

In this example p and N_i are the spectator variables.

Example 5.5 (Pressure as Potential) In this example S/V is replaced by T, and N_i/V by $\mu_C^{(i)}$ for all i. The transformation is obtained from

$$\begin{aligned} &-p\left(T, \mu_C^{(1)}, \ldots, \mu_C^{(n)}\right) \\ &= \inf_X \left\{ \frac{1}{V}\left(E(S, V, N_i) - TS - \sum_{i=1}^{n} \mu_C^{(i)} N_i \right) \right\} \ , \end{aligned} \tag{5.25}$$

where X stands symbolically for the set

$$X \equiv \left\{ \frac{S}{V}, \frac{N_1}{V}, \ldots \frac{N_n}{V} \right\} \ .$$

One confirms the relations, well-known by now,

$$\begin{aligned} \left.\frac{\partial p}{\partial T}\right|_{(\mu_C^{(1)},\ldots,\mu_C^{(n)})} &= \frac{S}{V} \ , \\ \left.\frac{\partial p}{\partial \mu_C^{(j)}}\right|_{(T,\mu_C^{(1)},\ldots,\hat{\mu}_C^{(j)},\ldots,\mu_C^{(n)})} &= \frac{N_j}{V} \ . \end{aligned}$$

This concludes the series of examples.

5.4 The Gibbs Phase Rule

One considers a thermodynamic system which consists of n substances and which can show r coexisting phases. The pressure, the temperature and the chemical potentials are chosen to be the variables,

$$p \ , \ T \ , \mu_C^{(1)} \ , \ \ldots \ , \ , \mu_C^{(n)} \ . \tag{5.26}$$

If there is only one phase the energy hypersurface has dimension $(n + 1)$. This is in agreement with the example of a single substance, $n = 1$, where the energy surface (and, likewise, the entropy surface) was two-dimensional. If there are two coexisting phases this hypersurface has dimension n. In the example of a single substance, $n = 1$, these were the boundaries between the ruled surfaces of the kind shown in Fig. 5.11.

Coexistence of r pure phases means that the states must lie on the intersection of $(r-1)$ such hypersurfaces. Up to exceptions the remaining hypersurface of possible states has the dimension

$$F = (n + 1) - (r - 1) = n - r + 2 \ . \tag{5.27}$$

This relation is the *Gibbs phase rule.*

Alternatively, the Gibbs rule can also be obtained by the following argument: Suppose the mixture consists of n substances with particle numbers N_1, N_2, …,N_n, respectively. Among the N_i particles of the substance "i" there are N_i^α of them in the phase α, with α taking the values 1 to r. As the particle numbers are constant, the sum of the particles which change the phase, is zero

$$\sum_{\alpha=1}^{r} \mathrm{d}N^{(i)\,\alpha} = 0\ . \tag{5.28a}$$

If in a system with r coexisting phases a state of equilibrium has been reached, the chemical potentials of a given species "i" of particles are all equal,

$$\mu_C^{(i),\alpha=1} = \mu_C^{(i),\alpha=2} = \cdots = \mu_C^{(i),\alpha=r}\ . \tag{5.28b}$$

These are $(r-1)$ equations per substance, hence $n(r-1)$ conditions. The chemical potentials $\mu_C^{(j),\alpha}$ of substance "j" in the phase α, are *intensive* quantities. Therefore, they can only depend on the ratios

$$\frac{N_j^\alpha}{\sum_{k=1}^{n} N_k^\alpha} \quad \text{with} \quad j = 1, 2, \ldots, n\,.$$

For every phase α there are $(n-1)$ ratios. Furthermore, the chemical potentials also depend on the variables p and T, and thus they depend on $r(n-1)+2$ variables. Subtracting the number of conditions (5.28b) from the total number of variables $r(n-1)+2$, one obtains

$$F = [r(n-1)+2] - n(r-1) = n - r + 2\ . \tag{5.28c}$$

This is seen to be the Gibbs phase rule (5.27).

Remarks

i) Gibbs' phase rule can only be applied if the decomposition of a mixed phase into pure phases is unique. This will be so whenever the mixed phase lies on a simplex. As we saw previously, in the case of a single substance this can only be a 2-simplex, i.e. a triangle. We refer to the article Wightman (1979) for some instructive counterexamples to the rule (5.27) .

ii) In the framework of statistical mechanics it turns out that the dynamics can and must be refined. The Hamilton operators or, in the classical case, the Hamiltonian functions on microscopic or semi-microscopic scales contain more information than the thermodynamic potentials. For instance, additional information is visible in the correlation functions of the system. Examples are magnetic systems which depend on semi-macroscopic variables such as the magnetization, or mixtures of ^{3}He and ^{4}He in the domain of coexistence in liquid and superfluid Helium.

5.5 Discrete Models and Phase Transitions

Realistic examples for phase transitions and their theoretical description are the subject of a theory of condensed matter which goes far beyond the framework of a textbook on the theory of heat. In this section we study only a few schematic, discrete models which allow to study, by means of examples, general aspects in relation to phase transitions. For a deeper understanding of the important field of phase transitions we refer to the more specialized literature, such as, e.g., Balian (2007), Thompson (1979), Binder and Landau (2005). Our choice of examples is based primarily on Thompson (1979).

5.5.1 A Lattice Gas

We consider a gas consisting of a finite number N of particles and attempt to describe it by means of a discrete lattice. This is perhaps the simplest microscopic model of a thermodynamic system in equilibrium. The model is specified as follows.

Let a lattice with V lattice sites be given. (We choose the letter V because, in the limit of a continuum, V will related to the volume of the lattice.) The N particles are disposed on the lattice sites in such a way that there is at most one particle per site. The sites are numbered by an index $p \in V$. One introduces an occupation parameter n_p which can only take the values zero or one.

A *configuration*

$$\{n\} = \bigl(n_1, n_2, \ldots, n_V |\, (n_p = 0 \text{ or } 1), p \in V\bigr) \tag{5.29}$$

is defined by giving the occupation numbers n_1 to n_V with the constraint

$$\sum_{p=1}^{V} n_p = N \,. \tag{5.30}$$

Regarding the *interaction* between two gas particles we assume that it is different from zero only if the particles are immediate neighbours, that is to say for two arbitrary lattice sites $p_i, p_k \in V$ the interaction potential is

$$U(i,k) = \begin{cases} +\infty \,, & \text{if } p_i \text{ and } p_k \text{ are occupied and } i = k \,, \\ -A \,, & \text{if } p_i \text{ and } p_k \text{ are nearest neighbours,} \\ 0 \,, & \text{if separated by more than one lattice site.} \end{cases} \tag{5.31}$$

(The first of these conditions guarantees that at a given lattice site there can never be more than one particle.)

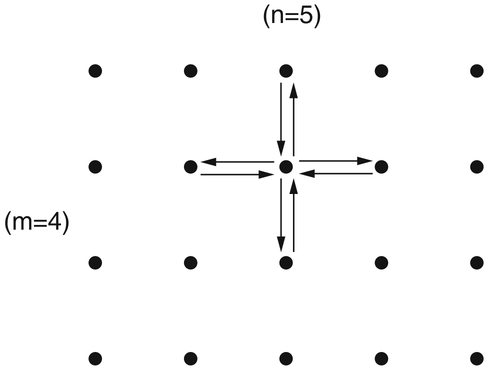


Fig. 5.15 Model for a lattice gas in the plane. Every particle at an (inner) lattice site interacts only with its four direct neighbours

The strength of the interaction is characterized by a coupling constant A which, as yet, is unknown. The energy as a function of the configuration is then given by

$$E(\{n\}) = -A\,\Sigma'_{i,k}\,n_i n_k \quad \text{with} \quad \sum_{i=1}^{V} n_i = N\,. \tag{5.32}$$

The notation $\Sigma'_{i,k}$ means that one sums only over pairs of neighbouring lattice sites.

As an example we consider a lattice in the *plane*. The example shown in Fig. 5.15 consists of $m = 4$ rows and $n = 5$ columns. Any lattice site which is an inner point, has four neighbours, i.e. four valences, $v_0 = 4$, which must be counted in the sum Σ'. However, every inner bond occurs twice but should be counted only once. Thus, with a total of $N_0 = n \cdot m$ lattice points, the sum of the nearest-neighbour relations is $\sum' = N_0(v_0/2)$. Disregarding boundary effects there would be 40 relations in the example of Fig. 5.15. The bonds pointing outside the lattice which are contained in this sum must be subtracted, of course. Thus, the number of neighbour relations is

$$\sum{}' = N_0\tfrac{v_0}{2} - (n + m)\,, \tag{5.33}$$

and therefore, in our example, $40 - 9 = 31$. The additional term on the right-hand side is a typical boundary term whose contribution decreases with the size of the lattice so that, eventually, it can be neglected.

If interpreted as a *canonical* ensemble, the gas would be described by the partition function

$$Z_{\text{can.}}(T, V, N) = \sum \mathrm{e}^{-\beta E(\{n\})}$$

$$\text{with} \quad \beta = \frac{1}{kT} \quad \text{and} \quad \sum_{p=1}^{V} n_p = N\,. \tag{5.34}$$

The constraint $\sum_{p=1}^{V} n_p = N$ may also be incorporated in the partition function by expanding the partition function of the *grand canonical* ensemble in terms of the particle number. According to (2.13) and (4.28c) one has

$$Z_{\mathrm{G}} = \mathrm{e}^{-\beta K(T,\mu_C,V)} \quad \text{with} \quad \beta K = \beta H - \beta\mu_C N = \beta H - \alpha N \; ,$$

where H is the Hamilton operator (or the Hamiltonian function). Thereby the partition function is turned into a series of *canonical* ensembles,

$$\begin{aligned} Z_{\mathrm{G}} &= \sum \mathrm{e}^{-\beta H + \alpha N} = \sum_N z^N \sum \mathrm{e}^{-\beta H} \\ &\equiv \sum_N z^N Z_{\mathrm{can.}}(T,V,N) \; . \end{aligned} \tag{5.35}$$

The expansion parameter of this series,

$$z = \mathrm{e}^{\alpha} \; , \tag{5.36}$$

is called *fugacity*.

Applying this idea to the example of the lattice gas one obtains

$$Z_{\mathrm{G}}(T,z,V) = \sum_{\{n\}} z^{\left(\sum_p n_p\right)} \mathrm{e}^{-\beta E(\{n\})} \; . \tag{5.37}$$

The constraint (5.30) is now built in the partition function. We continue the analysis of this example further below.

5.5.2 Models of Magnetism

Suppose the constituents of a lattice carry magnetic moments

$$\boldsymbol{\mu}_i = g\mu_B \boldsymbol{s}_i ,$$

with μ_B the Bohr magneton and g the gyromagnetic ratio. In correspondence with the values $s^{(3)} = \pm 1/2$ of the spin component along the 3-axis, the magnetic moments can take two orientations that we denote by $+1$ or $\uparrow$ and -1 or $\downarrow$, respectively. An instructive model for such a lattice is one where the magnetic moments, except for interactions with external fields $\boldsymbol{B}$, interact only if they are immediate neighbours. The energy of a given configuration then takes the form

$$E(\{\mu\}) = -J\,\Sigma'_{i,k}\mu_i\mu_k - B\,\Sigma_i\mu_i \; , \qquad (B = |\mathbf{B}|) \; , \tag{5.38}$$

where the sum Σ' is taken over nearest behaviours only. Without loss of generality and for the sake of simplicity one may assume that the "magnetic moments" μ_i take the values $+1$ and -1. Depending on how the nearest neighbours are aligned, parallel or antiparallel, one has

$$-J\mu_i\mu_k = \begin{cases} -J \text{ for } \uparrow\uparrow \text{ and } \downarrow\downarrow\,, \\ +J \text{ for } \uparrow\downarrow \text{ and } \downarrow\uparrow\,. \end{cases}$$

If J is positive, the configuration with spins parallel is the energetically preferred one. In this case and with a total of N magnetic moments, the ground state energy is

$$E_0 = \inf_{\{\mu\}} E(\{\mu\}) = -\frac{1}{2}v_0 NJ - N|B|\,.$$

(Like in (5.33) the number of neighbouring sites is v_0.) Thus, for $J > 0$ the expression (5.38) is a model for a *ferromagnet*. With a parameter $J < 0$ one obtains a model for an *antiferromagnet.*

In the simplest case of a one-dimensional lattice and if the lattice is open at its ends, the energy is

$$E(\{\mu\}) = -J\sum_{i=1}^{N-1}\mu_i\mu_{i+1} - B\sum_{i=1}^{N}\mu_i\,. \tag{5.39a}$$

If the lattice is closed to a ring, see Fig. 5.16b, a, the energy is

$$E(\{\mu\}) = -J\sum_{i=1}^{N}\mu_i\mu_{i+1} - B\sum_{i=1}^{N}\mu_i \quad \text{with} \quad \mu_{N+1} = \mu_1\,, \tag{5.39b}$$

The latter case corresponds to the assumption of periodic boundary conditions.

In the case of a lattice in two dimensions the total energy is a sum over all occupied lattice sites. Thus, for a fully occupied $m \times n$-lattice the energy is given by

$$\begin{aligned} E(\{\mu\}) = &-J\left\{\sum_{i=1}^{m-1}\sum_{k=1}^{n}\mu_{ik}\mu_{(i+1)k} + \sum_{i=1}^{m}\sum_{k=1}^{n-1}\mu_{ik}\mu_{i(k+1)}\right\} \\ &- B\sum_{i,k}\mu_{ik}\,. \end{aligned} \tag{5.40a}$$

The partition function of the corresponding grand canonical ensemble is obtained from the formula (5.37).

By analogy to (5.39b) also this model can be provided with periodic boundary conditions by bending the two-dimensional lattice to a torus T^2, as shown in Fig. 5.16b. With m rows and n columns of the initially plane lattice, this is equivalent

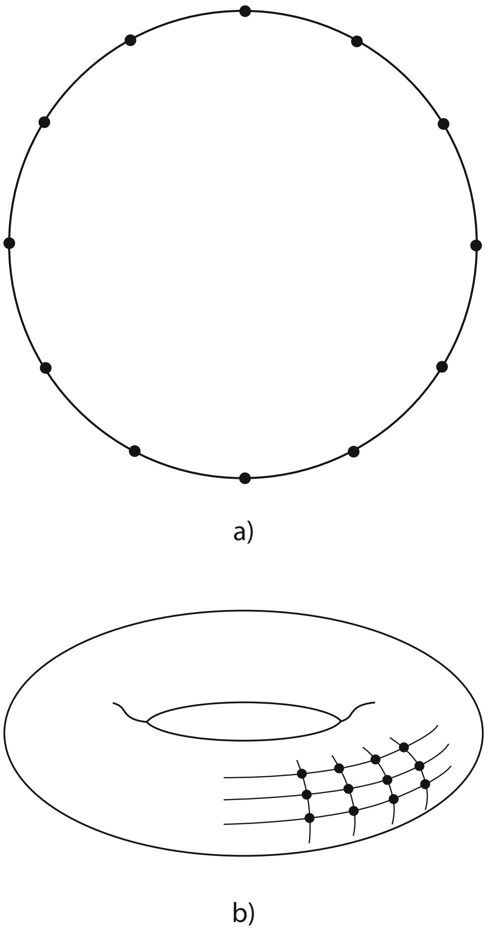


Fig. 5.16 **(a)** A linear chain of magnetic moments with nearest-neighbour interaction which may also be bent together to form a ring. **(b)** A lattice in two dimensions with periodic boundary conditions can be soldered to a torus

to the assumption

$$\mu_{(m+1)k} = \mu_{1k} \quad \text{and} \quad \mu_{i(n+1)} = \mu_{i1}\ . \tag{5.40b}$$

As a first application one shows that the lattice gas of the preceding Sect. 5.5.1 is of this type (5.38). To see this relate the occupation number n_i of the lattice gas to the magnetic moments μ_i by the formula

$$n_i = \frac{1}{2}(1 - \mu_i)\,.$$

The partition function of the grand canonical ensemble (5.37), together with the formula (5.32) for the energy, then yields

$$
\begin{aligned}
Z_{\mathrm{G}} &= \sum_{\{n\}} z^{\Sigma_i(1-\mu_i)/2} \exp\left\{\beta A \frac{1}{4} \Sigma'_{ik}(1-\mu_i)(1-\mu_k)\right\} \\
&= \exp\left\{\tfrac{1}{2} V \ln z - \tfrac{1}{2}\Sigma_i \mu_i \ln z + \beta A \tfrac{1}{8} v_0 V - \tfrac{1}{4} v_0 \beta A \Sigma_i \mu_i + \tfrac{1}{4}\beta A \Sigma' \mu_i \mu_k\right\} ,
\end{aligned}
$$

where we used the sums over nearest neighbours

$$
\Sigma'_{ik} 1 = \frac{1}{2} v_0 V \quad \text{and} \quad \Sigma'_{ik}\mu_i = \frac{1}{2} v_0 \sum_i \mu_i .
$$

As before v_0 is the number of nearest neighbours for every inner point on the lattice. Finally, one defines

$$
A =: 4J , \qquad -\frac{1}{2}\ln z - \frac{1}{4} v_0 \beta A =: \beta B \tag{5.41}
$$

and thereby obtains a direct analogue of the model (5.40a),

$$
\begin{aligned}
Z_{\mathrm{G}}(T, z, V) &= \exp\left\{\tfrac{1}{2} V \ln z + \tfrac{1}{8} v_0 \beta V A\right\} \\
&\quad \times \sum_{\{n\}} \exp\left\{\beta J \Sigma' \mu_i \mu_k + \beta B \sum_i \mu_i\right\} \\
&= \exp\left\{\tfrac{1}{2} V \ln z + \tfrac{1}{8} v_0 \beta V A\right\} Z_{\mathrm{can.}}(T, V, N)
\end{aligned} \tag{5.42}
$$

taking into account the formulae (5.35) and (5.37) for Z_{G}.

Given a grand canonical partition function, various state and material properties can be computed. Here are some examples: According to the formula (5.20) the pressure is obtained from

$$
\beta p = \frac{1}{V} \ln Z_{\mathrm{G}} = -\frac{1}{V} \beta K . \tag{5.43a}
$$

This function is derived from the formula (5.42),which has the form $Z_{\mathrm{G}} = \exp\{\Phi(z, V)\} Z_{\mathrm{can.}}$. Here $\Phi(z, V)$ stands for

$$
\begin{aligned}
\Phi(z, V) &= \tfrac{1}{2} V \ln z + \tfrac{1}{8} v_0 \beta V A \\
&= -\beta V \left(B + \frac{1}{8} v_0 A\right) = -\beta V \left(B + \frac{1}{2} v_0 J\right) .
\end{aligned}
$$

Note that in the second step we used the definitions (5.41) for B and J, respectively. From (5.42) one concludes

$$p\beta = -\beta\left(B + \frac{1}{2}v_0 J\right) + \frac{1}{V}\ln Z_{\text{can.}}(T, V, N) \ . \tag{5.43b}$$

Up to the sign and to the factor β the last term on the right-hand side is the free energy f per spin

$$\beta f = -\frac{1}{V}\ln Z_{\text{can.}}(T, V, N) \ , \tag{5.43c}$$

so that the pressure is given by $p = -f - B - v_0 J/2$.

In much the same way one obtains the density ϱ from the formula

$$\varrho = z\frac{\partial}{\partial z}\left(\frac{1}{V}\ln Z_{\text{G}}\right) \ . \tag{5.44}$$

More examples will be given below.

