TEXTBOOK

Wolfgang Cassing

Theoretical Physics Compact IV

Quantum Statistics and Thermodynamics

Springer

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ISBN 978-3-031-95517-4 e-ISBN 978-3-031-95518-1
https://doi.org/10.1007/978-3-031-95518-1

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Dedicated to Prof. Dr. Achim Weiguny

Preface

This book provides a textbook on quantum statistics and thermodynamics and is in particular suited for bachelor students in their last year of bachelor studies in theoretical physics. Prerequisites are a knowledge of classical Hamilton dynamics, quantum mechanics and its formulations in different representations. Elementary knowledge about electrodynamics is welcome in particular about elementary electric and magnetic dipoles and their interactions with external electromagnetic fields.

Somewhat contrary to standard books about thermodynamics we will not start with the phenomenological thermodynamics, but directly from quantum dynamics with the definition of the statistical operator in the many-particle Hilbert space. This opens up the possibility to define the entropy as the statistical average of the negative logarithm of the statistical operator and to set up the framework for irreversible processes in macro-systems even if the basic equations of motion for elementary particles obey micro-reversibility. Statistical ensembles then are specified by the postulate of maximum entropy and microcanonical, canonical, grand-canonical and general ensembles are defined, which depend on the knowledge about energy, particle number and volume. If some of these quantities are only known on average, then corresponding Lagrange parameters are introduced, that guarantee the average values, respectively. These Lagrange parameters will be related to temperature, chemical potential and pressure later on.

Another important issue of quantum mechanics is the exchange symmetry of many-body states of identical particles, which has no counterpart in classical mechanics, i.e. the exchange symmetry with respect to particle exchange: the wave functions have to be symmetric or antisymmetric with respect to particle exchange, which leads to the separation of bosons and fermions with different quantization rules for the definition of creation and annihilation operators. This splitting of the Hilbert space in bosons and fermions has important consequences e.g. for the specific heat, the thermal expansion coefficient and the single-particle occupation numbers at low temperatures. Only in case of low densities and/or high temperatures these different quantities merge to the classical limit. Independently, the different ensembles go over to the classical distribution functions, if the particle number N becomes large, since the relative fluctuations in energy and particle number scale as $1/\sqrt{N}$.

In line with the different ensembles thermodynamic potentials are defined as a function of the natural variables and their total differentials are specified. This leads to a couple of Maxwell relations that can be employed to compute thermodynamic quantities. The three laws of thermodynamics are formulated and proven and it is shown that the classical ideal gas violates the 3rd law of thermodynamics at low temperatures. Isochoric, isobaric, isothermal and adiabatic changes of state are discussed and employed for the thermodynamics of the Carnot cycle and the Otto engine.

Furthermore, small deviations from equilibrium are investigated and the connection between spontaneous fluctuations of physical quantities around their average values in statistical equilibrium and forced deviations from the average values due to disturbances of the balance by external perturbations. It is shown that these two phenomena are closely linked for weak external perturbations and find their expression in the fluctuation-dissipation theorem. To this aim we will introduce the thermodynamic perturbation theory and compute response functions for various examples like the electric conductivity or the resistance noise.

The ideal Fermi gas and Bose gas provide important examples for the different properties of Bose and Fermi systems at low temperatures and it is shown, that these systems are consistent with the 3rd law of thermodynamics. The equations of state show important differences in comparison to the classical limit and the Bose-Einstein condensation—in case of bosons—is found at low temperatures. As important example for Bose systems the photon gas in a large container is investigated and Planck’s radiation law is derived explicitly. Another example are phonons in solids, which correspond to the quantized vibrations of the building blocks (atoms or molecules).

Furthermore, the framework for the description of real interacting systems is presented in terms of the Virial expansion and the resulting equations of state are derived. In particular the classical Van der Waals system is investigated as well as ‘nuclear matter’ as an example for an interacting Fermi system. Both systems are found to show a liquid-gas phase transition of 1st order.