5.5.3 One-Dimensional Models with and Without Magnetic Field

Although models for magnetism in one dimension are not very realistic, they have the advantage that they are exactly soluble. We start with a chain of spins, but without a magnetic field, $B = 0$, which interact only with their nearest neighbours. With the same assumptions as in Sect. 5.5.2 let the partition function for a canonical ensemble of N spins be defined as follows,

$$\begin{aligned} Z^{(N)}_{\text{can.}} &= \exp\{-\beta E(\{\mu\})\} \\ &= \sum_{\mu_1=-1}^{+1}\cdots\sum_{\mu_N=-1}^{+1}\exp\{x(\mu_1\mu_2 + \mu_2\mu_3 + \ldots \mu_{N-1}\mu_N)\} \end{aligned} \tag{5.45}$$

with $x = \beta J$. Performing first the sum over $\mu_N = \pm 1$, taking account of the fact that

$$\sum_{\mu_N=-1}^{+1} \mathrm{e}^{x\mu_{(N-1)}\mu_N} = \mathrm{e}^{x\mu_{(N-1)}} + \mathrm{e}^{-x\mu_{(N-1)}} = \mathrm{e}^{x} + \mathrm{e}^{-x} = 2\cosh x \ ,$$

independently of whether $\mu_{(N-1)}$ equals plus or minus one, one obtains

$$Z^{(N)}_{\text{can.}} = (2\cosh x)\, Z^{(N-1)}_{\text{can.}} \ .$$

This elementary recurrence formula can be continued and one obtains

$$Z^{(N)}_{\text{can.}} = 2\,(2\cosh x)^{N-1} \ . \tag{5.46}$$

The factor of 2 follows from the trivial case $N = 2$ where $Z^{(2)}_{\text{can.}} = 4\cosh x$ (reader please verify!). This is the simplest version of what is called the *Ising model*. This model was developed by Ernst Ising in 1925.[2]

Using the formula (5.43c) one now computes the free energy per spin. In the limit $N \to \infty$ one finds

$$-\beta f = -\frac{f}{kT} = \lim_{N\to\infty} \frac{1}{N} \ln Z^{(N)}_{\text{can.}} = \ln(2\cosh x) \ , \tag{5.47}$$

where $x = J/(kT)$. This function is analytic for all positive values of the temperature, $T > 0$.

There is no phase transition in dimension 1.

Another simple one-dimensional model is a periodic chain with N links. This is obtained by identification of the last and the first spin, $\mu_{N+1} = \mu_1$. In contrast to the previous model we allow the magnetic moments to interact with an external magnetic field. The partition function then takes the form

$$Z^{(N)}_{\text{can.}} = \sum_{\{\mu\}} \exp\left\{ x \sum_{i=1}^{N} \mu_i \mu_{i+1} + y \sum_{i=1}^{N} \mu_i \right\} \tag{5.48}$$
$$\text{with} \quad x = \beta J \quad \text{and} \quad y = \beta B \ .$$

The contribution of two neighbouring links to the partition function is

$$M(\mu_i, \mu_{i+1}) = \exp\left\{ x\mu_i\mu_{i+1} + \tfrac{1}{2} y (\mu_i + \mu_{i+1}) \right\} \ . \tag{5.49a}$$

As μ_i and μ_{i+1} can take the values $+1$ and -1 only, this is a 2×2-matrix which can be written as follows

$$\begin{aligned} M &= \begin{pmatrix} M(+,+) & M(+,-) \\ M(-,+) & M(-,-) \end{pmatrix} = \begin{pmatrix} \mathrm{e}^{x+y} & \mathrm{e}^{-x} \\ \mathrm{e}^{-x} & \mathrm{e}^{x-y} \end{pmatrix} \\ &= \mathrm{e}^{x} \cosh y \mathbb{1}_2 + \mathrm{e}^{x} \sinh y \sigma_3 + \mathrm{e}^{-x} \sigma_1 \ , \end{aligned} \tag{5.49b}$$

---

[2] E. Ising Beiträge zur Theorie des Ferromagnetismus, Z. Physik (1925), vol. 31, p. 253.

where σ_3 and σ_1 are two of the three Pauli matrices,

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} , \quad \sigma_2 = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix} , \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} .$$

All factors $M(\mu_i, \mu_{i+1})$ have the same form (5.49b) and, in fact, are all equal. Furthermore, since we have $\mu_{N+1} = \mu_1$, that is to say, as the chain closes, the partition function equals the trace of the N-fold product of M with itself. Therefore, one has

$$Z_{\text{can.}}^{(N)} = \operatorname{tr}\left(M^N\right) = \lambda_1^N + \lambda_2^N , \tag{5.50}$$

where (λ_1, λ_2) are the eigenvalues of the matrix M. These eigenvalues are easily calculated. The first term in (5.49b) is already diagonal and is proportional to the unit matrix. An orthogonal transformation A which diagonalizes the sum of the two remaining terms,

$$A\left(\mathrm{e}^x \sinh y \sigma_3 + \mathrm{e}^{-x}\sigma_1\right) A^T = \operatorname{diag}(\varrho, -\varrho)$$

$$\text{with} \quad \varrho = \sqrt{\mathrm{e}^{2x} \sinh^2 y + \mathrm{e}^{-2x}}$$

leaves invariant the first term. Indeed, the eigenvalues of this second part are easily determined: the matrix

$$\mathrm{e}^x \sinh y \sigma_3 + \mathrm{e}^{-x}\sigma_1 \equiv \begin{pmatrix} a & b \\ b & -a \end{pmatrix}$$

has trace zero. Thus, its eigenvalues (ϱ_1, ϱ_2) are equal and opposite. Their product is equal to the determinant, $\det(\cdots) = -(a^2 + b^2)$ and one concludes $\varrho_1 = -\varrho_2 = \sqrt{a^2 + b^2}$.

Using these results the eigenvalues of M are found to be

$$\left.\begin{matrix} \lambda_1 \\ \lambda_2 \end{matrix}\right\} = \mathrm{e}^x \cosh y \pm \sqrt{\mathrm{e}^{2x} \sinh^2 y + \mathrm{e}^{-2x}} . \tag{5.51}$$

For all positive values of x the eigenvalue λ_1 is strictly larger than λ_2. Therefore, for large values of N the first term in (5.50), λ_1^N, is the dominant term. So, for example, the free energy per spin is given by

$$\begin{aligned} \lim_{N\to\infty} \frac{1}{N} \ln Z_{\text{can.}}^{(N)} &= \lim_{N\to\infty} \frac{1}{N} \ln \left\{ \lambda_1^N \left(1 + \left(\tfrac{\lambda_2}{\lambda_1}\right)^N \right) \right\} \\ &= \ln \lambda_1 + \lim_{N\to\infty} \ln \left(1 + \left(\tfrac{\lambda_2}{\lambda_1}\right)^N \right) \end{aligned}$$

$$= \ln\left\{ \mathrm{e}^{x}\cosh y + \sqrt{\mathrm{e}^{2x}\sinh^2 y + \mathrm{e}^{-2x}} \right\} \ . \tag{5.52}$$

For vanishing magnetic field, $y = 0$, the partition function (5.50) is

$$Z^{(N)}_{\text{can.}}(y=0) = (\cosh x)^N + (\sinh x)^N \tag{5.53}$$

and, at first, does not coincide with the result (5.46) for the open chain. Only for $N \to \infty$, in what is called the *thermodynamic limit,* the two expressions (5.46) and (5.53) tend towards each other.

5.5.4 Ising Model in Dimension Two

Another version of the Ising-model may be defined by means of a two-dimensional lattice with m rows and n columns. Furthermore, this lattice is thought to be bent to a cylinder in such a way that the $(n+1)$-st column is identified with column number 1 as shown in Fig. 5.17. The interaction energy between nearest neighbours and with an external magnetic field B is given by

$$\begin{aligned} E(\{\mu\}) = &-J\sum_{i=1}^{m-1}\sum_{k=1}^{n}\mu_{ik}\mu_{(i+1)k} - J\sum_{i=1}^{m}\sum_{k=1}^{n}\mu_{ik}\mu_{i(k+1)} \\ &- B\sum_{i=1}^{m}\sum_{k=1}^{n}\mu_{ik} \end{aligned} \tag{5.54}$$

It is useful to collect the magnetic moments of the k-th column in one symbol,

$$S_k := (\mu_{1k}, \mu_{2k}, \ldots, \mu_{mk}) \equiv (\mu_1, \ldots, \mu_m) \ . \tag{5.55}$$

The interaction *within* this column then is

$$U^{(\text{vertical})}(S_k) = -J\sum_{i=1}^{m-1}\mu_{ik}\mu_{(i+1)k} - B\sum_{i=1}^{m}\mu_{ik} \ , \tag{5.56a}$$

while the nearest-neighbour interaction between column number k and column number $k+1$ is given by

$$U^{(\text{neighbour})}(S_k, S_{k+1}) = -J\sum_{i=1}^{m}\mu_{ik}\mu_{i(k+1)} \ . \tag{5.56b}$$

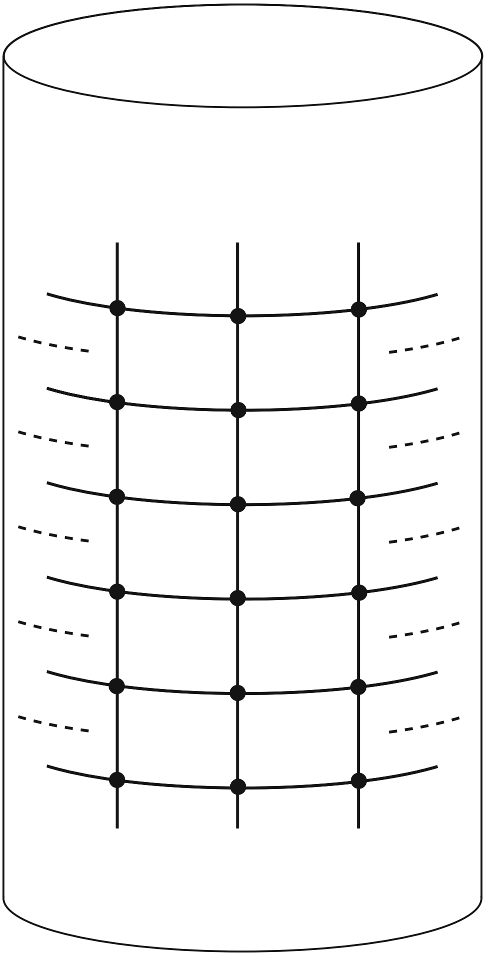


Fig. 5.17 A plane lattice of magnetic moments with periodic boundary conditions is soldered to a cylinder

The total energy (5.54) is the sum of these contributions,

$$E(\{\mu\}) = \sum_{k=1}^{n} \Big\{ U^{(\text{vertical})}(S_k) + U^{(\text{neighbour})}(S_k, S_{k+1}) \Big\} \,. \tag{5.56c}$$

Therefore, the canonical partition function is

$$\begin{aligned} Z^{(m,n)}_{\text{can.}} &= \sum_{\{\mu\}} \mathrm{e}^{-\beta E(\{\mu\})} \\ &= \sum_{S_1, \cdots, S_n} \mathrm{e}^{-\beta \sum_{k=1}^{n} \{ U^{(\text{vertical})}(S_k) + U^{(\text{neighbour})}(S_k, S_{k+1}) \}} \,. \end{aligned} \tag{5.57}$$

Like in the previous example the partition function can be written as the n-fold product of a symmetric $2^m \times 2^m$ matrix M. Thus, if the lattice is deformed to a cylinder, the partition function is the trace of this product. This is seen as follows: Defining the matrix

$$M(S,S') := \mathrm{e}^{-(\beta/2)U^{(\text{vertical})}(S)}\,\mathrm{e}^{-\beta U^{(\text{neighbour})}(S,S')}\,\mathrm{e}^{-(\beta/2)U^{(\text{vertical})}(S')} \tag{5.58}$$

one sees that the partition function is given by

$$Z_{\text{can.}}^{(m,n)} = \sum M(S_1,S_2)M(S_2,S_3)\cdots M(S_{n-1},S_n)M(S_n,S_1)\ . \tag{5.59a}$$

Writing down the matrix M for two neighbouring columns S and S', using the abbreviation (5.55), that is, $S_k \equiv (\mu_1,\dots,\mu_m)$ and $S_{k+1} \equiv (\mu'_1,\dots,\mu'_m)$, one has

$$M(S_k,S_{k+1}) = \exp\left\{(x/2)\sum_{i=1}^{m-1}\mu_i\mu_{i+1} + (y/2)\sum_{i=1}^{m}\mu_i\right\}$$

$$\times\exp\left\{x\sum_{i=1}^{m}\mu_i\mu'_i\right\}\exp\left\{(x/2)\sum_{i=1}^{m-1}\mu'_i\mu'_{i+1} + (y/2)\sum_{i=1}^{m}\mu'_i\right\}$$

with $x = \beta J$ and $y = \beta B$. As the moments μ_i can only take the values ±1, every column S_k contains 2^m configurations. Therefore, the matrices $M(S,S')$ in (5.59a) are symmetric $2^m \times 2^m$-matrices and they are all equal. Thus, the partition function is given by

$$Z_{\text{can.}}^{(m,n)} = \operatorname{tr}(M^n) = \sum_{k=1}^{2^m}\lambda_k^n\ , \tag{5.59b}$$

where $\lambda_1,\dots,\lambda_{2^m}$ are the eigenvalues of M. These eigenvalues are numbered in decreasing order.

$$\lambda_1 > \lambda_2 \geq \lambda_3 \geq \cdots \geq \lambda_{2^m}\ .$$

In the thermodynamic limit only the largest eigenvalue λ_1 matters. For example, the free energy per spin is found to be

$$-\frac{f}{kT} = \lim_{m\to\infty}\lim_{n\to\infty}\frac{1}{mn}Z_{\text{can.}}^{(m,n)} = \lim_{m\to\infty}\frac{1}{m}\ln\lambda_1$$

$$+\lim_{m\to\infty}\left\{\lim_{n\to\infty}\frac{1}{mn}\ln\left(1+\sum_{k=2}^{2^m}\left(\tfrac{\lambda_k}{\lambda_1}\right)^n\right)\right\}\ . \tag{5.60}$$

Actually, solving this problem is an involved and cumbersome task. In the special case of zero magnetic field, $y = 0$, an analytic solution for λ_1 exists but the published solutions are rather intricate. A method originally developed by Onsager and which makes use of techniques based on Lie algebras is described, e.g., in Thompson (1979), in an appendix. We skip the detailed derivation. We quote the result and draw a few conclusions from it. For more details and a complete exposition of Onsager's method and other, combinatoric, approaches we refer to Thompson (1979).

In the case of vanishing magnetic field, $B = 0$, the highest eigenvalue is

$$\lambda_1 = (2\sinh(2x))^{m/2} \exp\bigl\{\tfrac{1}{2}(\gamma_1 + \gamma_3 + \cdots + \gamma_{2m-1})\bigr\} , \tag{5.61a}$$

where $x := \beta J = J/(kT)$. The parameters γ_k are to be taken from the equations

$$\cosh \gamma_k = \cosh(2x)\coth(2x) - \cos(\pi k/m) \ . \tag{5.61b}$$

The free energy per spin then becomes

$$\begin{aligned} -\frac{f}{kT} &= \lim_{m\to\infty} \frac{1}{m} \ln \lambda_1 \\ &= \frac{1}{2}\ln[2\sinh(2x)] + \lim_{m\to\infty} \frac{1}{2m} \sum_{l=0}^{m-1} \gamma_{2l+1} , \end{aligned} \tag{5.62}$$

whose second term, in the limit $m \to \infty$, goes over into an integral,

$$\lim_{m\to\infty} \frac{1}{2m} \sum_{l=0}^{m-1} \gamma_{2l+1} = \frac{1}{2\pi} \int_0^{\pi} \mathrm{d}\theta \ \cosh^{-1}[\cosh(2x)\coth(2x) - \cos\theta] \ .$$

Making use of the identity

$$\cosh^{-1}(|u|) = \frac{1}{\pi} \int_0^{\pi} \mathrm{d}\theta' \ \ln\bigl[2(u - \cos\theta')\bigr] ,$$

the free energy per spin goes over into

$$\begin{aligned} -\frac{f}{kT} &= \frac{1}{2}\ln[2\sinh(2x)] + \frac{1}{2}\ln 2 \\ &+ \frac{1}{2\pi^2} \int_0^{\pi}\!\!\int_0^{\pi} \mathrm{d}\theta\,\mathrm{d}\theta' \ \ln\bigl[\cosh(2x)\coth(2x) - \cos\theta - \cos\theta'\bigr] \ . \end{aligned} \tag{5.63a}$$

If one partially resolves the logarithms, this formula takes a manifestly symmetric form in the variables θ and θ',

$$\begin{aligned}
-\frac{f}{kT} &= \ln 2 + \frac{1}{2}\ln\bigl(\sinh(2x)\bigr) \\
&+ \frac{1}{2\pi^2}\int_0^\pi\int_0^\pi \mathrm{d}\theta\,\mathrm{d}\theta'\;\ln\left\{\cosh^2(2x) - \sinh(2x)\left[\cos\theta + \cos\theta'\right]\right\} \\
&- \frac{1}{2\pi^2}\ln\bigl(\sinh(2x)\bigr)\int_0^\pi\int_0^\pi \mathrm{d}\theta\,\mathrm{d}\theta' \\
&= \ln 2 + \frac{1}{2\pi^2}\int_0^\pi\int_0^\pi \mathrm{d}\theta\,\mathrm{d}\theta'\;\ln\left\{\cosh^2(2x) - \sinh(2x)\left[\cos\theta + \cos\theta'\right]\right\}\;.
\end{aligned} \tag{5.63b}$$

In Fig. 5.18 we show the curves

$$f_1(x) = \cosh^2(2x) = \frac{1}{4}\left(\mathrm{e}^{4x} + 2 + \mathrm{e}^{-4x}\right)\;, \tag{5.64a}$$

$$f_2(x) = 2\sinh(2x) = \mathrm{e}^{2x} - \mathrm{e}^{-2x}\;, \tag{5.64b}$$

$$d(x) := f_1(x) - f_2(x) = (1 - \sinh(2x))^2\;. \tag{5.64c}$$

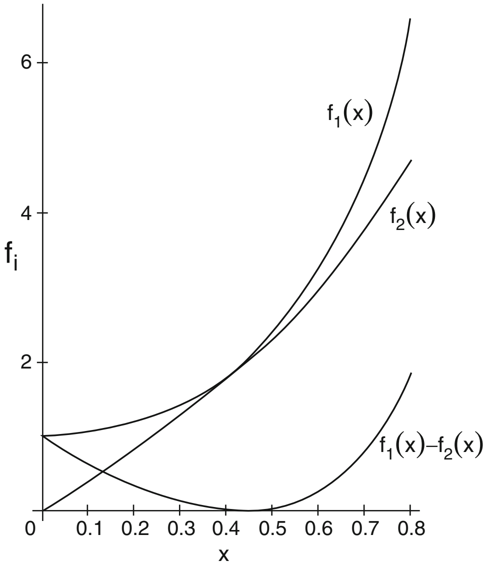


Fig. 5.18 Graphs of the functions (5.64a)–(5.64c) versus the variable $x = \beta J$

One notes from (5.64a) and (5.64b) as well as from the figure that f_1 and f_2 are tangent if $\sinh(2x_\mathrm{c}) = 1$, i.e. at the value

$$x_\mathrm{c} = \frac{J}{(kT_\mathrm{c})} \simeq 0.44013\ ; \tag{5.65}$$

Everywhere else f_2 lies below f_1 (see exercise 5.4). The argument of the logarithm in the integrand of (5.63b) can only come close to zero (from above) if the two angles of integration θ and θ' approach the lower limit of integration. Indeed, for $\theta \to 0^+$ and, simultaneously, $\theta' \to 0^+$, the integrand on the right-hand side of (5.63b) becomes

$$\ln\left\{d(x) + \sinh(2x)\left[(1-\cos\theta) + (1-\cos\theta')\right]\right\} \simeq \ln d(x)$$

with $d(x)$ from (5.64c). This function has a zero at the value x_c, (5.65). For all other values of x, of θ and of θ', the argument of the logarithm is positive.

That there is indeed a singularity in this particular constellation can be seen from the first derivative of the free energy by x. To witness, calculate, e.g., the inner energy from the partial derivative of the free energy per spin by the temperature,

$$\begin{aligned} E &= kT^2 \frac{\partial}{\partial T}\left(\frac{f}{kT}\right) = J\frac{\partial}{\partial x}\left(\frac{f}{kT}\right) \\ &= -J\coth(2x)\left\{1 + \left(\sinh^2(2x) - 1\right)\right. \\ &\left.\cdot \frac{1}{\pi^2}\int_0^\pi\!\!\int_0^\pi \mathrm{d}\theta\,\mathrm{d}\theta'\, \frac{1}{d(x) + \sinh(2x)\left[(1-\cos\theta) + (1-\cos\theta')\right]}\right\}\ . \end{aligned} \tag{5.66}$$

Choosing x very close to the zero x_c of $d(x)$, $d(x) \simeq \varepsilon$ with $\varepsilon \ll 1$, one sees that the integral in (5.66) exhibits a logarithmic singularity in the neighbourhood of $(\theta = 0, \theta' = 0)$. In Exercise 5.5 the reader is invited to show that in this limit the integral in (5.66) is proportional to $\ln\varepsilon$,

$$\begin{aligned} &\int_0^\pi\!\!\int_0^\pi \mathrm{d}\theta\,\mathrm{d}\theta'\, \frac{1}{d(x) + \sinh(2x)\left[(1-\cos\theta) + (1-\cos\theta')\right]} \\ &\simeq -\frac{2}{\pi\,\sinh(2x)}\ln\varepsilon\ . \end{aligned}$$

Note, however, that in (5.66) this integral is multiplied by the factor $(\sinh^2(2x) - 1)$ which has a zero at $x = x_\mathrm{c}$. Thus, the inner energy is continuous at this point. In the neighbourhood of x_c it has the form

$$E \simeq -J\coth(2x)\left\{1 + C(x - x_\mathrm{c})\ln|x - x_\mathrm{c}|\right\}\ , \tag{5.67}$$

where C is a constant. Calculating the specific heat (2.18), instead,

$$C_V = \frac{\partial E}{\partial T} \simeq \text{const.} \ln |x - x_\mathrm{c}| \ , \tag{5.68}$$

one sees that it diverges logarithmically at the critical value x_c. The essential conclusion is the following:

While the Ising model in one dimension shows no phase transition, in dimension two there is a phase transition at T_c, (5.65)*. This phase transition is visible in the specific heat and in other physical quantities.*

Analytic solutions of this same model in two dimensions with nonzero magnetic field, or in dimensions higher than 2, with or without magnetic field, are not known. However, the model described here has further applications and generalizations that are worked out in, e.g., Thompson (1979).

This schematic model leaves open the question which microscopic phenomena are responsible for phase transitions to occur. Another approach which allows to answer this question, at least to some extent, consists in studying the two-body correlation functions

$$\langle \mu_i \mu_k \rangle = \frac{1}{Z^{(N)}_{\text{can.}}} \sum_{\{\mu\}} \mu_i \mu_k \, \mathrm{e}^{-\beta E(\{\mu\})} \tag{5.69}$$

of the magnetic lattice model. Phase transitions are often related to qualitative changes of correlation functions. An example are the occurrence of effects of long range in the neighbourhood of the critical point. Since these matters lead beyond the scope of this book, we leave this topic here.

5.6 Stability of Matter

This section deals with a mathematical question which is of central importance for physics and whose solution is found in a wonderful synthesis of quantum theory, thermodynamics and statistical physics:

> *Why is condensed matter stable on our familiar, macroscopic scales? Conversely, under which circumstances would everyday matter tend to explode or to implode?*

A satisfactory answer to this question which is essential for the existence of life on earth, the possibility of doing experiments and, after all, pursuing research, was given only late (Dyson and Lenard 1967), about 40 years after the discovery of quantum mechanics and, somewhat later, the Pauli exclusion principle. After the pioneering work of F.J. Dyson and A. Lenard, who solved this problem with due mathematical rigor, there appeared a number of publications, illuminating partial aspects of this important problem. This work can be traced back from the book Lieb (2004). Our strongly simplified treatment is based, to some extent, on the review article Thirring (1986)). It aims at giving a heuristic understanding of some of the most important mathematical and physical results.

5.6.1 Assumptions and First Thoughts

If one wants to understand its stability it is sufficient to describe macroscopic matter as consisting of electrons and point-like nuclei. The finite extension of nuclei plays a less important role although the electrostatic potential of a realistic model of the nucleus has no singularity at $r = 0$—in contrast to the Coulomb potential of a point-like nucleus. In a first approach it might be adequate to use nonrelativistic kinematics. Under normal circumstances relativistic corrections give only slight refinements of the estimates.

Intuitively one expects *Heisenberg's uncertainty relations* and *Pauli's exclusion principle* to play in important role for the stability. Also the fact that electrostatic interactions, depending on the relative signs of electric charges, can be attractive or repulsive, may help to prevent the collapse of matter. But what is the role of gravitational forces which are always *attractive*? While gravitation can often be neglected in the description of microscopic physics, this is not admissible in macroscopic systems in which a very large number of massive particles are involved. Both electrostatic and gravitational interactions have long range. In contrast, weak and strong interactions have very short ranges and play no role for the stability of matter. It seems justified, therefore, to describe the interaction between the constituents of macroscopic matter in terms of the following potential:

$$U = \sum_{i>j} \frac{\kappa_{\mathrm{C}}\, q_i q_j - G_{\mathrm{N}} m_i m_j}{\left|\boldsymbol{x}_i - \boldsymbol{x}_j\right|} \,. \tag{5.70}$$

In this expression q_i and q_j are the electric charges two particles, m_i and m_j are their masses, respectively, and G_{N} is Newton's constant. The factor κ_{C} depends on the system of physical units one is using. In the Gauss system, for instance, it is equal to 1 (see e.g. Classical Field Theory, Sect. 1.5.4).

Whenever nonrelativistic kinematics is sufficient for the description of condensed matter, the relevant equation of motion is, of course, the Schrödinger equation

$$\mathrm{i}\hbar\dot{\Psi}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N) = H\Psi(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N) \,, \tag{5.71}$$

with the many-body Hamilton operator

$$H = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m_i} + \sum_{i>j} \frac{q_i q_j - G_{\mathrm{N}} m_i m_j}{\left|\boldsymbol{x}_i - \boldsymbol{x}_j\right|} \,, \quad (\kappa_{\mathrm{C}} = 1) \,. \tag{5.72}$$

In judging the stability of a system consisting of N nuclei and N electrons the primary objective is to find out in which way the energy of the ground state depends on the particle number N. If matter is stable one expects the energy of its lowest state to be a homogeneous function of degree 1 of the particle number, viz.

$$E_0 = E_0(N, V, S) \propto -N\,. \tag{5.73a}$$

Furthermore, the volume taken by the system should grow linearly with the particle number N so that its characteristic linear dimension increases by the third root,

$$R_{\min} \propto N^{1/3}\,. \tag{5.73b}$$

Any higher power of N would mean that the system has a tendency to explosion, any smaller power would signal tendency to implosion.

Heisenberg's uncertainty relation is the main reason why bound quantum systems are stable and do not collapse in space. As an example we quote the one-dimensional harmonic oscillator, for which one has

$$(\Delta q)(\Delta p) \geq \frac{\hbar}{2} \quad \text{with} \quad (\Delta q)^2 = \left\langle q^2 \right\rangle,\ (\Delta p)^2 = \left\langle p^2 \right\rangle\,.$$

The expectation value of the energy,

$$E = \langle H \rangle = \frac{1}{2m}\left\langle p^2 \right\rangle + \frac{1}{2} m\omega^2 \left\langle q^2 \right\rangle\,,$$

is estimated from below by a limit which is just compatible with the uncertainty relation. For the details of this estimate see, e.g., [Quantum Physics, Sect. 1.2.3]. The estimate yields the lower limit $E \geq (1/2)\hbar\omega$. In this case this is precisely the energy of the ground state of the harmonic oscillator.

The uncertainty relation for the radial momentum p_r and the radial coordinate r, $(\Delta p_r)(\Delta r) \geq \hbar/2$, yields a lower bound for the energy spectrum of the Hamiltonian

$$H = \frac{p_r^2}{2m} + \frac{\ell^2}{2mr^2} - \frac{e^2}{r}$$

with $\ell = 0$. The minimum of $\langle H \rangle$ is found at $(\Delta r) = \hbar^2/(4me^2)$ and from this one finds the bound

$$E = \langle H \rangle > -\frac{2me^4}{\hbar^2}\,.$$

(Note that this is four times the true binding energy of the hydrogen atom.) This simple estimate can be applied to the N-body system. Write the Hamilton operator (5.72) as a sum over effective single particle systems,

$$\begin{aligned} H^{(N)} &= \sum_{i=1}^{N} \sum_{j \neq i} \left\{ \frac{\boldsymbol{p}_i^2}{2m_i(N-1)} + \frac{q_i q_j - G_{\mathrm{N}} m_i m_j}{2\left|\boldsymbol{x}_i - \boldsymbol{x}_j\right|} \right\} \\ &= \sum_{i=1}^{N} \sum_{j \neq i} H^{(1)}(\boldsymbol{x}_i, \boldsymbol{x}_j) \; . \end{aligned} \tag{5.74a}$$

The operator $H^{(1)}$ has the form of the Hamilton operator of the Hydrogen atom provided one makes the replacements

$$\begin{aligned} &m_i \quad \text{by} \quad \mu \equiv m_i(N-1) \; , \\ &e^2 \quad \text{by} \quad \alpha \equiv -\frac{1}{2}\left(q_i q_j - G_{\mathrm{N}} m_i m_j\right) \; . \end{aligned}$$

With $\left\langle p_r^2 \right\rangle \geq (\Delta p_r)^2$ and using the uncertainty relation one has

$$E^{(i)} = \left\langle H^{(1)} \right\rangle > \frac{\hbar^2}{8\mu(\Delta r)^2} - \frac{\alpha}{(\Delta r)} \; .$$

The minimum of the right-hand side is reached for

$$(\Delta r) = \frac{\hbar^2}{4\mu\alpha} = \frac{\hbar^2}{4m_i(N-1)\alpha} \; .$$

Inserting this into $H^{(1)}$ yields the lower bound for $\left\langle H^{(1)} \right\rangle$

$$\left\langle H^{(1)} \right\rangle > -\frac{2\mu\alpha^2}{\hbar^2} = -\frac{2m_i(N-1)\alpha^2}{\hbar^2} \; . \tag{5.74b}$$

The double sum in (5.74a) provides this estimate with another factor $N(N-1)$, so that one obtains the lower bound

$$\left\langle H^{(N)} \right\rangle > -c\, N(N-1)^2 \quad \text{with} \quad c > 0 \; . \tag{5.74c}$$

If the energy of the ground state were indeed proportional to $-cN^3$, matter could not be stable. In what follows the aim will be to improve and to refine this rough estimate.

5.6.2 Kinetic and Potential Energies

The arguments of the preceding section show that although the uncertainty relation guarantees the stability of the individual atom, it is not sufficient, by far, to keep a macroscopic piece of matter stable. In order to improve the rough estimate (5.74c) we assume that the N particles are uniformly distributed over a given volume

$$V = \text{const.}\, R^3 \,,$$

where R is a length characteristic for the spatial extension of the system. Given the particle number N, how does this radius R adjust itself? Is it finite, when N becomes large, does it tend to infinity or to zero? To answer these questions one proceeds as follows: One estimates both the kinetic energy and the potential energy of the N particle system as functions of R and of N and determines the minimum of the total energy

$$\left\langle H^{(N)} \right\rangle = \langle T_{\text{kin}} \rangle + \langle U \rangle \,. \tag{5.75}$$

For the sake of simplicity we choose units such that $\hbar = 1$. The *kinetic* energy is estimated using the uncertainty relation between position and momentum. With the convention $\hbar = 1$ this takes the form

$$(\Delta p)\,(\Delta q) \geq \frac{1}{2} n \,. \tag{5.76}$$

Recalling the definitions

$$(\Delta p)^2 = \left\langle p^2 \right\rangle - \langle p \rangle^2 \,, \quad (\Delta q)^2 = \left\langle q^2 \right\rangle - \langle q \rangle^2 \,,$$

one sees that $\left\langle p^2 \right\rangle \geq (\Delta p)^2$. In the case of *bosons* the uncertainty in the coordinate can be maximal, $(\Delta q) = R$. From this one obtains

$$\left\langle p^2 \right\rangle \geq (\Delta p)^2 \geq \frac{1}{4R^2} \,.$$

Thus, the kinetic energy of the N-particle system varies like

$$\langle T_{\text{kin}} \rangle = \left\langle \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m_i} \right\rangle \sim \frac{N}{R^2} \qquad \text{(bosons).} \tag{5.77a}$$

If, in contrast, the particles are *fermions,* the Pauli principle is taken care of by dividing the volume V into N cells and by assigning each of the N fermions to one of these cells. The uncertainty in one component of the position variable can at most be

$$(\Delta q) = \frac{R}{N^{1/3}} \,.$$

This limitation changes the dependence of the kinetic energy on N. One obtains the estimate

$$\langle T_{\text{kin}} \rangle \sim \frac{N^{5/3}}{R^2} \qquad \text{(fermions).} \tag{5.77b}$$

Also, it is not difficult to estimate the *potential* energy. If there is only gravitational interaction, then pairs of particles attract each other. Therefore, one expects the behaviour

$$\langle U \rangle \sim -\kappa \frac{N^2}{R} \quad \text{with} \quad \kappa = G_{\text{N}} m_i m_j \,. \tag{5.78a}$$

If there is only electrostatic interaction and if the system contains approximately as many positively charged and negatively charged particles, one may argue as follows. An arbitrarily chosen particle essentially feels only its immediate neighbourhood. Any charge located somewhere further away, is screened. The spatial extension of the neighbourhood is characterized by a radius on the order of $R/N^{1/3}$. Summing over all N particles, one obtains

$$\langle U \rangle \sim -N \left(\frac{\alpha}{R/N^{1/3}} \right) = -\alpha \frac{N^{4/3}}{R} \,, \quad \text{with} \quad \alpha = -q_i q_j \,. \tag{5.78b}$$

Collecting results, one obtains an estimate of the expectation value of the total energy in the general form of

$$\left\langle H^{(N)} \right\rangle = \langle T_{\text{kin}} \rangle + \langle U \rangle = c_{\text{kin}} \frac{N^k}{R^2} - c_{\text{pot}} \frac{N^p}{R} \,, \tag{5.79}$$

where the exponents k for the kinetic energy and p for the potential energy can be read off from the formulae above.

The minimum of the expectation value (5.79) as a function of the radius R is reached for $R_{\text{min}} \propto N^{k-p}$. It is equal to

$$\left\langle H^{(N)} \right\rangle_{\text{min}} = -\frac{c_{\text{pot}}^2}{4c_{\text{kin}}} N^{2p-k} \quad \text{at} \quad R_{\text{min}} = \frac{2c_{\text{kin}}}{c_{\text{pot}}} N^{k-p} \,. \tag{5.80}$$

We discuss the various cases for bosons and for fermions.

(i) For *bosons* one has $k = 1$ and $\langle T_{\text{kin}} \rangle = N/R^2$.

- With electrostatic interaction only one has $p = 4/3$, the potential energy is estimated by (5.78b). Then (5.80) yields

$$R_{\text{min}} \sim N^{-1/3}\,, \quad E \equiv \left\langle H^{(N)} \right\rangle_{\text{min}} \sim -N^{5/3}\,. \tag{5.81}$$

- With gravitational interaction only one has $p = 2$, the potential energy is estimated by (5.78a). From (5.80) one concludes

$$R_{\text{min}} \sim N^{-1}\,, \quad E \equiv \left\langle H^{(N)} \right\rangle_{\text{min}} \sim -N^{3}\,. \tag{5.82}$$

(ii) For *fermions* one has $k = 5/3$, the kinetic energy is $\langle T_{\text{kin}} \rangle = N^{5/3}/R^2$.

- Like for bosons, with electrostatic interaction only, one has $p = 4/3$, the potential energy is also estimated by means of (5.78b). Therefore, from (5.80) one obtains

$$R_{\text{min}} \sim N^{+1/3}\,, \quad E \equiv \left\langle H^{(N)} \right\rangle_{\text{min}} \sim -N\,. \tag{5.83}$$

- With gravitational interaction one has $p = 2$ like in the case of bosons. The potential energy is estimated by the same formula (5.78a). From (5.80) one concludes

$$R_{\text{min}} \sim N^{-1/3}\,, \quad E \equiv \left\langle H^{(N)} \right\rangle_{\text{min}} \sim -N^{7/3}\,. \tag{5.84}$$

The first two results (5.81) and (5.82) show that matter which consists of bosons only, cannot be stable under any circumstance. In contrast, the results (5.83) and (5.84) show that matter made of fermions which interact by electrostatic forces may become stable. In all other cases matter is inclined to implosion. Stability seems to be the exception, instability the rule.

Remarks

i) It is remarkable that it is the kinetic energy of fermions, in the case (5.83), which may guarantee stability at all.
ii) Note, however, that the estimates also depend on the form of the electrostatic potential. For example, if one modifies the Coulomb potential in such a way that $v(|\boldsymbol{x}_i - \boldsymbol{x}_j|)$ stays finite at zero, then one has

$$\sum_{i>j} q_i q_j v(|\boldsymbol{x}_i - \boldsymbol{x}_j|) = \frac{1}{2} \sum_i \sum_j q_i q_j v(|\boldsymbol{x}_i - \boldsymbol{x}_j|) - \frac{1}{2} v(\boldsymbol{0}) \sum_i q_i^2\,.$$

The first term in this expression is the total electrostatic energy of all charges and, hence, is positive. Therefore,

$$\sum_{i>j} q_i q_j v(|\boldsymbol{x}_i - \boldsymbol{x}_j|) > -\frac{1}{2} v(\boldsymbol{0}) \sum_i q_i^2 \, .$$

The individual charges q_i are likely to be bounded from above, $|q_i| \le Z_{\max} e$ with e the elementary charge. From this one would infer a lower bound, viz.

$$\left\langle H^{(N)} \right\rangle \ge -\frac{1}{2} N v(\boldsymbol{0}) Z_{\max}^2 e^2 \, .$$

A system of this kind will be stable for both fermions and bosons.

iii) If one replaces the electrostatic interaction by attractive forces of short range which follow from a nonsingular potential, then there is instability in any case, also with fermions. The reader is invited to show this in Exercise 5.6.

5.6.3 Relativistic Corrections

If with increasing number of particles N, a system becomes unstable and eventually implodes, then the momenta become so large that the nonrelativistic expression $T_{\text{kin}}^{\text{n.r.}}$ must be replaced by

$$T_{\text{kin}}^{\text{rel}} = \sqrt{\boldsymbol{p}^2 + m^2} - m \, . \tag{5.85}$$

For estimates it is sufficient to keep only the first term $\sqrt{\boldsymbol{p}^2 + m^2}$, the second term giving a constant which is unimportant. If one estimates $\boldsymbol{p}^2$ like in Sect. 5.6.2 by $(\Delta p)^2$ and via the uncertainty relation by $1/(\Delta q)^2$ one obtains

$$\left\langle H^{(N)} \right\rangle \simeq N \sqrt{m^2 + \frac{N^{k-1}}{R^2}} - c_{\text{pot}} \frac{N^p}{R} \, . \tag{5.86}$$

The exponents k and p, as well as the constant c_{pot} have the same meaning as in (5.79). The minimum of this expression as a function of the radius R is easily determined. One finds

$$R = R_{\min} = \frac{1}{m c_{\text{pot}}} N^{k-p} \sqrt{1 - c_{\text{pot}}^2 N^{2p-k-1}} \, , \tag{5.87a}$$

$$\left\langle H^{(N)} \right\rangle_{\min} = N m \sqrt{1 - c_{\text{pot}}^2 N^{2p-k-1}} \, . \tag{5.87b}$$

If the radicand is positive, i.e. $1 - c_{\text{pot}}^2 N^{2p-k-1} > 0$, then R_{min} is the minimal radius of the system. If it is smaller than or equal to zero, i.e. $1 - c_{\text{pot}}^2 N^{2p-k-1} \leq 0$, then $R_{\text{min}} = 0$. The minimum of the energy (5.86) tends to minus infinity.

As a matter of example, consider bosonic matter with electrostatic interaction. From (5.77a) or from (5.78b), respectively, one has $k = 1$ and $p = 4/3$. The radicand in (5.87a) is $(1 - c_{\text{pot}}^2 N^{2/3})$. It becomes negative as soon as N gets larger than $1/c_{\text{pot}}^3$. Hence, the limit of the length R is $R_{\text{min}} = 0$, whereas $E_{\text{min}} = -\infty$.