This volume closes with a derivation of kinetic theories for interacting Fermi systems, which describe the processes that pave the way from systems out-off equilibrium to the statistical equilibrium. This will lead to the Vlasov-Uehling-Uhlenbeck equation for Fermi systems or the Boltzmann equation in the classical limit. The solution of these equations can conveniently be achieved within the test-particle framework.

Acknowledgements This book results from the collaboration with many students and collaborators throughout about 35 years of common teaching and research. It follows the drafts of my teacher Prof. Dr. Achim Weiguny to whom this volume is dedicated. Special thanks go to my daughter Marie for preparing some of the figures and helpful comments on notations and presentations.

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October 2024

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W. Cassing, *Theoretical Physics Compact IV*
https://doi.org/10.1007/978-3-031-95518-1_1

1. Statistical Ensembles

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Statistical mechanics has the goal to calculate the macroscopic properties of systems with a lot of particles based on the microscopic structure of matter. The central point is the concept of the **statistical ensemble:** instead of describing the actual system one considers a large number of copies of this system, which all may be in different states, but fulfill the macroscopic conditions (e.g. constant total energy and/or particle number for a closed system). A statistical ensemble then is characterized by the probabilities, with which the individual states (often also called **micro-states**) are represented in the whole ensemble, that is characterized by the macroscopic conditions. Macroscopic properties, that imply a space-time average of an associated observable, then are understood as average values over the statistical ensemble. The concept of the statistical ensemble–together with the classical equations of motion–provides the framework for **classical statistical mechanics**.

The limits of classical statistical mechanics are reached, if the particles of the system to be examined must be described in terms of quantum theory (regardless of whether the system consists of many or only a few particles), which itself has a probabilistic character. Even with maximum information about the system, i.e. the knowledge of the wave function Ψ, we only get probabilistic information about an ensemble of systems, which are prepared in a similar and complete way. In this case we denote the system also by a **pure ensemble**. Often–especially in the case of many particles–we don’t know the state of the system completely, we only know that it is realized with certain probabilities p_m in the states $|\Psi_m\rangle$. (Example: probabilities for the two spin polarizations in a partially polarized beam of free electrons). Such a **mixed ensemble** is described by the **statistical operator** $\rho = \sum_m p_m |\Psi_m\rangle\langle\Psi_m|$, where $|\Psi_m\rangle$ denote the different micro-states. The expectation value of an observable A is obtained by first forming the matrix elements $\langle\Psi_m|A|\Psi_m\rangle$ (**quantum mechanical average**) and then summing up the values obtained with the weights p_m (**statistical average**). In this book we will, starting from quantum mechanics, formulate the quantum statistics and then derive the classical statistical mechanics and its particular results.

Statistical mechanics can be roughly divided into two areas: the treatment of **statistical equilibrium** $(\partial\rho/\partial t = 0)$ and the description of **non-equilibrium phenomena** $(\partial\rho/\partial t \neq 0)$, especially the transition into statistical equilibrium. The focus of this book will be on the treatment of statistical equilibrium and calculation of more concrete, macroscopic properties such as the specific heat or susceptibilities. Only towards the end of the book concepts of statistical mechanics for dynamical systems far from equilibrium are presented for weakly interacting particles.

The **statistical mechanics** provides–in comparison to the **phenomenological thermodynamics**–a significant advantage: thermodynamics delivers only relations between different macroscopic quantities, whereas the statistical mechanics allows for the calculation of macroscopic quantities directly from the underlying microscopic properties of the system under consideration.

W. Cassing, *Theoretical Physics Compact IV*
https://doi.org/10.1007/978-3-031-95518-1_2

2. Identical Particles

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In this chapter we first want to describe systems of identical particles, i.e. systems that e.g. only contain electrons, only nucleons or only ^4He atoms. More complicated systems, such as a mixture of gases, then can be built up in a straight forward manner.