For bosons and for fermions, respectively, one finds, using relativistic kinematics,

i) For bosonic matter and purely electromagnetic interaction one has $k = 1$, $p = 4/3$ so that

$$\langle T_{\text{kin}} \rangle = N \sqrt{m^2 + \frac{1}{R^2}} , \quad \langle U \rangle_{\text{e.m.}} = -\alpha \frac{N^{4/3}}{R} . \tag{5.88a}$$

The formula (5.87a) for R shows that the radicand vanishes for $N = \alpha^{-3}$. For $N > \alpha^{-3}$ there is a minimum at $R_{\text{min}} = 0$, the energy (5.86) tends to minus infinity.

The analogous analysis with purely gravitational interaction gives

$$\langle U \rangle_{\text{grav.}} = -\kappa \frac{N^2}{R} \tag{5.88b}$$

and shows that R tends to $R_{\text{min}} = 0$ whenever $N > \kappa^{-1}$.

ii) In the case of fermions with purely electromagnetic interaction one has $p = 4/3$ so that

$$\langle T_{\text{kin}} \rangle = N \sqrt{m^2 + \frac{N^{2/3}}{R^2}} , \quad \langle U \rangle_{\text{e.m.}} = -\alpha \frac{N^{4/3}}{R} . \tag{5.89a}$$

As long as $|\alpha|$ stays smaller than 1 there is indeed a smallest spatial extension which is related to the lowest value of the energy,

$$R_{\text{min}} = \frac{N^{1/3}}{m\alpha} \sqrt{1 - \alpha^2} , \quad \langle H_{\text{min}} \rangle = Nm\sqrt{1 - \alpha^2} . \tag{5.89b}$$

(Note that this is indeed a bound state since the second term in (5.89b) contains the rest mass!)

With gravitational interaction only, one has $k = 5/3$, $p = 2$. The potential energy is again given by (5.88b) and one concludes that the system collapses to zero and that its energy tends to minus infinity as soon as N exceeds $\kappa^{-3/2}$.

Remarks

i) For the sake of illustration consider a system which consists of N protons which interact gravitationally only. Using the numerical values

$$G_\mathrm{N} = 6.672 \times 10^{-11}\,\mathrm{m^3kg^{-1}s^{-2}} \mathrel{\widehat{=}} 6.707 \times 10^{-39}\,\mathrm{GeV^{-2}}$$
$$m_p = 0.9383\,\mathrm{GeV}$$
$$\text{there follows } \kappa = G_\mathrm{N} m_p^2 = 5.9 \times 10^{-39}\,.$$

Protons are fermions. Therefore, the critical value of N equals $\kappa^{-3/2}$. The system would ultimately collapse for $N > 2 \times 10^{57}$.

ii) It is instructive to consider the role of the masses in these estimates. The following estimates are easily derived

$$\sqrt{\boldsymbol{p}^2 + m^2} - 2m \le |\boldsymbol{p}| - m \le \sqrt{\boldsymbol{p}^2 + m^2} - m \le \frac{\boldsymbol{p}^2}{2m}\,, \tag{5.90a}$$

$$Nm + \sum_{i=1}^{N} |\boldsymbol{p}_i| \ge \sum_{i=1}^{N} \sqrt{\boldsymbol{p}_i^2 + m^2} \ge \sum_{i=1}^{N} |\boldsymbol{p}_i|$$
$$\ge -Nm + \sum_{i=1}^{N} \sqrt{\boldsymbol{p}_i^2 + m^2}\,. \tag{5.90b}$$

One concludes from the first inequality (5.90a) that stability does not depend on the mass. The second inequality tells us that the minimum of the energy $E_\mathrm{min}(m \neq 0)$ in the massive case on the one hand, and the minimum $E_\mathrm{min}(m = 0)$ with massless particles, on the other hand, differ at most by terms of the order of Nm. In the massless case (5.86) implies that the energy of the ground state is proportional to R^{-1},

$$\left\langle H^{(N)} \right\rangle = \frac{C}{R}\,. \tag{5.91}$$

Thus, if C is negative then $\left\langle H^{(N)} \right\rangle$ goes to minus infinity when $R \to 0$. Furthermore, taking into account the inequality

$$\sum_{i=1}^{N} \sqrt{\boldsymbol{p}_i^2 + m^2} \le \frac{\boldsymbol{p}_i^2}{2m} + Nm\,,$$

one sees that in the case of nonrelativistic kinematics, instability implies $\left\langle H^{(N)} \right\rangle^{\text{rel.}}(m \neq 0) < 0$. But then also $\left\langle H^{(N)} \right\rangle^{\text{rel.}}(m=0)$ is negative and by (5.91) tends to $-\infty$. In turn, this means that

$$\left\langle H^{(N)}\right\rangle^{\text{rel.}}(m \neq 0) \longrightarrow -\infty\,.$$

Note, however, that the converse of these arguments does not hold: If a nonrelativistic system is stable, one cannot conclude stability in a domain with relativistic kinematics. For instance, a fermionic system with electrostatic interaction is stable in the nonrelativistic regime for all α. The same system in a relativistic regime is stable only if $|\alpha| < 1$.

iii) It is instructive to study a gas consisting of fermions with electrostatic interaction and to calculate some of its state variables. Denoting the energy and matter densities by

$$\varepsilon = \frac{E}{V} \quad \text{and} \quad \varrho = \frac{N}{V},$$

respectively, one concludes from (5.77b), (5.78b), and (5.79), using $V \propto R^3$,

$$\begin{aligned} E = \left\langle H^{(N)}\right\rangle &= N\left(\frac{N^{2/3}}{R^2} - \alpha\frac{N^{1/3}}{R}\right) \\ &= N\left(\left(\frac{N}{V}\right)^{2/3} - \alpha\left(\frac{N}{V}\right)^{1/3}\right)\,. \end{aligned} \tag{5.92a}$$

Written differently, the densities fulfill the equation

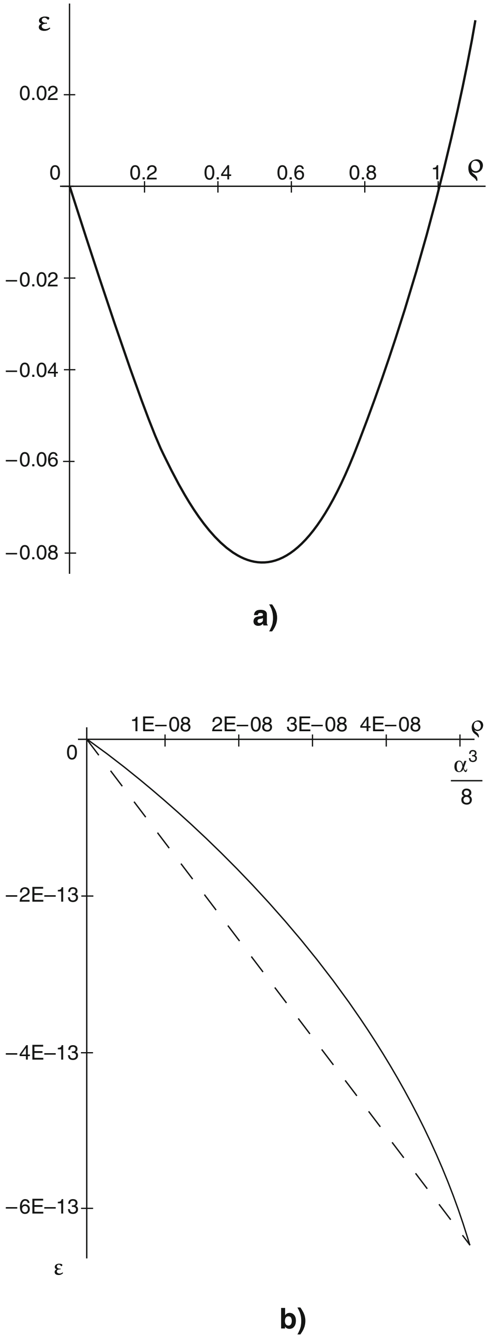
$$\varepsilon = \varrho^{5/3} - \alpha\varrho^{4/3}\,. \tag{5.92b}$$

The energy is homogeneous, that is to say, partial domains with equal density also have equal energy densities. One has $E = \varepsilon V = \varepsilon(V_1 + V_2) = E_1 + E_2$. Calculating the pressure from this, using (2.3a), one finds

$$\begin{aligned} p = -\frac{\partial E}{\partial V} &= -\varepsilon + \varrho\frac{\partial\varepsilon}{\partial\varrho} \\ &= \frac{2}{3}\varrho^{5/3} - \frac{1}{3}\alpha\varrho^{4/3}\,. \end{aligned} \tag{5.93}$$

This formula shows that in the interval $0 < \varrho < \alpha^3/8$ the pressure is *negative*. The graph of $\varepsilon(\varrho)$ which is plotted in Fig. 5.19b, shows an unexpected behaviour in this range, too. In order to substantiate this observation, calculate

Fig. 5.19 **(a)** Graph of the function $\varepsilon(\varrho)$ in the (unrealistic) case $\alpha = 1$; **(b)** The function $\varepsilon(\varrho)$, now drawn with $\alpha = 0.0073$, is concave in the range between 0 and $\varrho = (\alpha/2)^3$ and, therefore, is unphysical. In this domain it must be replaced by its convex hull, that is, the straight line (5.96)



the isothermal compressibility (2.20)

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial p} = -\frac{1}{V}\left(\frac{\partial p}{\partial V}\right)^{-1} = \left(\varrho\frac{\partial p}{\partial \varrho}\right)^{-1}$$
$$= \left(\varrho^2\frac{\partial^2 \varepsilon}{\partial \varrho^2}\right)^{-1} = \frac{9}{2}\varrho^{-4/3}\left(5\varrho^{1/3} - 2\alpha\right)^{-1} . \tag{5.94}$$

This function is negative for all $\varrho < 8\alpha^3/125$. One concludes from this that the section of the curve $\varepsilon(\varrho)$ from $\varrho = 0$ and $\varrho = \alpha^3/8$ is unphysical. The function $\varepsilon(\varrho)$ is concave, as can be seen quite well in Fig. 5.19b. The upper figure holds for the unrealistic case $\alpha = 1$, the lower for $\alpha = 0.0073$. This can be understood by means of the following argument: The system may be decomposed into a linear combination of subsystems whose densities and energies are, respectively, ϱ_i and $\varepsilon(\varrho_i)$. The energy must be a convex combination of the energies of the subsystems, i.e. in the sense of Definition 5.2

$$\varepsilon\Big(\sum_i t_i\varrho_i\Big) \le \sum_i t_i\varepsilon\left(\varrho_i\right) \ , \quad (t_i > 0, \sum_i t_i = 1) \ . \tag{5.95a}$$

In particular, if the volume V is decomposed into partial volumes V_i, defining $t_i = V_i/V$, so that $V = \sum_i V_i$, the energy (5.92a) must fulfill the inequality

$$\big\langle H^{(N)}\big\rangle(V) \le \sum_i \big\langle H^{(N_i)}\big\rangle(V_i) \, . \tag{5.95b}$$

If, in turn, $\varepsilon(\varrho)$ is concave, then (5.95b) holds with the $\geq$-sign. Thus, putting N_i particles in the partial volume V_i, the energy as a whole decreases. The quantity E calculated above does not correspond to the ground state. This argument shows that in the interval $(0, \alpha^3/8)$ the function ε must be replaced by its convex hull. This is the straight line

$$\varepsilon = \varrho\frac{\partial \varepsilon}{\partial \varrho} \ , \tag{5.96}$$

which is drawn as a dashed line in Fig. 5.19b. Equation (5.93) shows that the pressure is zero along this straight line. Apparently, the system decomposes into parts where the pressure vanishes, $p = 0$, and others where the density vanishes, $\varrho = 0$, i.e. where there will be no particles.

iv) An analogous analysis can also be made for the other cases contained in (5.80). One finds the same qualitative results for the pressure and the compressibility. However, in case of instability, the system does not decompose into subsystems but contracts to one single system.

5.6.4 Matter at Positive Temperatures

Up to this point we have been using essentially only the characteristic zero-point energy of quantum mechanics and the indistinguishability of bosons and fermions. When the temperature of a macroscopic body increases and takes positive values, the total energy is composed of the quantum mechanical energy and the thermodynamic energy. For the latter we use the variables S (entropy), V (volume) and N (particle number), as well as the function $E^{\text{thermo}}(S, V, N)$. In a system of natural units where the Boltzmann constant k as well as Planck's constant are equal to 1, using the definition (1.10) and the formula $S = k \ln \Omega \equiv \ln \Omega$, one has

$$\Omega = e^S = \frac{1}{N!} \int d^{3N}q \int d^{3N}p \; \Theta\left(E^{\text{thermo}} - \sum \boldsymbol{p}_i^2/(2m_i)\right) . \tag{5.97}$$

In this formula Θ is the Heaviside step function, $\Theta(x) = 1$ for $x > 0$, $\Theta(x) = 0$ for $x \leq 0$. We calculate the quantity Ω in the limit of a very large number of particles and for one kind of particles only whose masses are $m_i = m$.

The integral over the coordinates yields a factor V^N. The integral over the momenta is best calculated in spherical polar coordinates in dimension $M \equiv 3N$. The volume element in coordinate space gives

$$\int d^M x \; \cdots = \frac{2\pi^{M/2}}{\Gamma(M/2)} \int_0^\infty r^{M-1}\, dr \; \cdots . \tag{5.98a}$$

This follows from the formulae in Sect. 1.3. Alternatively, the result (5.98a) can be obtained as follows. One calculates an integral with integrand e^{-r^2} in two different ways, first from the product of M one-dimensional integrals, viz.

$$\int d^M x \; e^{-r^2} = \prod_{k=1}^{M} \left(\int_{-\infty}^{+\infty} dx_k \; e^{-x_k^2} \right) = \pi^{M/2} , \tag{5.98b}$$

and, second, using spherical polar coordinates, viz.

$$\int d^M x \; e^{-r^2} = X \int_0^\infty r^{M-1}\, dr \; e^{-r^2} = X \cdot \frac{1}{2} \Gamma(\tfrac{M}{2}) . \tag{5.98c}$$

Comparison of the results (5.98b) and (5.98c) yields the factor X,

$$X = \frac{2\pi^{M/2}}{\Gamma(M/2)} . \tag{5.98d}$$

Using this one now calculates the expression (5.97) and determines its asymptotic form for $N \to \infty$. We define $\boldsymbol{x}_i^2 := \boldsymbol{p}_i^2/(2m)$, insert the formulae above and obtain

$$\Omega = \frac{V^N}{N!} \frac{(\pi 2mE^{\text{thermo}})^{3N/2}}{\Gamma(3N/2+1)} \tag{5.99}$$

The asymptotics is obtained by means of Stirling's formula for the Γ-functions in the denominator,

$$\begin{aligned} N!\Gamma\left(\frac{3N}{2}+1\right) &= \Gamma(N+1)\Gamma\left(\frac{3N}{2}+1\right) \\ &\sim 2\pi \left(\tfrac{3}{2}\right)^{3N/2} N^{(5N+3)/2} \mathrm{e}^{-5N/2} \ . \end{aligned}$$

One obtains, up to a multiplicative constant,

$$\Omega \sim \frac{V^N (2mE^{\text{thermo}})^{3N/2} \mathrm{e}^{5N/2}}{(3/2)^{3N/2} N^{5N/2} N^{3/2}} = \frac{V^N}{N^N} \left(\frac{4mE^{\text{thermo}}\,\mathrm{e}}{3N}\right)^{3N/2} N^{-3/2} \mathrm{e}^N \ .$$

For large values of N, and solving the formula (5.97) for the energy, one obtains

$$E^{\text{thermo}}(S,N,V) \simeq c_0 N \left(\frac{N}{V}\right)^{2/3} \mathrm{e}^{2S/(3N)} \tag{5.100}$$

up to a multiplicative positive constant. For fermions, using (5.78b) and $R = V^{1/3}$, the total energy takes the form

$$E(S,V,N) \simeq \frac{N^{5/3}}{V^{2/3}} \left(1 + c\,\mathrm{e}^{2S/(3N)}\right) - \alpha \frac{N^{4/3}}{V^{1/3}} \ . \tag{5.101a}$$

Replacing $E(S, V, N)$ by the energy density $\varepsilon = E/V$, expressed as a function of the matter density $\varrho = N/V$ and of the entropy per unit of volume $\sigma = S/V$, one has

$$\varepsilon(\sigma,\varrho) = \varrho^{5/3} \left(1 + c\,\mathrm{e}^{2\sigma/(3\varrho)}\right) - \alpha \varrho^{4/3} \ . \tag{5.101b}$$

The pressure is obtained from the partial derivative of E by V, $p = -\partial E/\partial V$, so that

$$p = \frac{2}{3} \varrho^{4/3} \left\{ \varrho^{1/3} \left(1 + c\,\mathrm{e}^{2\sigma/(3\varrho)}\right) - \frac{\alpha}{2} \right\} \ . \tag{5.102a}$$

The pressure vanishes if ϱ and σ are related by

$$\varrho^{1/3} = \frac{\alpha}{2} \left[1 + c\,\mathrm{e}^{2\sigma/(3\varrho)}\right]^{-1} \ . \tag{5.102b}$$

This equation can be solved for the corresponding value of the entropy density σ_c to obtain

$$\sigma_c = \frac{3}{2}\varrho \ln\left\{\frac{1}{c}\left(\frac{\alpha}{2\varrho^{1/3}} - 1\right)\right\} \ . \tag{5.103}$$

As c is positive, $\varrho_0 = \alpha^3/8$ is the value beyond which p has no zero. However, if $\varrho < \varrho_0$ one must replace the expression (5.101b) at $\sigma < \sigma_c$ by $\varepsilon(\sigma, \varrho_c)$, i.e. for $\varrho < \alpha^3/8$

$$\sigma > \sigma_c : \quad \varepsilon = \varrho^{5/3}\left(1 + c\,\mathrm{e}^{2\sigma/(3\varrho)}\right) - \alpha\varrho^{4/3} \ , \tag{5.104a}$$

$$\sigma < \sigma_c : \quad \varepsilon = -\varrho\frac{\alpha^2}{4}\left(1 + c\,\mathrm{e}^{2\sigma/(3\varrho)}\right)^{-1} \ . \tag{5.104b}$$

One can then calculate the specific heat as well as other thermodynamic properties. For the specific heat (2.17a) one has the relation

$$C_V = T\frac{\partial S}{\partial T} = T\left(\frac{\partial^2 \varepsilon}{\partial \sigma^2}\right)^{-1} \tag{5.105a}$$

and, therefore, from (5.104a) and (5.104b)

$$\sigma > \sigma_c : \quad \frac{T}{C_V} = \frac{4c}{9}\varrho^{-1/3}\,\mathrm{e}^{2\sigma/(3\varrho)} \ , \tag{5.105b}$$

$$\sigma < \sigma_c : \quad \frac{T}{C_V} = \frac{\alpha^2 c}{9\varrho}\,\mathrm{e}^{2\sigma/(3\varrho)}\,\frac{1 - c\,\mathrm{e}^{2\sigma/(3\varrho)}}{(1 + c\,\mathrm{e}^{2\sigma/(3\varrho)})^3} \ . \tag{5.105c}$$

The specific heat proper is obtained by calculating the temperature separately by means of (2.1a). One finds

$$\sigma > \sigma_c : \quad T = \frac{\partial \varepsilon}{\partial \sigma} = \frac{2c}{3}\varrho^{2/3}\,\mathrm{e}^{2\sigma/(3\varrho)} \ , \tag{5.106a}$$

$$\sigma < \sigma_c : \quad T = \frac{\alpha^2 c}{6}\,\frac{\mathrm{e}^{2\sigma/(3\varrho)}}{(1 + c\,\mathrm{e}^{2\sigma/(3\varrho)})^2} \ . \tag{5.106b}$$

Obviously, the temperature is always positive. However, if $\varrho < \alpha^3/8$, then (5.105c) shows that C_V becomes *negative* in the interval

$$\frac{3\varrho}{2}\ln\left(\tfrac{1}{c}\right) < \sigma < \sigma_c \, . \tag{5.107}$$

Then, (5.105a) shows that the energy density ε, when interpreted as a function of σ, is *concave* in this interval. In case only electrostatic interactions must be taken into account, the system can decompose, as we have seen, into subsystems with differing properties. In a decomposable system every part acts like a heat reservoir for the other parts. Therefore, if in a subsystem C_V is negative, this subsystem delivers energy while heating up until the local specific heat is positive again. As the energy is homogeneous, the lowest state is reached as a minimum of

$$E = \sum_i E(S_i, V_i, N_i) \tag{5.108a}$$

with the boundary conditions

$$\sum_i S_i = S\,, \quad \sum_i N_i = N\,, \quad \sum_i V_i = V\,. \tag{5.108b}$$

This is tantamount with replacing the function $\varepsilon(\sigma, \varrho)$ by

$$\overline{\varepsilon}(\sigma, \varrho) = \inf \sum_i \alpha_i \varepsilon(\sigma_i, \varrho_i) \quad (\alpha_i = \tfrac{V_i}{V}) \tag{5.109}$$

$$\text{with} \quad \sum_i \alpha_i = 1\,, \sum_i \alpha_i \sigma_i = \sigma \quad \text{and} \quad \sum_i \alpha_i \varrho_i = \varrho\,.$$

The domain in which ε is concave, is replaced by its convex hull. The physical interpretation is as follows: The system which is assumed to be isolated, is decomposed into a mixture of differing phases. The apparent instability that one infers from the behaviour of the function $\varepsilon(\sigma, \varrho)$, is neutralized by phase transitions.

Remarks

i) The preceding considerations are particularly interesting for the physics of stars dominated by gravitational interaction. Replacing the electrostatic interaction by the gravitational interaction means that the factor α in the second term on the right-hand side of (5.101b) must be replaced by $\kappa N^{2/3}$. This follows from (5.79) with the exponent $p = 2$. The energy is no longer a homogeneous function of degree 1. The system does not decompose. The phenomenon of negative specific heat does really occur. In falling towards a center the particles heat up, the temperature rises even though the energy decreases.

   Of course, one wishes to know more about the realm where this is relevant. Gravitation dominates over electrostatic interaction when $\kappa N^{2/3} > e^2$. The numerical example in the first remark in Sect. 5.6.3, together with the dimensionless coupling strengths

$$\alpha_{\mathrm{G}} = \frac{G_{\mathrm{N}} m_p^2}{\hbar c} = 5.9 \times 10^{-39}\,,$$

$$\alpha_{\mathrm{S}} = \frac{e^2}{\hbar c} = \frac{1}{137.036} \quad \text{(Sommerfeld's constant)}\,,$$

show that this condition yields a number of particles (which are protons in our example) on the order of 1.4×10^{54}. The mass of the planet Jupiter is of that order of magnitude, 1×10^{54} protons. Roughly, one may say that systems with a comparatively small number of particles can be stable, while for systems with very large numbers of particles instability prevails.

ii) Note that in relation with the stability of matter, Theorem 5.1 is of decisive importance. Here we apply this theorem in the form of an obvious corollary:

A function $f(X)$ is called homogeneous of degree 1, if it satisfies

$$f(\mu X) = \mu f(X)\ . \tag{5.110a}$$

(This is the same property as in (5.4a).)
A function is said to be *subadditive*, if it satisfies the inequality

$$f(X_2 + X_1) \le f(X_2) + f(X_1)\ . \tag{5.110b}$$

(This is the counterpart of superadditivity (5.4b).)
It is *convex* if it fulfills the inequality

$$f\left(tX_2 + (1-t)X_1\right) \le tf(X_2) + (1-t)f(X_1)\ . \tag{5.110c}$$

(This is the complement of (5.4c).)

The result of Theorem 5.1 remains unchanged: If a function has any two of these properties then it has also the third property.

If one knows that the energy, as a function of the particle number, behaves like $E \sim -N^{\alpha}$, the question remains whether the limit

$$E_{\infty}(S;N;V) = \lim_{\mu\to\infty} \mu^{-\alpha} E\left(\mu S, \mu N, \mu V\right)$$

actually exists. Let us assume that this is indeed so and let us take α to be 1. We set $X = (S,N,V)$ and $f(X) \equiv E_{\infty}(S,N,V)$. One can then show that with $E \sim -N$ the volume grows linearly with N, $V \sim N$. The property (5.110a) can be interpreted as a criterion for stability against *implosion*.

Convexity of the energy function, (5.110c), is tantamount to *thermodynamic* stability of the system.

Subadditivity, (5.110b) tells us that it is energetically unfavourable to put the system apart into subsystems. This is equivalent to stability against *explosion*. Theorem 5.1, in the form adapted to the situation discussed here, relates the three criteria for stability. For instance, if subadditivity holds generally, the systems which are thermodynamically stable are precisely those whose energy is extensive, i.e. is a homogeneous function of degree one.

Given the technical difficulties of the problem of the stability of matter we could only give a heuristic discussion. The results we obtained from simple estimates, in essence, are correct. They are very interesting, indeed, because they show that the stability of our world presupposes a subtle balance. Matter, if it appears in large objects, is intrinsically unstable. At very large scales gravitation dominates over all other interactions. Both properties, stability at small scales, instability at large scales, provide the conditions which seem necessary for the existence of life in the universe, and, by the same token, for a chance for us to ponder these fundamental questions.

Finally, let us note that the analysis of the stability of matter makes use of a wonderful synthesis of classical mechanics, quantum physics and thermodynamics.

Exercises, Hints and Selected Solutions

6

Exercises Chap. 1

1.1 Prove the formula (1.8a) in Sect. 1.3,

$$\int \mathrm{d}^n x \;=\int_0^{+\infty} \mathrm{d}r\, r^{n-1} \int_0^{2\pi} \mathrm{d}\phi \prod_{k=1}^{n-2} \int_0^{\pi} \mathrm{d}\theta_k \sin^k(\theta_k) \tag{1.1}$$

by means of induction.
Hint: The formula is known to yield the correct result for dimensions $n = 2$ and $n = 3$. One assumes that it is valid for some $n > 3$, then proves that it is correct in dimension $(n + 1)$, choosing $\tilde{r} = r \sin\theta_{n-1}$ and $x^{n+1} = r \cos\theta_{n-1}$.

1.2 As an alternative to the derivation of (1.8b) in Sect. 1.3, write the volume of the ball with radius R in dimension n as $V^n(R) = \alpha_n R^n$ and imagine the ball $D^n(R)$ decomposed into thin discs of radius $\sqrt{R^2 - z^2}$ and thickness dz. You will obtain a recurrence formula for the coefficients α_n that can easily be solved.

Solution Let $(x_1, x_2, \ldots, x_{n-1}, x_n \equiv z)$ be the coordinates of an arbitrary point on the surface of $D^n(R)$, so that $R^2 = x_1^2 + \ldots x_{n-1}^2 + z^2$. At an arbitrary point z on the z-axis with $0 \le z \le R$, we have a disc of radius $\sqrt{R^2 - z^2}$ and thickness dz whose volume is $V^{(n-1)}(\sqrt{R^2 - z^2})$ dz. We have with $z = R\lambda$

$$\begin{aligned} V^{(n)} &= \int_{-R}^{R} \mathrm{d}z\; V^{(n-1)}(\sqrt{R^2 - z^2}) = \alpha_{n-1} \int_{-R}^{R} \mathrm{d}z\; (R^2 - z^2)^{(n-1)/2} \\ &= \alpha_{n-1} R^n \int_{-1}^{1} \mathrm{d}\lambda\; (1 - \lambda^2)^{(n-1)/2} = \alpha_{n-1} R^n \frac{\sqrt{\pi}\,\Gamma((n+1)/2)}{\Gamma((n+2)/2)}\,. \end{aligned}$$

F. Scheck, *Statistical Theory of Heat*, Graduate Texts in Physics,
DOI 10.1007/978-3-319-40049-5_6

The integral over λ is seen to be a Beta-function

$$\int_{-1}^{1} \mathrm{d}\lambda\ (1-\lambda^2)^{(n-1)/2} = \int_{0}^{1} \mathrm{d}t\ t^{-1/2}(1-t)^{(n-1)/2}$$
$$= B\left(\frac{1}{2}, \frac{(n+1)}{2}\right) = \frac{\Gamma(1/2)\Gamma((n+1)/2)}{\Gamma((n+2)/2)}.$$

Inserting $\alpha_2 = \pi$ one obtains by recurrence $\alpha_n = \pi^{n/2}/\Gamma(1+n/2)$. This is the desired result.

1.3 A swarm of particles is described by the Hamiltonian function

$$H(q,p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2 \equiv \frac{1}{2}\left(P^2 + Q^2\right)$$
$$\text{with} \quad P = \frac{p}{\sqrt{m}}, \ Q = \sqrt{m}\omega^2 q^2 .$$

Calculate the volume of phase space for the interval $(E-\Delta, E)$ of the energy and determine the density function of the microcanonical ensemble. Using this result calculate the mean values $\langle T\rangle$ of the kinetic energy and $\langle U\rangle$ of the potential energy. *Hint:* For a single particle the volume of phase space—in the variables (Q, P)—is a ring between two circles with radii $R_1 = \sqrt{2(E-\Delta)}$ and $R_2 = \sqrt{2E}$, respectively. For a swarm of N particles it is the part of a ball enclosed between $S_{R_1}^{2N-1}$ and $S_{R_2}^{2N-1}$. Knowing this one calculates Ω in a way analogous to Sect. 1.3.

1.4 Starting from the definitions (1.26) and (1.30) for temperature and pressure, respectively, and making use of the theorem on implicit functions prove the relation

$$p = -\frac{\partial E}{\partial V} .$$

Hint: The number of particles N is held fixed. Note that in comparing the definitions of temperature and pressure one is using the variables S and V in the first case, E and V in the second. Hence E must be solved for S or vice versa. Hence the minus sign.

1.5 Derive the Gaussian fundamental integral,

$$\int_{-\infty}^{+\infty} \mathrm{d}x\ \mathrm{e}^{-x^2} = \sqrt{\pi} , \tag{1.2}$$

by calculating first its square using polar coordinates in the plane. This then allows to calculate the more general integral

$$\int_0^{+\infty} \mathrm{d}x\, x^{2n}\ \mathrm{e}^{-x^2}$$

as well as the special cases given in the Example 1.7, (1.53c).

1.6 Suppose the energy E of a particle moving in the potential of the harmonic oscillator is given. By considering the most general solution for fixed energy, one shows that the oscillator fulfills the hypothesis of ergodicity.

Solution The Hamiltonian and the most general solution read, respectively,

$$H(p,q) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2\ , \qquad q(t) = A\sin(\omega t + \phi)\ .$$

The *time average*

$$\langle q^2 \rangle_{\text{time}} := \lim_{t\to\infty} \frac{1}{\tau}\int_0^{\tau} \mathrm{d}t\, q^2(t)$$

is calculated from the elementary integral

$$\begin{aligned}\frac{1}{\tau}\int_0^{\tau} \mathrm{d}t\, q^2(t) &= A^2 \frac{1}{\tau}\int_0^{\tau} \mathrm{d}t\ \sin^2(\omega t + \phi)\\ &= \frac{A^2}{2} - \frac{A^2}{4\omega\tau}\left(\sin(2\omega t + 2\phi) - \sin(2\phi)\right)\ .\end{aligned}$$

In the limit $\tau \to \infty$ the second term vanishes and one obtains

$$\langle q^2 \rangle_{\text{time}} = \frac{1}{2}A^2\ . \tag{1.3}$$

The time average of q^2 over a period τ is plotted in Fig. A.1 as a function of τ.

We assume a constant probability distribution on phase space, i.e. "equal a priori probabilities": $\rho(q,p) = \text{const.}$, so that the probability to find the system in a given cell of phase space is proportional to the volume of that cell. For a harmonic oscillator whose energy lies in the range $[E, E+\Delta]$, the allowed region in phase space is the shell between the two ellipses $E_0 = p^2/2m + 1/2m\omega^2 q^2$ with $E_0 = E$ and $E_0 = E + \Delta$, respectively. As the observable that we consider does not depend on p, we need to find a suitable probability density $\mathcal{P}(q)$ in configuration space. This is obtained by integrating the momentum variable over its allowed domain. Taking the positive square root, we have $p(q,E) = \sqrt{2mE - m^2\omega^2 q^2}$, so that, taking into

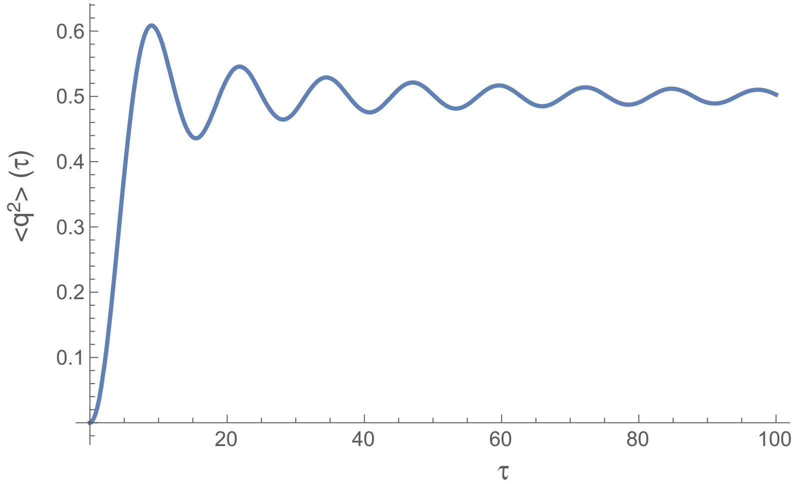


Fig. A.1 Time average of q^2 over a period τ as a function of τ

account the symmetry of the problem and introducing a normalization constant α,

$$\begin{aligned}\mathcal{P}(q)\Delta q &= \alpha\,(p(q,E+\Delta E) - p(q,E))\,\Delta q \\ &\approx \alpha\frac{\partial p}{\partial E}\Delta E\Delta q.\end{aligned}$$

Thus, for an oscillator with maximal amplitude A, and using

$$\frac{\partial p}{\partial E} = \frac{m}{\sqrt{2mE - m^2\omega^2q^2}},$$

we obtain

$$\mathcal{P}(q) = \frac{1}{\pi A}\frac{1}{\sqrt{1-(q/A)^2}}\,.$$

Note that ΔE is absorbed in the normalization constant. From this we obtain:

$$\begin{aligned}\langle q^2\rangle_{\text{space}} &:= \int_{-A}^{A} q^2\mathcal{P}(q)dq = \frac{1}{\pi A}\int_{-A}^{A}\frac{q^2}{\sqrt{1-(q/A)^2}}dq \\ &= \frac{A^2}{\pi}\int_{-1}^{1}\frac{x^2}{\sqrt{1-x^2}} = \frac{1}{2}A^2\,. \end{aligned} \tag{1.4}$$

Comparison with (1.3) shows the expected result.

1.7 An integral representation for the Gamma function, valid for positive arguments, reads

$$\Gamma(z) = \int_0^\infty \mathrm{d}t\, t^{z-1}\,\mathrm{e}^{-t} \quad (z > 0)\,. \tag{1.5}$$

1. Prove the functional equation $\Gamma(z+1) = z\Gamma(z)$. Use this result to derive its form for integer argument, $n! = \Gamma(n+1)$. Evaluate $\Gamma(\frac{1}{2})$.
2. Making use of the substitution $\nu = \ln t/z$ derive the leading term in the asymptotic form of the Gamma function,

$$\Gamma(z) \sim \sqrt{2\pi}\, z^{z-1/2}\,\mathrm{e}^{-z} \quad \text{(Stirling's formula)}. \tag{1.6}$$

Hint: From $t = \mathrm{e}^{\nu z}$ one has $\mathrm{d}t = z\mathrm{e}^{\nu z}\mathrm{d}\nu = zt\,\mathrm{d}\nu$ and

$$\Gamma(z) = z\int_{-\infty}^{+\infty} \mathrm{d}\nu\ \mathrm{e}^{f(\nu)} \quad \text{with} \quad f(\nu) = \nu z^2 - \mathrm{e}^{\nu z}\,.$$

An estimate of the function at large values of z is obtained by replacing $f(\nu)$ by its maximum, i.e. choosing $f'(\bar{\nu}) = 0$. From

$$\frac{\mathrm{d}f(\nu)}{\mathrm{d}\nu} = z\,(z - \mathrm{e}^{\nu z}) = 0 \quad \text{follows} \quad \bar{\nu} = \frac{\ln z}{z}\,.$$

If one replaces the variable ν by $y := \nu - \ln z/z$, one obtains

$$\Gamma(z) = z^{z+1}\,\mathrm{e}^{-z}\int_{-\infty}^{+\infty} \mathrm{d}y\ \mathrm{e}^{-\left[\frac{1}{2}z^3y^2+\ldots\right]}.$$

Gauß's formula, cf. Exercise 1.5 yields $\int_{-\infty}^{+\infty}\mathrm{d}x\,\mathrm{e}^{-\lambda x^2} = \sqrt{\pi/\lambda}$. The asymptotics (1.6) follows from this.

1.8 As an example for symplectic geometry on phase space, determine and then sketch the Hamiltonian vector field X_H for the one-dimensional harmonic oscillator. Compare with the gradient field $\sum_i (\nabla H)^i \partial_i$. What is the form of the orbits in phase space?

1.9 The barometric formula describes the variation of air pressure (or of the density of particles) as a function of the height z above sea level. Under conditions of equilibrium the temperature is everywhere the same. Assuming the air to be an ideal gas derive an equation for the pressure gradient at the height z and derive from it the barometric formula.
Derive the same formula on the basis of the probability density of the canonical ensemble.

Solution

1. Let z be the height above sea level, $n(z)$ the density of particles at z and m the mass of the air molecules, so that the mass density is $\varrho(z) = mn(z)$. The gradient of pressure is equal to the gravitational force per unit of volume,

$$\frac{\mathrm{d}p(z)}{\mathrm{d}z} = -\varrho(z)g \ .$$

With air as an ideal gas, one has $p = nkT$, cf. (1.31). Inserting this one has

$$\varrho(z) = \varrho_0 \, \mathrm{e}^{-mgz/(kT)} = \varrho_0 \, \mathrm{e}^{-U(z)\beta} \ ,$$

where $U(z)$ denotes the potential energy. The result is proportional to the probability $\varrho(z)\,\mathrm{d}z$ to find an air molecule in the interval $(z, z + \mathrm{d}z)$.

2. Air may be treated as a canonical ensemble provided the temperature is the same everywhere and remains constant. The density function is then as given by (1.39), with

$$H = \sum_{i=1}^{N} \left(\frac{\boldsymbol{p}^{(i)\,2}}{2m} + m\boldsymbol{g} \cdot \boldsymbol{q}^{(i)} \right) \quad \text{and} \quad \boldsymbol{g} = (0, 0, -g)^T \ .$$

Like in Example 1.7 one integrates over all variables except for the one whose distribution one wishes to calculate, i.e. the height in space. Equation (1.39) shows that the probability to find a particle in the interval $(z, z + \mathrm{d}z)$ is proportional to $\exp\{-mgh(z)/(kT)\}\,\mathrm{d}z = \exp\{-\beta U(z)\}$.

1.10 Maxwell himself derived the distribution of velocities (1.53d) named after him, in the following manner. The assumptions are:

(i) The probability for the i-th component of the velocity to lie in the interval $(v_i, v_i + \mathrm{d}v_i)$ is given by $\varrho(v_i)\,\mathrm{d}v_i$.
(ii) The distribution depends only on the modulus of the velocity, i.e. one has

$$\varrho(v_1^2)\varrho(v_2^2)\varrho(v_3^2)\;\mathrm{d}v_1\,\mathrm{d}v_2\,\mathrm{d}v_3 = \varphi(v_1^2 + v_2^2 + v_3^2)\;\mathrm{d}v_1\,\mathrm{d}v_2\,\mathrm{d}v_3 \ .$$

With these assumptions Maxwell showed that ϱ must be of the form

$$\varrho(v_i^2) = C\,\mathrm{e}^{-Bv_i^2} \ .$$

Solution In a first step, take $v_2 = v_3 = 0$ and note that $\varrho(x^2)$ must be the same function $\varphi(x^2)$ up to the factor $(\varrho(0))^2$. With $z \equiv x^2$ one then has $\ln \varphi(z) = \ln \varrho(z) + 2 \ln \varrho(0)$. If, in turn, one sets $v_1^2 = v_2^2 = v_3^2 \equiv z$, one obtains

$$\ln \varphi(3z) = 3 \ln \varrho(z) = \ln \varrho(3z) + 2 \ln \varrho(0) \ , \quad \text{or}$$

$$\ln \varrho(3z) = 3 \ln \varrho(z) - 2 \ln \varrho(0) \ .$$

A function $f(z)$ fulfilling the condition $f(3z) = 3f(z) - 2f(0)$, or, written differently,

$$f(z) - f(0) = \frac{1}{3}\left[f(3z) - f(0)\right] ,$$

must be linear in z. Therefore $\ln \varrho(z) = az + b$ and from this $\varrho(v^2) = C\mathrm{e}^{av^2}$ with $C = \mathrm{e}^b$. The constant a must be negative by the following argument: The mean value of $\boldsymbol{v}^2$ is calculated from

$$\left\langle \boldsymbol{v}^2 \right\rangle = \int \mathrm{d}^3v\ \boldsymbol{v}^2 \varrho(\boldsymbol{v}^2) = \frac{\mathrm{d}}{\mathrm{d}a} \ln\left(\int \mathrm{d}^3v\ \mathrm{e}^{a\boldsymbol{v}^2}\right) .$$

The integral on the right-hand side is proportional to $a^{-3/2}$, its logarithmic derivative gives $\left\langle \boldsymbol{v}^2 \right\rangle = -3/(2a)$.