2.1 Concept of Identical Particles

(a) Classical mechanics

For the basic comparison between the classical mechanics and quantum mechanics it is sufficient to look at two identical particles. We call two particles **identical**, if all observables A are symmetric with respect to particle exchange,

$$A_{cl.}(1,2) = A_{cl.}(2,1). \tag{2.1}$$

In the context of classical mechanics the two identical particles move on individual trajectories, which are clearly defined as long as we know the symmetric Hamiltonian function,

$$H_{cl.}(1,2) = H_{cl.}(2,1), \tag{2.2}$$

and the position and momentum of both particles at any time $t = t_0$. The equations of motion then uniquely provide the trajectories $\mathbf{r}_1(t)$ and $\mathbf{r}_2(t)$. Since they are identical particles it remains initially unclear, which particle is assigned to which trajectory. But this arbitrariness does not represent any difficulty: if at time t an assignment is made, this is retained in time; each particle moves on **its own** trajectory. In this sense identical particles in classical mechanics are **distinguishable**.

(b) Quantum mechanics

Since in quantum mechanics the concept of a trajectory–due to the disintegration of wave packets–gets lost, identical particles in quantum theory are **indistinguishable.** To examine the consequences of this fact, we note that–in analogy to classical mechanics–any observable of a system of identical particles must be symmetric with respect to particle exchange,

$$A(\xi_1, \xi_2) = A(\xi_2, \xi_1), \tag{2.3}$$

otherwise there would be the possibility of differentiation. Here ξ_1, ξ_2 stand for the coordinates of the particles under consideration, position, spin, isospin etc. This also applies to the Hamilton operator:

$$H(\xi_1, \xi_2) = H(\xi_2, \xi_1), \tag{2.4}$$

and with any solution $\Psi(\xi_1, \xi_2; t)$ of the Schrödinger equation,

$$\boxed{i\hbar \frac{\partial}{\partial t}\ \Psi(\xi_1, \xi_2; t) = H(\xi_1, \xi_2)\Psi(\xi_1, \xi_2; t),} \tag{2.5}$$

also $\Psi(\xi_2, \xi_1; t)$ is a solution of (2.5). For a system of identical particles–apart from degeneracies known from the single-particle problem–another degeneracy appears: the **exchange degeneracy**.

Example: For two independent, identical particles–moving in an oscillator potential–one particle may be in the 1 s—state, the other in the 1p—state. The wave functions

$$\Psi(\xi_1, \xi_2) = \varphi_{1s}(\xi_1)\varphi_{1p}(\xi_2) \tag{2.6}$$

and

$$\Psi(\xi_2, \xi_1) = \varphi_{1s}(\xi_2)\varphi_{1p}(\xi_1) \tag{2.7}$$

then are degenerate.

Since this exchange degeneracy cannot be clarified experimentally, it destroys the possibility for a unique description of a completely prepared system by a single Hilbert vector. In order to maintain this fundamental assumption of quantum theory, one must add another postulate in the case of identical particles, i.e. the **Pauli principle**:

> For a system of identical particles only such states can be realized, which are either totally symmetric or totally antisymmetric with respect to particle

exchange.

For the case of two identical particles this means, that as possible states only the combinations

$$\Psi_s(\xi_1,\xi_2) = \frac{1}{\sqrt{2}}(\Psi(\xi_1,\xi_2) + \Psi(\xi_2,\xi_1)) \tag{2.8}$$

for bosons and

$$\Psi_a(\xi_1,\xi_2) = \frac{1}{\sqrt{2}}(\Psi(\xi_1,\xi_2) - \Psi(\xi_2,\xi_1)) \tag{2.9}$$

for fermions are acceptable. Such a classification of the possible states of a system of identical particles in two classes–**bosons** and **fermions**–does not exist in classical mechanics!