1.11 If it is known that the Maxwell distribution is normalized to one and that the mean value of the kinetic energy equals $3kT/2$, determine the constants C and B of the preceding Exercise 1.10.

1.12 A particle with energy E moves freely with an arbitrary velocity in a box whose volume is V. Calculate the volume $\Phi(E)$ of phase space that the particle sweeps.

Solution The volume is $V4\pi R^2$ where $R^2 = (E/c)^2 - (mc)^2$. If the motion is only weakly relativistic then $E \simeq mc^2 + E_{\text{n.r}}$ and $R^2 \simeq 2mE_{\text{n.r}}$.

1.13 Determine the Legendre transform of the function $f(x) = x^\alpha/\alpha$. From this follows the inequality

$$x \cdot z \leq \frac{x^\alpha}{\alpha} + \frac{z^\beta}{\beta} ,$$

which holds for all positive x and z as well as for all pairs (α, β) fulfilling the following conditions:

$$\alpha > 1\ , \ \beta > 1 \quad \text{and} \quad \frac{1}{\alpha} + \frac{1}{\beta} = 1 .$$

Solution

1. The Legendre transform of $f(x) = (1/\alpha)x^\alpha$, with $z = f'(x)$, is given by

$$\begin{aligned}\Phi(z) &= x(z)z - f\left(x(z)\right) = z^{1/(\alpha-1)}z - \frac{1}{\alpha}z^{\alpha/(\alpha-1)} \\ &= \frac{\alpha-1}{\alpha}z^{\alpha/(\alpha-1)} \equiv \frac{1}{\beta}z^\beta \quad \text{where} \quad \frac{1}{\alpha} + \frac{1}{\beta} = 1 .\end{aligned}$$

2. One constructs the "hybrid" function $F(x, z) = xz - f(x)$ and compares the graphs of the function $y = f(x)$ and of the straight line $y = zx$ (at fixed z). The condition $\partial F(x, z)/\partial x = 0$ yields the point $x(z)$ at which the vertical distance of the two graphs is maximal. At this point one has $x(z)z - f(x(z)) = \Phi(z)$. In all other points one has $xz - f(x) < \Phi(z)$ ($f(x)$ is convex!). Thus, under these assumptions one finds

$$xz \le f(x) + \Phi(z) .$$

Illustrations for this example may be found in (Scheck, Mechanics 2010, Problem 2.14 and its solution).

1.14 Two ideal gases containing of N_1 and N_2 particles occupying the fixed volumes V_1 and V_2, respectively, are brought to contact. Initially these two microcanonical systems have energies E_1 and E_2, respectively. After they have come to equilibrium, the temperatures are equal, $T^0 = T_1 = T_2$, the energies are $E_i^0 = (E_1 + E_2)N_i/(N_1 + N_2)$. The combined system is again microcanonical. Assume the particle numbers to be on the order of 10^{23}. Estimate the size of typical fluctuations Δ about the mean values (normalized to the energy).
Hint: Calculate the entropies S_1 and S_2 for $E_1 = E_1^0 + \Delta$ (and thus $E_2 = E_2^0 - \Delta$) with $\Delta \ll E_i^0$, that is to say, the coefficient in the formula

$$\Omega_i = (\Omega_i)_{(\max)}\, \mathrm{e}^{-\alpha\Delta^2} , \quad i = 1, 2 .$$

1.15 Work out the same estimate, Exercise 1.14 for the ideal gas considered as a canonical ensemble, that is for an ideal gas in a heat bath. What you need to show is that the probability

$$w = \frac{1}{Z}\, \mathrm{e}^{-\beta(E-TS)} ,$$

to find the gas with equilibrium energy E^0 corresponding to temperature T, is practically equal to one.

1.16 The atoms of a gas in a box are assumed to move according to the Maxwell distribution of velocities. How many atoms hit a unit area per second?

Exercises Chap. 2

2.1 This problem is instructive in relation to the definition of entropy (in the statistical sense). Show that the functional equation

$$\sigma(x \cdot y) = \sigma(x) + \sigma(y) \tag{2.7a}$$

admits the unique differentiable solution

$$\sigma(x) = c\ \ln x \quad \text{with} \quad c \quad \text{a constant.}$$

One may even show the stronger assertion: If for all x_i and all y_k whose sums are normalized to one, the functional equation

$$\sum_{i,k} x_i y_k \sigma(x_i \cdot y_k) = \sum_i x_i \sigma(x_i) + \sum_k y_k \sigma(y_k) \tag{2.7b}$$

holds, then $\sigma(x)$ is proportional $\ln x$.

Solution

(a) Obviously, the function $\sigma(x) = c \ln x$ satisfies the functional equation (2.7a). Conversely, taking the derivative of (2.7a) by x at the point $x = 1$, there follows the differential equation

$$y\sigma'(y) = \sigma'(1) = c\ .$$

Its solution is $\sigma(y) = c \ln y$. (b) The condition $(\sum_k y_k = 1)$ is taken care of if one multiplies the first term on the right-hand side of (2.7b) by this sum. Similarly, the subsidiary condition $(\sum_i x_i = 1)$ is introduced as a factor of the second term on the right-hand side of this equation so that one obtains the differential equation

$$\sum_{i,k} x_i y_k [\sigma(x_i y_k) - \sigma(x_i) - \sigma(y_k)] = 0\ .$$

This expression vanishes term by term and one obtains the same equation (2.7a) for x_i and y_k which was solved in the first part.

2.2 Suppose an arbitrary scale for temperature Θ is chosen and the functions $\partial p/\partial\Theta|_V$ and $T\ \partial S/\partial V|_\Theta$ are given.

1. One has $\mathrm{d}S = (\mathrm{d}E + p\,\mathrm{d}V)/T$, T and V are independent variables. Show that

$$T\frac{\partial p}{\partial T} = \frac{\partial E}{\partial V} + p \quad \text{and} \quad T(\Theta) = T_0\,\mathrm{e}^{J(\Theta)} \quad \text{with}$$

$$J(\Theta) = \int_{\Theta_0}^{\Theta} \mathrm{d}\Theta\ \frac{\partial p/\partial\Theta'|_V}{\partial E/\partial V|_{\Theta'} + p}\ .$$

2. Alternatively, the denominator of the integrand can be written as $T \left.\frac{\partial S}{\partial V}\right|_{\Theta}$. Show that

$$T = (T_1 - T_0)\frac{e^J}{e^{J_1} - 1} \; . \qquad (2.8)$$

How must the interval $(T_1 - T_0)$ (which corresponds to the interval $(\Theta_1 - \Theta_0) = 100°$) be chosen to obtain the Kelvin scale?

Solution

1. One has $T\,dS = dE + p\,dV$ (first law) so that the partial derivative by V at constant temperature is

$$T \left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial E}{\partial V}\right|_T + p \; .$$

If one makes use of the grand canonical potential (2.7b), for instance, (2.8a) and (2.8b) yield the Maxwell relation

$$\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial p}{\partial T}\right|_V$$

and hence the equation

$$T \left.\frac{\partial p}{\partial T}\right|_V = \left.\frac{\partial E}{\partial V}\right|_T + p \; .$$

If one replaces T by some other temperature Θ defined differently, one obtains in a similar way

$$T \left.\frac{\partial p}{\partial \Theta}\right|_V = \left.\frac{\partial E}{\partial V}\right|_{\Theta} + p \; .$$

If Θ is fixed, so is T and vice versa. The Maxwell relation which follows from (2.8a) and (2.8b), looks similar to the previous one,

$$\left.\frac{\partial S}{\partial V}\right|_{\Theta} = - \left.\frac{\partial^2 K}{\partial T \partial V}\right|_{\Theta} = \left.\frac{\partial p}{\partial T}\right|_V \; .$$

The derivative on the right-hand side is rewritten as

$$\left.\frac{\partial p}{\partial T}\right|_V = \left.\frac{\partial p}{\partial \Theta}\right|_V \left.\frac{\partial \Theta}{\partial T}\right|_V = \left.\frac{\partial p}{\partial \Theta}\right|_V \frac{d\Theta}{dT} \; ,$$

and one obtains the differential equation

$$\frac{\mathrm{d}T}{\mathrm{d}\Theta} = T\frac{\partial p/\partial\Theta|_V}{\partial E/\partial V|_\Theta + p} .$$

Integrating this equation yields the formula given above.

2. With $T(\Theta) = T_0\,\mathrm{e}^{J(\Theta)}$, with $T_1 > T_0$ an arbitrary reference temperature, and with $J_0 \equiv J(\Theta_0) = 0, J_1 = I(\Theta_1)$ one obtains the formula (2.8).

Adjusting the temperature to the Kelvin scale is described in the main text, in Sect. 1.5.

2.3 Alternative formulations of the second law are:

> (C) Heat can never be transmitted from a cooler to a hotter body, unless there is some other change of the system which is related to this process.
> (due to Rudolf Clausius)
>
> (P) There can be no periodically working machine whose effect is no more than lifting a load and cooling of a heat reservoir, i.e. there is no *perpetual motion machine* of the second kind.
> (due to Max Planck)

Prove that these assertions are equivalent: Assume that (P) is not valid and show that also (C) is not. For the converse, i.e. if (C) is not true then also (P) is false, consider a thermodynamic engine which takes the amount of heat Q_1 from the warmer body and delivers the amount Q_2 to the cooler body while delivering the work $A = Q_1 - Q_2$.

2.4 An ideal gas has the molar specific heat c_V at constant volume. The specific heat does not depend on temperature. The ratio of the specific heats at constant pressure and at constant volume, respectively, is denoted by $\gamma = c_p/c_V$. The gas is thermally isolated, it expands quasi-statically from the initial volume V_i at temperature T_i to its final volume V_f.

1. Use the relation $pV^\gamma = \text{const}$ to determine the final temperature.
2. Calculate the temperature T_f in the final state by making use of the fact that the entropy is constant in this process.

2.5 A gas, assumed to be an ideal gas, fills a cylindrical vessel with cross section A. The vessel is placed vertically. The atmospheric pressure is p_0. The gas supports a movable piston of mass m which has the same cross section as the vessel, in equilibrium with gravity and gas pressure. In this state the gas occupies the volume V_0. If the piston is moved slightly out of equilibrium it starts oscillating about the equilibrium position with frequency ν. (These oscillations are slow so that the gas stays in equilibrium, and yet fast enough so that the gas does not exchange heat

with the ambient space.) All changes of pressure and volume are quasi-static and adiabatic.
Calculate γ as a function of m, g, p_0, A, V_0 and ν. Note that this experiment can serve to measure γ.

Solution The gas pressure acts in positive z-direction, its modulus is pA, the pressure of the atmosphere acts along the negative z-direction with modulus p_0A, like gravity whose modulus is mg. Thus, the equation of motion reads

$$m\ddot{z} = (p - p_0)A - mg \ .$$

The process being adiabatic one has $pV^\gamma = $ const., equilibrium is realized when $V = V_0$ and $p^{(0)} = p_0 + mg/A$. Therefore

$$pV^\gamma = \left(p_0 + \frac{mg}{A}\right) V_0^\gamma \ .$$

With $z = (V - V_0)/A$ one has

$$m\ddot{z} = (Ap_0 + mg)\left(\frac{V_0}{V_0 + zA}\right)^\gamma - (Ap_0 + mg) \ .$$

There will be small oscillations if the condition $|(V - V_0)/V_0| \ll 1$, i.e. $|zA| \ll V_0$ is fulfilled. One can then approximate

$$\left(\frac{V_0}{V_0 + zA}\right)^\gamma = \left(1 + \frac{zA}{V_0}\right)^{-\gamma} \simeq 1 - \gamma\frac{zA}{V_0} \ .$$

The equation of motion is reduced to the differential equation of the harmonic oscillator,

$$m\ddot{z} \simeq -\frac{\gamma A}{V_0}(Ap_0 + mg)\, z = -m\omega^2 z \ ,$$

whose frequency is given by

$$\nu = \frac{1}{2\pi}\sqrt{(p_0A + mg)\frac{\gamma A}{mV_0}} \ .$$

Solving for the exponent γ one obtains

$$\gamma = \frac{4\pi^2\nu^2 mV_0}{(p_0A + mg)A} \ .$$

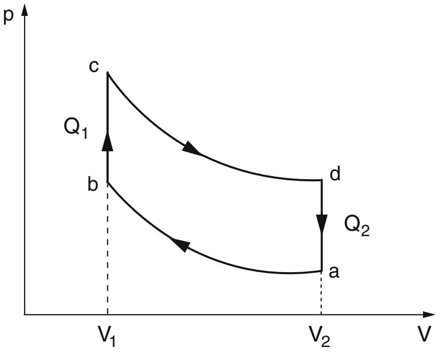


Fig. A.2 Schematic model for a car engine, see Exercise 2.6

2.6 As a model for periodic motion of a motor consider the idealized circular process $a \to b \to c \to d$ in the (V, p)-plane of Fig. A.2. The branch $a \to b$ represents the adiabatic compression of the gasoline-air mixture, the branch $b \to c$ describes the increase of pressure at constant volume, caused by the explosion, the branch $c \to d$ represents the adiabatic expansion of the mixture while the motor delivers mechanical work, and the branch $d \to a$ describes the cooling process at constant volume. We assume that this circular process is performed quasi-statically with a fixed quantity of gas.
Calculate the efficiency of the motor and express the result in terms of V_1, V_2 and $\gamma = c_p/c_V$.

Solution There is no exchange of heat, positive or negative, on the two branches $a \to b$ and $c \to d$, i.e. $\mathrm{d}E = -p\,\mathrm{d}V$. For an ideal gas one has $E = c_V T$. Therefore, the amounts of work A_{ab} and A_{cd} delivered or absorbed on these branches are determined by the differences of temperature $T_b - T_a$ and $T_d - T_c$, respectively. Using the relation $pV^{\gamma-1} =$ const. these differences are converted to the volumes V_1 and V_2. The quantity of heat absorbed on the branch $b \to c$ is $Q_1 = E_c - E_b$ and, therefore, is proportional to $T_c - T_b$. The efficiency is

$$\eta = \frac{A_{ab} + A_{cd}}{Q_1} = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1} .$$

2.7 A gas which is diluted such that the interaction of its molecules can be neglected, can be considered an ideal gas. In this exercise one is invited to show that this system can be described as a grand canonical ensemble with variable number of particles N. The partition function is

$$Y(T, V, \mu_C) = \sum_N Z(T, V, N)\,\mathrm{e}^{\mu_C N/(kT)} , \tag{2.9}$$

where $Z(T, V, N)$ is the partition function of the canonical distribution of N particles in the volume V at the temperature T.

1. Show that Y, when expanded in terms of N, is equal to

   $$Y(T, V, \mu_C) = 1 + Z(T, V, 1)\,\mathrm{e}^{\mu_C/(kT)} + Z(T, V, 2)\,\mathrm{e}^{2\mu_C/(kT)} + \dots$$

   and that $\mathrm{e}^{\mu_C/(kT)} \ll 1$ so that it is sufficient to consider only the first term

   $$\ln Y = Z(T, V, 1)\,\mathrm{e}^{\mu_C/(kT)} + \dots .$$

   For this purpose calculate $Z(T, V, 1)$ and N from derivatives of the function $\ln Y$. Show that

   $$N = \frac{V}{\lambda^3}\,\mathrm{e}^{\mu_C/(kT)} \quad \text{with} \quad \lambda = \frac{2\pi\hbar}{\sqrt{2\pi mkT}} . \tag{2.10}$$

   The quantity λ is called *thermal de Broglie wave length.*
2. One knows that for the grand canonical potential $K = -kT \ln Y$ one has

   $$\mathrm{d}K = -S\,\mathrm{d}T - p\,\mathrm{d}V - N\,\mathrm{d}\mu_C .$$

   Use this to calculate the entropy S, the pressure p and the number of particles N. Write entropy and chemical potential as functions of T, V and N.

Compare the thermal de Broglie wave length with the mean distance $(V/N)^{1/3}$ of the particles. Calculate the second term in the expansion of $\ln Y$. The result one obtains for one or two particles is sufficient for the description of a system with $N \gg 1$.

2.8

1. One mole of an ideal gas with initial temperature T_1 and molar volume V_1, by some mechanism, is taken to temperature T_2 and volume V_2. Show that the entropy changes as follows,

   $$\Delta S = c_V \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right) .$$

2. The gas is assumed to follow a three-step circular process in a volume-pressure (V, p)-diagram: (i) Adiabatic expansion from $A = (V_1, p_1)$ to $B = (V_2, p_2)$; (ii) Compression along the isobaric $p_2 = \text{const.}$ from B to $C = (V_1, p_2)$; (iii) Increase of pressure, at constant volume V_1, from C back to A.

Sketch this process in the (V, p)-plane and calculate the amounts of work delivered on the paths $A \to B$ and $B \to C$, as well as the amount of heat absorbed on the path $C \to A$. Show that the thermal efficiency is given by

$$\eta = 1 - \gamma \, \frac{V_2/V_1 - 1}{p_1/p_2 - 1} \, .$$

(Recall that the coefficient γ is the ratio of c_p to c_V.)

Solution

1. For the ideal gas we have $pV = RT$. The formula for the change in entropy follows from the equation $\mathrm{d}S = (\mathrm{d}E + pdV)/T$.
2. The work delivered on the section of adiabatic $A \to B$ and on the section of isobaric $B \to C$ is

   $$A = \int_A^B \mathrm{d}V \, p + p_2(V_1 - V_2) \, .$$

   Inserting the relations $pV = RT$ and $c_p = c_V + R$ which hold for the ideal gas, the first term yields

   $$\begin{aligned}\int_A^B \mathrm{d}V \, p &= -\int_A^B \mathrm{d}T \, c_V = -c_V(T_2 - T_1) \\ &= \frac{1}{1-\gamma} \left(p_2 V_2 - p_1 V_1\right) \, ,\end{aligned}$$

   with $\gamma = c_p/c_V$, hence for the total work

   $$A = \frac{1}{1-\gamma} \left[\gamma p_2 \left(V_2 - V_1\right) + V_1 \left(p_2 - p_1\right)\right] \, .$$

   The furnished amount of heat is

   $$\begin{aligned}Q = \int_C^A \mathrm{d}S \, T &= \int_C^A \mathrm{d}T \, c_V = c_V(T_1 - T_2) \\ &= \frac{1}{1-\gamma} V_1 \left(p_2 - p_1\right) \, .\end{aligned}$$

   The assertion then follows from $\eta = A/Q$.

2.9 Prove the formulae (2.28a) and (2.28b) by means of the method of Jacobi determinants.

Solution

1. The general formula that we use here, is given in (2.27). Thus,

$$\frac{\partial(p,S)}{\partial(V,S)} = \left\{ \frac{\partial(p,S)/\partial(p,T)}{\partial(V,S)/\partial(V,T)} \right\} \frac{\partial(p,T)}{\partial(V,T)} \, .$$

If one inserts the definitions of c_p and of c_V, cf. the formulae right after (2.27), as well as the formulae

$$\kappa_S = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_S = -\frac{1}{V}\frac{\partial(V,S)}{\partial(p,S)} \, ,$$

$$\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_T = -\frac{1}{V}\frac{\partial(V,T)}{\partial(p,T)} \, ,$$

one obtains

$$\frac{\kappa_T}{\kappa_S} = \frac{\partial(p,S)/\partial(V,S)}{\partial(p,T)/\partial(V,T)} \, .$$

The expression between curly brackets in the first equation above is the ratio of the specific heats so that $\kappa_T/\kappa_S = c_p/c_V$.

2. The specific heat c_V can be transcribed as

$$\begin{aligned} c_V &= T\frac{\partial(S,V)/\partial(T,p)}{\partial(T,V)/\partial(T,p)} \\ &= \frac{T}{\partial V/\partial p|_T}\left[\left.\frac{\partial S}{\partial T}\right|_p \left.\frac{\partial V}{\partial p}\right|_T - \left.\frac{\partial S}{\partial p}\right|_T \left.\frac{\partial V}{\partial T}\right|_p \right] . \end{aligned}$$

Taking the difference $c_p - c_V$, making use of the Maxwell relation

$$\left.\frac{\partial S}{\partial p}\right|_T = \left.\frac{\partial V}{\partial T}\right|_p \, ,$$

which follows from the mixed second derivatives of the free enthalpy (2.5c), and inserting the definitions (2.20) and (2.21), one finds indeed the relation (2.28b).

Exercises Chap. 3

3.1 Consider a Hamiltonian system with one degree of freedom, $f = 1$, with Hamiltonian function $H(q,p)$. The phase space $\mathbb{P}$ is described by coordinates q and p. Consider the one-form

$$\theta = p\,\mathrm{d}q \, . \qquad (3.11)$$

1. Evaluate the form (3.11) on the general solution of the equation of motion for $H = (p^2 + q^2)/2$.
2. Calculate the two-form

$$\omega = -\,\mathrm{d}\theta\ . \tag{3.12}$$

   The Hamiltonian vector field is defined by

$$X_H = \begin{pmatrix} \partial H/\partial p \\ -\partial H/\partial q \end{pmatrix}\ . \tag{3.13}$$

   Evaluate $\omega(X_H, \cdot)$ and compare the result with the exterior derivative $\mathrm{d}H$ of H. (The dot stands for a missing argument.)
3. With $f(q,p)$ and $g(q,p)$ two smooth functions on the phase space $\mathbb{P}$ construct the vector fields

$$V^{(f)} = \begin{pmatrix} \partial f(q,p)/\partial p \\ -\partial f(q,p)/\partial q \end{pmatrix}\ , \quad V^{(g)} = \begin{pmatrix} \partial g(q,p)/\partial p \\ -\partial g(q,p)/\partial q \end{pmatrix}\ .$$

   Evaluate $\omega(V^{(f)}, V^{(g)})$. Which function is generated in this way? Examples: $f(q,p) = H(q,p)$ and $g(q,p) = q$ or $g(q,p) = p$.

Solution

1. The most general solution reads

$$q(t) = a\cos(t+\varphi)\ , \quad p(t) = -a\sin(t+\varphi)\ .$$

   Evaluating the one-form on the vector $(q(t), p(t))$ yields $\theta(q(t), p(t)) = p^2(t) = a^2\sin^2(t+\varphi)$.
2. One has $\omega = -\mathrm{d}p \wedge \mathrm{d}q = \mathrm{d}q \wedge \mathrm{d}p$ and $\omega(X_H, \cdot) = p\,\mathrm{d}p + q\,\mathrm{d}q = \mathrm{d}H$.
3. $\omega(V^{(f)}, V^{(g)}) = \mathrm{d}q(V^{(f)})\,\mathrm{d}p(V^{(g)}) - \mathrm{d}q(V^{(g)})\,\mathrm{d}p(V^{(f)}) = \{g,f\}$, the Poisson bracket is defined as in Scheck Mechanics (2010). With $f = H(q,p)$ the examples give

$$\omega(H,q) = \{q,H\} = -\frac{\partial H}{\partial p}\ , \quad \omega(H,p) = \{p,H\} = \frac{\partial H}{\partial q}\ .$$

3.2 Let v and w be two vector fields on the manifold Σ. Show that their commutator $vw - wv =: z$ is also a vector field on Σ.
Hint: The key for the solution of this exercise is given by the Leibniz rule for vector fields,

$$\text{With } v \text{ a vector field, } f \text{ and } g \text{ two functions and } x \in \Sigma :$$
$$v(f \cdot g)(x) = v(f)(x)g(x) + f(x)v(g)(x)\ .$$

One verifies that the product vw does not fulfill this rule but the commutator $vw - wv$ does.

3.3 Given the following one-forms, decide whether they are exact or not.

$$\begin{aligned}\omega_1 &= \frac{-y}{x^2+y^2}\,\mathrm{d}x + \frac{x}{x^2+y^2}\,\mathrm{d}y\ ,\\ \omega_2 &= (y-x^2)\,\mathrm{d}x + (x+y^2)\,\mathrm{d}y\ ,\\ \omega_3 &= (2y^2-3x)\,\mathrm{d}x + 4xy\,\mathrm{d}y\ .\end{aligned}$$

If one of these forms is exact find the function $f(x,y)$ for which one has $\omega = \mathrm{d}f$.

Solution With $\omega = f(x,y)\,\mathrm{d}x + g(x,y)\,\mathrm{d}y$ one has

$$\begin{aligned}\mathrm{d}\omega &= \frac{\partial f(x,y)}{\partial y}\,\mathrm{d}y\wedge\mathrm{d}x + \frac{\partial f(x,y)}{\partial x}\,\mathrm{d}x\wedge\mathrm{d}y\\ &= \left(\frac{\partial f(x,y)}{\partial x} - \frac{\partial f(x,y)}{\partial y}\right)\mathrm{d}x\wedge\mathrm{d}y\end{aligned}$$

Thus, for the three forms above one obtains

$$\begin{aligned}\mathrm{d}\omega_1 &= \frac{y^2-x^2}{(x^2+y^2)^2}\,\mathrm{d}y\wedge\mathrm{d}x + \frac{y^2-x^2}{(x^2+y^2)^2}\,\mathrm{d}x\wedge\mathrm{d}y = 0\ ,\\ \mathrm{d}\omega_2 &= \mathrm{d}y\wedge\mathrm{d}x + \mathrm{d}x\wedge\mathrm{d}y = 0\ ,\\ \mathrm{d}\omega_3 &= 4y\,(\mathrm{d}y\wedge\mathrm{d}x + \mathrm{d}x\wedge\mathrm{d}y) = 0\ .\end{aligned}$$

As the plane is singly connected there is no obstruction to the application of Poincaré's lemma to ω_2 and ω_3. Therefore, these two forms are not only closed but also exact. One has

$$\begin{aligned}&\omega_i = \mathrm{d}f_i = \frac{\partial f_i}{\partial x}\,\mathrm{d}x + \frac{\partial f_i}{\partial y}\,\mathrm{d}y\ ,\ i=1,2\,,\\ &\text{with}\, f_2 = xy - \tfrac{1}{3}(x^3-y^3) + C_2\ ,\\ &\text{and}\, f_3 = 2xy^2 - \tfrac{3}{2}x^2 + C_3\ .\end{aligned}$$

Although the first form ω_1 can be written as a total differential as well, $\omega_1 = \mathrm{d}f_1(x,y)$ with $f_1 = -\arctan(x/y) + C_1$, Poincaré's lemma can be applied only to starlike domains which do not contain the straight line $y=0$.

3.4 Let a two-dimensional system Σ be described by means of the variables (V,T) or, alternatively, by (p,T). The one-form of heat then reads, respectively,

$$\alpha = \Lambda_V\,\mathrm{d}V + c_V\,\mathrm{d}T \quad\text{or}\quad \alpha = \Lambda_p\,\mathrm{d}p + c_p\,\mathrm{d}V\ . \tag{3.14}$$

1. The gradient field of a function f is $\nabla f = (\partial_1 f, \partial_2 f)^T$; tangent and normal vectors of a curve defined by $S =$ const. are proportional to

$$\boldsymbol{v} \propto (-\partial_2 S, \partial_1 S) \quad \text{or} \quad \boldsymbol{n} \propto (\partial_1 S, \partial_2 S) \ .$$

   Show that for $\alpha = T\,\mathrm{d}S$ and for two smooth functions f and g,

$$\frac{\alpha \wedge \mathrm{d}f}{\alpha \wedge \mathrm{d}g} = \left.\frac{\mathrm{d}f}{\mathrm{d}g}\right|_S \ .$$

2. Furthermore, one has $(\mathrm{d}T \wedge \mathrm{d}p)/(\mathrm{d}T \wedge \mathrm{d}V) = \mathrm{d}p/\mathrm{d}V|_T$. Prove the relation

$$\left.\frac{\mathrm{d}p}{\mathrm{d}V}\right|_{\text{adiabatic}} = \left.\frac{\mathrm{d}p}{\mathrm{d}V}\right|_T \ .$$

   Prove the formula

$$\left.\frac{\mathrm{d}p}{\mathrm{d}V}\right|_{\text{adiabatic}} = \gamma \left.\frac{\mathrm{d}p}{\mathrm{d}V}\right|_{\text{isothermal}} \ ,$$

   making use of (3.14).

Hint: Note that we are dealing with systems in only two dimensions. For example, choose the variables (V, T). If the function $S(V, T)$ is constant then $\mathrm{d}V$ and $\mathrm{d}T$ are related by $\mathrm{d}S = 0$ so that

$$\mathrm{d}f = \frac{\mathrm{d}V}{\partial S/\partial T}\left(\frac{\partial f}{\partial V}\frac{\partial S}{\partial T} - \frac{\partial f}{\partial T}\frac{\partial S}{\partial V}\right) ,$$

and likewise for g. This gives for the ratio

$$\left.\frac{\mathrm{d}f}{\mathrm{d}g}\right|_S = \left(\frac{\partial f}{\partial V}\frac{\partial S}{\partial T} - \frac{\partial f}{\partial T}\frac{\partial S}{\partial V}\right)\left(\frac{\partial g}{\partial V}\frac{\partial S}{\partial T} - \frac{\partial g}{\partial T}\frac{\partial S}{\partial V}\right)^{-1} \ .$$

On the other hand $\alpha \wedge \mathrm{d}f$ and $\alpha \wedge \mathrm{d}g$ are two-forms and, in dimension 2, have only one component. Their ratio is a function and is obviously equal to the ratio above.

3.5 Let a thermodynamic system Σ with $\dim \Sigma = 2$ be described by the variables T and V.

1. By making use of the relation $\mathrm{d}T \wedge \mathrm{d}S = \mathrm{d}p \wedge \mathrm{d}V$ prove

$$\left.\frac{\partial T}{\partial V}\right|_{\text{adiabatic}} = -\left.\frac{\partial p}{\partial S}\right|_V \quad \text{and} \quad \left.\frac{\partial S}{\partial V}\right|_{\text{isothermal}} = \left.\frac{\partial p}{\partial T}\right|_V \ .$$

2. The isothermal compressibility κ_T and the isobaric expansion coefficient α are contained in the formulae

$$\mathrm{d}V \wedge \mathrm{d}T = \kappa_T \,\mathrm{d}T \wedge \mathrm{d}p \quad \text{and} \quad \mathrm{d}V \wedge \mathrm{d}p = \alpha \,\mathrm{d}T \wedge \mathrm{d}p \,.$$

Prove the relation

$$c_p = c_V + VT\frac{\alpha^2}{\kappa_T} \,.$$

Solution

1. By evaluating $\mathrm{d}T \wedge \mathrm{d}S = \mathrm{d}p \wedge \mathrm{d}V$ on the base fields ∂_T and ∂_V one obtains immediately

$$(\mathrm{d}T \wedge \mathrm{d}S)\,(\partial_T, \partial_V) = \mathrm{d}S(\partial_V) = \left.\frac{\partial S}{\partial V}\right|_{T,N} \,,$$

$$(\mathrm{d}p \wedge \mathrm{d}V)\,(\partial_T, \partial_V) = \mathrm{d}p(\partial_T) = \left.\frac{\partial p}{\partial T}\right|_{V,N} \,.$$

This gives the second of the above relations. The first follows from

$$(\mathrm{d}T \wedge \mathrm{d}S)\,(\partial_V, \partial_S) = \mathrm{d}T(\partial_V) = \left.\frac{\partial T}{\partial V}\right|_{S,N} \,,$$

$$(\mathrm{d}p \wedge \mathrm{d}V)\,(\partial_V, \partial_S) = -\mathrm{d}p(\partial_S) = -\left.\frac{\partial p}{\partial S}\right|_{V,N} \,.$$

2. This is essentially the solution of Exercise 2.9, here again, but more consistently, in terms of Jacobi determinants. One starts from

$$c_p = T\frac{\mathrm{d}S \wedge \mathrm{d}p}{\mathrm{d}T \wedge \mathrm{d}p} \,, \quad c_V = T\frac{\mathrm{d}S \wedge \mathrm{d}V}{\mathrm{d}T \wedge \mathrm{d}V} \,,$$

and calculates from these formulae

$$\begin{aligned} \frac{1}{T}(c_p - c_V) &= \frac{\mathrm{d}S \wedge \mathrm{d}p}{\mathrm{d}T \wedge \mathrm{d}p} - \frac{\mathrm{d}S \wedge \mathrm{d}V}{\mathrm{d}T \wedge \mathrm{d}V} \\ &= \frac{\mathrm{d}T \wedge \mathrm{d}V}{\mathrm{d}T \wedge \mathrm{d}p}\left\{\frac{\mathrm{d}S \wedge \mathrm{d}p}{\mathrm{d}T \wedge \mathrm{d}V} - \frac{\mathrm{d}T \wedge \mathrm{d}p}{\mathrm{d}T \wedge \mathrm{d}V}\frac{\mathrm{d}S \wedge \mathrm{d}V}{\mathrm{d}T \wedge \mathrm{d}V}\right\} \,. \end{aligned}$$

The first term in curly brackets is evaluated separately as follows

$$\begin{aligned}\frac{\mathrm{d}S \wedge \mathrm{d}p}{\mathrm{d}T \wedge \mathrm{d}V} &= \frac{\partial S}{\partial T}\frac{\partial p}{\partial V} - \frac{\partial S}{\partial V}\frac{\partial p}{\partial T} \\ &= \frac{\mathrm{d}S \wedge \mathrm{d}V}{\mathrm{d}T \wedge \mathrm{d}V}\frac{\mathrm{d}p \wedge \mathrm{d}T}{\mathrm{d}V \wedge \mathrm{d}T} - \frac{\mathrm{d}S \wedge \mathrm{d}T}{\mathrm{d}V \wedge \mathrm{d}T}\frac{\mathrm{d}p \wedge \mathrm{d}V}{\mathrm{d}T \wedge \mathrm{d}V}\,.\end{aligned}$$

The first term on the right-hand side cancels against the second term in the curly brackets of the previous equation so that one obtains

$$\frac{1}{T}(c_p - c_V) = -\frac{\mathrm{d}T \wedge \mathrm{d}V}{\mathrm{d}T \wedge \mathrm{d}p}\frac{\mathrm{d}S \wedge \mathrm{d}T}{\mathrm{d}V \wedge \mathrm{d}V}\frac{\mathrm{d}p \wedge \mathrm{d}V}{\mathrm{d}T \wedge \mathrm{d}V}\,.$$

At this point one makes use of the Maxwell relation (cf. part 1)

$$\left.\frac{\partial S}{\partial V}\right|_T = \frac{\mathrm{d}S \wedge \mathrm{d}T}{\mathrm{d}V \wedge \mathrm{d}T} = \left.\frac{\partial p}{\partial T}\right|_V = \frac{\mathrm{d}p \wedge \mathrm{d}V}{\mathrm{d}T \wedge \mathrm{d}V}\,,$$

as well as relations of the type

$$\frac{\mathrm{d}p \wedge \mathrm{d}V}{\mathrm{d}T \wedge \mathrm{d}V} = \frac{\mathrm{d}p \wedge \mathrm{d}V}{\mathrm{d}p \wedge \mathrm{d}T}\frac{\mathrm{d}p \wedge \mathrm{d}T}{\mathrm{d}T \wedge \mathrm{d}V}\,,$$

so that one obtains

$$\frac{1}{T}(c_p - c_V) = \frac{(\mathrm{d}p \wedge \mathrm{d}V)^2}{(\mathrm{d}T \wedge \mathrm{d}p)^2}\frac{\mathrm{d}T \wedge \mathrm{d}p}{\mathrm{d}V \wedge \mathrm{d}T}\,.$$

The first factor on the right-hand side is to be compared with (2.21) and gives $V^2\alpha^2$. The second factor is proportional to the inverse of (2.20) and hence yields $1/(V\kappa_T)$. The assertion then follows.

3.6 If the one-form α fulfills neither $\mathrm{d}\alpha = 0$ nor $\alpha \wedge \mathrm{d}\alpha = 0$, then every point p can be linked to any other point q by a null curve, see Definition 3.6. Show this assertion by a suitable choice of the path from $p = (0,0,0)^T$ to $q = (a,b,c)^T$.

Solution Without loss of generality choose the standard form $\alpha = x^1\,\mathrm{d}x^2 + \mathrm{d}x^3$. The path from p to q is best decomposed in straight sections as follows:

(a) If $b \neq 0$: From $q = (0,0,0)^T$ to $q_1 = (-c/b,0,0)^T$ along the x^1-axis, then from q_1 to $q_2 = (-c/b,b,c)^T$ by means of

$$q(t) = \begin{pmatrix} -c/b \\ 0 \\ 0 \end{pmatrix} + (t-1)\begin{pmatrix} 0 \\ b \\ c \end{pmatrix}\,, \quad 1 \le t \le 2\,.$$

Finally, one moves from q_2 to $p = (a, b, c)^T$ via

$$q(t) = \begin{pmatrix} -c/b \\ b \\ c \end{pmatrix} + (t-2) \begin{pmatrix} a + c/b \\ 0 \\ 0 \end{pmatrix} , \quad 2 \leq t \leq 3 .$$

All these path integrals give zero.

(b) If $b = 0$ one moves from $(0, 0, 0)^T$ to $(1, c, 0)^T$ in three steps as before, then to $(1, 0, c)^T$ and, finally, to $(a, 0, c)^T$ along the x^1-axis.

(c) If both $b = 0$ and $c = 0$, one moves exclusively along the x^1-axis. The path integral vanishes in all cases.

3.7 For all one-forms α which do not belong to either of the classes (a) or (b) of Sect. 3.3.4, any two points p and q can be linked by a null curve. Show this assertion for the space $\mathbb{R}^6$.

Solution In the case of $\mathbb{R}^6$ one must study six different cases and use standard forms for α as follows

(a) $\alpha \neq 0$ and $d\alpha = 0$: standard form $\alpha = dx^3$.
(b) $d\alpha \neq 0$ and $\alpha \wedge d\alpha = 0$: standard form $\alpha = x^1\, dx^2$.
(c) $\alpha \wedge d\alpha \neq 0$ and $d\alpha \wedge d\alpha = 0$: standard form $\alpha = x^1\, dx^2 + dx^3$.
(d) $d\alpha \wedge d\alpha \neq 0$ and $\alpha \wedge d\alpha \wedge d\alpha = 0$:
standard form $\alpha = x^1\, dx^2 + x^4\, dx^5$.
(e) $\alpha \wedge d\alpha \wedge d\alpha \neq 0$ and $d\alpha \wedge d\alpha \wedge d\alpha = 0$:
standard form $\alpha = x^1\, dx^2 + x^4\, dx^5 + dx^3$.
(f) $d\alpha \wedge d\alpha \wedge d\alpha \neq 0$: standard form $\alpha = x^1\, dx^2 + x^4\, dx^5 + x^6\, dx^3$.

In the cases (c) to (f) it is always possible to link two arbitrarily chosen points $p = (0, 0, 0, 0, 0, 0)^T$ and $q = (x^1, x^2, x^3, x^4, x^5, x^6)^T$ by a null curve consisting of suitably chosen sections of straight lines. Using standard form (c): one stays in the subspace $x^4 = x^5 = x^6 = 0$ and moves from p to the point $(x^1, x^2, x^3, 0, 0, 0)^T$. Then, keeping x^1, x^2 and x^3 constant, move along a straight line to q. Standard form (e): In a first step proceed as above, then keep x^1 and x^2 constant and adjust x^4 and x^5. Along the curve $x^2 =$ const. the form α takes the same values as $x^4\, dx^5 + dx^3$ (compare with the case of $\mathbb{R}^3$). Then adjust x^6 while all other coordinates are held constant. Standard form (f): Suppose $x^6 \equiv r \neq 0$. In the subspace $x^1 = x^2 = x^3 = x^4 = x^5 = 0$ move to $p_1 = (0, 0, 0, 0, 0, r)^T$, then stay in the hyperplane $x^6 = r$. One has

$$\alpha' = x^1 dx^2 + x^4 dx^5 + r dx^3 \equiv x^1 dx^2 + x^4 dx^5 + dx'^3 \quad \text{with } x'^3 = r x^3$$

and continues like above. If $x^1 \neq 0$ or $x^4 \neq 0$, one proceeds in an analogous way. If q lies in the subspace $x^1 = x^4 = x^6 = 0$ then every curve from p to q is a null curve of α, as long as it is contained in this subspace. The standard form (d) is dealt with in an analogous manner. (see Bamberg and Sternberg 1990).

Exercises Chap. 4

4.1 Given a system of N semi-classical spins $s_3^{(i)} = \pm\frac{1}{2}$, $i = 1, 2, \dots, N$, all of which carry the magnetic moment μ, in an external magnetic field $\boldsymbol{B} = B\hat{\boldsymbol{e}}_3$. The interaction between these magnetic moments is neglected.

1. Calculate the energy levels and their degree of degeneracy $\Omega(E)$.
   Hint: $H = -\mu B \sum_i s_3^{(i)}$.
2. Making use of Stirling's formula (1.5) determine $\Omega(E)$ in the limit $N \gg 1$ and $|E| \ll N\mu B$.

Solution

1. The eigenstates of the Hamilton operator are product states $|\lambda_1, \dots, \lambda_N\rangle$ with $\lambda_i = \pm 1/2$. One has

$$s_3^{(i)}|\lambda_1, \dots, \lambda_N\rangle = \lambda_i|\lambda_1, \dots, \lambda_N\rangle \ ,$$

$$H|\boldsymbol{\lambda}\rangle = E_{\boldsymbol{\lambda}}|\boldsymbol{\lambda}\rangle \ , \quad E_{\boldsymbol{\lambda}} = -\mu B \sum_{i=1}^{N} \lambda_i = -\tfrac{1}{2}\mu B\,(N_+ - N_-) \ ,$$

   where N_+ denotes the number of "spins up" ↑, N_- denotes the number of "spins down" ↓. With $N_+ + N_- = N$, or $N_- = N - N_+$, one has

$$E_{\boldsymbol{\lambda}} = -\mu B\,(2N_+ - N) \ ,$$
$$N_+ = \frac{1}{2}N\left(1 - \frac{E_{\boldsymbol{\lambda}}}{\mu BN}\right) \ , \quad N_- = \frac{1}{2}N\left(1 + \frac{E_{\boldsymbol{\lambda}}}{\mu BN}\right) \ .$$

   The degree of degeneracy follows from the answer to the question in how many ways a number N_+ of ↑-spins can be distributed among the N possibilities, i.e.

$$\Omega(E_{\boldsymbol{\lambda}}) = \binom{N}{N_+} = \frac{N!}{N_+!\,N_-!} \ .$$

2. Using Stirling's formula one finds

$$\Omega \simeq \frac{1}{\sqrt{2\pi}} \frac{N^{N+1/2}}{N_+^{N_+ + 1/2}(N - N_+)^{N - N_+ + 1/2}} \ .$$

For $N \gg 1$ and $N \gg N_+$ this simplifies to

$$\Omega(E_\lambda) \simeq \frac{1}{\sqrt{2\pi N_+}\, N_+^{N_+}} \, .$$

4.2 Using the approximation for $\Omega(E)$ that was obtained in Exercise 4.1 in the limit ($N \gg 1, |E| \ll N\mu B$), calculate the entropy of this system. Derive the relation between the energy E of the system and its temperature T. When does T become negative? Use the result for the entropy in determining the magnetic moment $M = \mu \sum_i s_3^{(i)}$ as a function of N, B and T.

Solution With the result of Exercise 4.1 and in the approximation $\ln(N!) \simeq N(\ln N - 1) + \mathcal{O}(\ln N)$ the entropy is

$$\begin{aligned} S = k \ln \Omega &= k\left(\ln(N!) - \ln(N_+!) - \ln(N_-!)\right) \\ &\simeq k\left(N_+ \ln \frac{N}{N_+} + N_- \ln \frac{N}{N_-}\right) \, . \end{aligned}$$

Define $\Delta = N_+ - N_-$. Then

$$S \simeq \frac{1}{2}\left[(N+\Delta)\ln\left(\frac{2N}{N+\Delta}\right) + (N-\Delta)\ln\left(\frac{2N}{N-\Delta}\right)\right] \, .$$

The temperature is obtained from (1.26), i.e. from the equation $1/T = \partial S/\partial E = (\partial S/\partial \Delta)(\partial \Delta/\partial E)$, and from $E = -\mu B \Delta$

$$\begin{aligned} \frac{1}{T} &= -\frac{k}{\mu B}\frac{\partial S}{\partial \Delta} = \frac{k}{2\mu B}\ln\left(\frac{N+\Delta}{N-\Delta}\right) \\ &= \frac{k}{2\mu B}\ln\left(\frac{1 - E/(\mu B N)}{1 + E/(\mu B N)}\right) \, . \end{aligned}$$

This is solved for the energy

$$E_\lambda = -N\mu B \tanh\left(\frac{\mu B}{kT}\right) \, .$$

If $|E| \ll \mu B N$, then $T \to 0$. The temperature becomes *negative* when $N_+ < N_-$. This can also be seen from a plot of $\sigma := 2S/N$ in terms of the variable $\varepsilon := E_\lambda / N\mu B$. With $\Delta = -E_\lambda/(\mu B) = -N\varepsilon$ one has

$$\sigma = (1-\varepsilon)\ln\left(\frac{2}{2-\varepsilon}\right) + (1+\varepsilon)\ln\left(\frac{2}{2+\varepsilon}\right) \, .$$

This function is shown in Fig. A.3. For positive values of ε (or the energy) its derivative is negative.

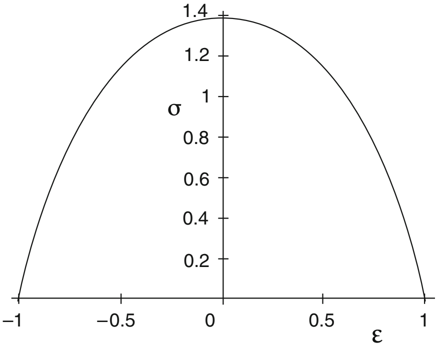


Fig. A.3 The function $\sigma(\varepsilon)$ from Exercise 4.2

The total magnetic moment is found to be

$$M = \frac{1}{2}\mu\Delta = -\frac{E_\lambda}{2B} = \frac{1}{2}N\mu\tanh\left(\frac{\mu B}{kT}\right) .$$

4.3 In classical dynamics of mechanics the expectation value of an observable is defined by $A(q,p)$

$$\langle A\rangle = \frac{1}{Z}\iint \mathrm{d}p\,\mathrm{d}q\, A(q,p)\,\mathrm{e}^{-\beta H(q,p)} , \tag{4.15}$$

with Z the canonical partition function and H the Hamilton function of the canonical ensemble. Show that

$$\left\langle H^2\right\rangle - \langle H\rangle^2 = kT^2 c_V . \tag{4.16}$$

Using this formula derive the assertion $c_V \geq 0$.

4.4 Given two identical particles which can take three states whose energies are

$$E_n = nE_0 \quad \text{with} \quad n = 0, 1, 2 . \tag{4.17}$$

The lowest state is doubly degenerate, the two remaining states are assumed to be non-degenerate. The thermodynamic system which is formed by a repartition of the particles onto the states (4.16), is assumed to be in equilibrium at the temperature T (i.e. it is a canonical system).

1. Calculate the partition function and the energy in the case where the particles obey Fermi-Dirac statistics. Sketch the six allowed configurations. (It is useful to represent the degeneracy in the ground state by symbols ↑ and ↓.)
2. How many states are there and what are their energies if the particles are bosons? Calculate the partition function and the energies.

3. If the particles obey Maxwell-Boltzmann statistics then there are 16 states. Describe these states graphically and specify which of these are degenerate in energy. Calculate partition function and energy.

In case $kT \gg E_0$ both bosons and fermions may be treated on the same footing, the energy becomes $(3/2)E_0$.

4.5 If a system has only discrete, non-degenerate energy levels E_n and if the measure takes the value 1 on every state, the partition function reads

$$Z = \sum_{n=0}^{\infty} \mathrm{e}^{-\beta E_n} \, . \tag{4.18}$$

1. What is the mean value $\langle E \rangle$ if it is expressed as a derivative by β or by the temperature T?
2. Study the example of the one-dimensional harmonic oscillator, $E_n = (n + 1/2)\hbar\omega$, in thermal equilibrium with a heat bath whose temperature is T. Show that
$$Z = \frac{2}{\sinh\left(\beta\hbar\omega/2\right)}$$
and calculate the mean value $\langle E \rangle$ and the fluctuation $\sqrt{(\langle E \rangle)^2}$.
3. Determine the limiting values of these quantities in the cases $kT \ll \hbar\omega$ and $kT \gg \hbar\omega$.

Hint: Write the inverse hyperbolic sine function as a geometric series.

4.6 In Example 4.9 and with $W = \ln Z$ as defined in (4.18a), show that

$$\frac{\partial W}{\partial V} \mathrm{d}V = -\beta\omega$$

where $\omega = -p\,\mathrm{d}V$ is the one-form of work.

4.7 When a particle is confined to a cuboid whose edges have lengths a_1, a_2 and a_3, respectively, (its volume then being $V = a_1 a_2 a_3$) a natural normalized base system is provided by the eigenfunctions of the momentum operator,

$$\varphi(\boldsymbol{p}, \boldsymbol{x}) = \frac{1}{\sqrt{V}} \mathrm{e}^{\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{x}/\hbar} \quad \text{with} \quad \boldsymbol{p} = 2\pi\hbar \left(\frac{n_1}{a_1}, \frac{n_2}{a_2}, \frac{n_3}{a_3} \right) \, .$$

The elementary volume in momentum space

$$\widetilde{V}_{\boldsymbol{p}} = \frac{(2\pi\hbar)^3}{a_1 a_2 a_3} = \frac{h^3}{V}$$

contains exactly one eigenstate of momentum. If $\underline{f}(\underline{q},\underline{p})$ is an operator with all momentum operators placed to the right of the position operators, show that its trace is given by

$$\mathrm{tr}\underline{f}(\underline{q},\underline{p}) = \frac{1}{V}\sum_{\boldsymbol{p}} \int \mathrm{d}^3 q\, f(\boldsymbol{q},\boldsymbol{p})\,.$$

In the classical limit one has $\sum_{\boldsymbol{p}} \tilde{V} \to \int \mathrm{d}^3 p$ and the replacement (4.74) applies.

4.8 A very diluted gas of N two-atomic molecules is enclosed in a volume V and has the temperature T. The two atoms of a molecule inside the volume are described by the Hamiltonian function

$$H(\boldsymbol{x}_1,\boldsymbol{x}_2,\boldsymbol{p}_1,\boldsymbol{p}_2) = \frac{1}{2m}\left(\boldsymbol{p}_1^2+\boldsymbol{p}_2^2\right) + \tfrac{1}{2}\alpha|\boldsymbol{x}_1-\boldsymbol{x}_2|^2$$

with $\alpha > 0$.

1. Calculate the classical canonical partition function and construct the equation of state in the variables (p, V, T).
2. Calculate the specific heat c_V and the quadratic mean square diameter of a molecule.

Solution

1. As there is no interaction between different molecules one has

$$Z_N(T,V) = \frac{1}{\hbar^{6N}(2N)!}\mathcal{J}^N \quad \text{where}$$

$$\mathcal{J} = \iiiint \mathrm{d}^3 p_1\, \mathrm{d}^3 p_3\, \mathrm{d}^3 x_1\, \mathrm{d}^3 x_2\; \mathrm{e}^{-\beta H}\ .$$

The integral $\mathcal{J}$ contains the following integrals in momentum- and position space, respectively:

$$I^{(p)} := \int \mathrm{d}^3 p\; \mathrm{e}^{-\beta \boldsymbol{p}^2/(2m)}\ , \quad I^{(x)} := \iint \mathrm{d}^3 x_1\, \mathrm{d}^3 x_2\, \mathrm{e}^{-\beta\alpha|\boldsymbol{x}_1-\boldsymbol{x}_2|^2}\ .$$

The first of these equals $I^{(p)} = (2\pi mkT)^{3/2}$. The second integral is calculated using center-of-mass and relative coordinates, $\boldsymbol{R} = (\boldsymbol{x}_1 + \boldsymbol{x}_2)/2$ and $\boldsymbol{r} = \boldsymbol{x}_1 - \boldsymbol{x}_2$, respectively. Then $\int \mathrm{d}^3R \cdots$ yields a factor V. The integral over $r \equiv |\boldsymbol{x}_1 - \boldsymbol{x}_2|$ has an exponentially decreasing integrand and may therefore be extended to infinity. Thus,

$$I^{(x)} = V4\pi \int_0^\infty r^2 \mathrm{d}r \; \mathrm{e}^{-\beta\alpha r^2/2} = V \left(\frac{2\pi}{\beta\alpha}\right)^{3/2} .$$

The partition function is found to be

$$Z_N(T,V) = C(N) V^N (kT)^{9N/2} \quad \text{with} \quad C(N) = \frac{(2\pi\sqrt{2\pi}m)^{3N}}{\hbar^{6N}(2N)!\alpha^{3N/2}} .$$

According to (1.51) the free energy is $F(T,N,V) = -kT \ln Z_N(T,V)$. Using this, one calculates from (2.2b)

$$p = -\left.\frac{\partial F}{\partial V}\right|_T = kT\frac{N}{V} .$$

The diluted gas behaves like an ideal gas.

2. This is also confirmed by the value of the specific heat which is calculated from the (inner) energy

$$E = -\frac{\partial}{\partial\beta} \ln Z_N(T,V) = \frac{9}{2}NkT$$

by means of the formula (2.18) ,

$$c_V = \left.\frac{\partial E}{\partial T}\right|_V = \frac{9}{2}NkT .$$

The mean square distance is obtained from the mean value, weighted with the partition function

$$\begin{aligned} \langle r^2 \rangle &= \frac{\iint \mathrm{d}^3x_1\,\mathrm{d}^3x_2\; |\boldsymbol{x}_1 - \boldsymbol{x}_2|^2 \exp\{-(\alpha\beta/2)|\boldsymbol{x}_1 - \boldsymbol{x}_2|^2\}}{\iint \mathrm{d}^3x_1\,\mathrm{d}^3x_2\; \exp\{-(\alpha\beta/2)|\boldsymbol{x}_1 - \boldsymbol{x}_2|^2\}} \\ &= -\frac{2}{\alpha}\frac{\partial}{\partial\beta} \ln I^{(x)} = \frac{3}{\alpha\beta} = \frac{3}{\alpha}kT . \end{aligned}$$

Here we used $\mathrm{d}E = T\,\mathrm{d}S$ and $\mathrm{d}V = 0 = \mathrm{d}N$.

Exercises Chap. 5

5.1 Consider a linear chain with N links for N very large, $N \gg 1$. Every link of the chain can take two possible states: either aligned along the chain, in which case it has the length a, or perpendicular to it in which case the length is 0. The two ends of the chain have the distance Nx.

1. Construct the entropy $S(x)$ of the system as a function of x.
2. The temperature T being given, the chain is exposed to a tension F such that the length Nx is kept unchanged. The difference in energy of a link between its position perpendicular and its position parallel is Fa. Find the mean length ℓ of a link at the temperature T.

   This yields an equation which relates the length $L = N\ell$ to F and T.
3. In which limit does the result yield Hooke's law?

Solution

1. If the momentary length is Nx then $M = Nx/a$ links are oriented along the chain, $N - M$ links are perpendicular to it. The number of micro-states is

   $$\Omega = \frac{N!}{M!(N-M)!} \; .$$

   Thus, the entropy is

   $$S = k \ln \Omega = k \ln \left(\frac{N!}{(Nx/a)!(N - Nx/a)!} \right) \; .$$

2. The links of the chain can have only one of two possible positions, either perpendicular to the chain with energy $-Fa$, or parallel to it with energy zero. The partition function is

   $$Z = 1 + \exp\{ \mathrm{e}^{\beta Fa} \} \; ,$$

   (cf. Example 4.5 and (4.44c)). At the temperature T the mean length of a link is

   $$\ell = \frac{a \, \mathrm{e}^{Fa/(kT)}}{1 + \mathrm{e}^{Fa/(kT)}} \; ,$$

   from which the relation between the length of the chain and the temperature is seen to be $L = N\ell$ with ℓ as obtained above.
3. At high temperatures the function L can be expanded,

   $$L \simeq \frac{1}{2} Na \left(1 + \frac{Fa}{kT} \right) \; .$$

   This is Hooke's law.

5.2 The reader is invited to complete the following settings by the appropriate Maxwell relation: Choose as the thermodynamic potential

1. the energy $E(S,N,V)$, with

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu_C\,\mathrm{d}N\,,$$

$$T = \frac{\partial E}{\partial S}\,, \quad p = -\frac{\partial E}{\partial V}\,, \quad \mu_C = \frac{\partial E}{\partial N}\,;$$

2. the free energy $F(T,N,V) = E - TS$, with

$$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu_C\,\mathrm{d}N\,;$$

3. the enthalpy $H(S,N,p) = E + pV$, with

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \mu_C\,\mathrm{d}N\,;$$

4. the free enthalpy $G(T,N,p) = E - TS + pV$, with

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu_C\,\mathrm{d}N\,;$$

5. The grand canonical potential $K(T,\mu_C,V) = E - TS - \mu_c N$, with

$$\mathrm{d}K = -S\,\mathrm{d}T - p\,\mathrm{d}V - N\,\mathrm{d}\mu_C\,.$$

5.3 Given a system which possesses the critical temperature T_c. The (V,T)-diagram that applies to this substance, is assumed to be known. Let its qualitative behaviour be as sketched in Fig. A.4. If one joins two noninteracting copies of the same substance then, in equilibrium, they will reach the same temperature. How does

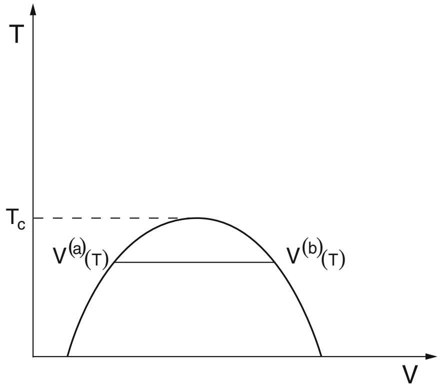


Fig. A.4 Qualitative (V,T)-diagram of a single substance (Exercise 5.3) the (V_1, V_2, T)-diagram of the combined system look like? It is assumed that the coexisting pure phases $(T, V^{(a)}(T))$ and $(T, V^{(b)}(T))$, with $T < T_\mathrm{c}$, have the same free energy. Does Gibbs's phase rule hold true?

5.4 Determine the zero of the function (5.64c)

$$d(x) = (1 - \sinh(2x))^2$$

by means of a numerical method.
Hint: As an example one might use Newton's iteration formula. One chooses a trial value x_0 for the zero, then calculates $d(x_0)$ and $d'(x_0)$. The tangent in the point $(x_0, d(x_0))$ intersects with the x-axis in the point x_1. This point is used for the next iteration. One continues this procedure until the approximations x_n and x_{n+1} differ by less than a given ε. The iteration equation is

$$x_{n+1} = x_n - \frac{d(x_n)}{d'(x_n)} \, .$$

The procedure converges as long as the modulus of the derivative stays smaller than 1, $|d'(x)| < 1$. (The case at stake needs a little care because $d'(x)$ vanishes at the zero.) The answer is given in (5.65).

5.5 Study the integral in (5.66) in the neighbourhood of the singularity.

5.6 If the forces between fermions are non-singular at distance zero, if they are of short range and always attractive, the potential energy varies like $-N^2$. The system collapses. Give a plausibility argument for this assertion.

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Index

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