The restriction expressed by the Pauli principle of separating the space of states to totally **symmetric** or totally **antisymmetric** states is compatible with the dynamics, i.e. a symmetric state remains symmetric for all times and an antisymmetric state remains antisymmetric. From (2.4) follows that

$$[H, P_{12}] = 0, \tag{2.10}$$

if P_{12} denotes the particle exchange operator. The eigenstates of H can therefore always be chosen to be also eigenstates of P_{12}: the equations

$$H(\xi_1,\xi_2)\Psi(\xi_1,\xi_2) = E\ \Psi(\xi_1,\xi_2) \tag{2.11}$$

$$P_{12}\Psi(\xi_1,\xi_2) = p\ \Psi(\xi_1,\xi_2) \tag{2.12}$$

can be solved simultaneously. Since twice permutation leads to the initial state

$$P_{12}^2\Psi(\xi_1,\xi_2) = P_{12}\Psi(\xi_2,\xi_1) = \Psi(\xi_1,\xi_2) \tag{2.13}$$

we get for the eigenvalues of P_{12}

$$p^2 = 1 \rightarrow p = \pm 1. \tag{2.14}$$

The eigenvalues $p = \pm 1$ of P_{12}, which correspond exactly to the only possible states according to the Pauli principle, are **good quantum numbers** due to (2.10), i.e. the Pauli principle is compatible with the dynamics of the system. Even by an external perturbation of the system in the form of a perturbation H' no transition between symmetric and antisymmetric states is possible, since

$$\langle \Psi_s | H' | \Psi_a \rangle = \langle \Psi_s | P_{12} H' | \Psi_a \rangle = \langle \Psi_s | H' P_{12} | \Psi_a \rangle = -\langle \Psi_s | H' | \Psi_a \rangle = 0, \tag{2.15}$$

and in analogy to (2.4) $H'(\xi_1, \xi_2) = H'(\xi_2, \xi_1)$ must hold. Thus the consistency of the Pauli principle and quantum theory is proven.

2.2 Statistics

The difference in the concept of identical particles in classical mechanics and quantum mechanics is not an academic one, but rather has severe consequences, which the following simple **example** shows explicitly: We consider a system of two identical particles that can only occupy two single-particle states: α, β. Then there are the following possibilities:

1. Classical particles

Here we can have

(1) both particles in the state α
(2) both particles in the state β
(3) one particle in α, the other in β.

Case (3) can be realized in two ways because the particles can be distinguished. Therefore the three possibilities–in the statistical average–have the following weights:

$$\begin{array}{lll} (1) & (2) & (3) \\ \frac{1}{4} & \frac{1}{4} & \frac{1}{2} \end{array} \tag{2.16}$$

2. Fermions

Here the options (1) and (2) are forbidden, thus the weight factors are:

$$\begin{array}{lll} (1) & (2) & (3) \\ 0 & 0 & 1 \end{array} \tag{2.17}$$

and case (3) is realized by the wave function
$\frac{1}{\sqrt{2}}(\varphi_\alpha(\xi_1)\varphi_\beta(\xi_2) - \varphi_\alpha(\xi_2)\varphi_\beta(\xi_1))$.

3. Bosons
Cases (1) and (2) are possible, but in contrast to classical statistics case (3) can only be realized in a single way, since the state must be symmetric. Thus the weight factors and wave functions are:

$$\begin{array}{lll} \frac{1}{3} & \varphi_\alpha(\xi_1)\varphi_\alpha(\xi_2) & (1) \\ \frac{1}{3} & \varphi_\beta(\xi_1)\varphi_\beta(\xi_2) & (2) \\ \frac{1}{3} & \frac{1}{\sqrt{2}}(\varphi_\alpha(\xi_1)\varphi_\beta(\xi_2) + \varphi_\beta(\xi_1)\varphi_\alpha(\xi_2)) & (3) \end{array} \tag{2.18}$$

2.3 Pauli Principle for *N* Identical Particles

In analogy to the case of two particles we require for *N* identical particles, that only such states are possible for which–for any selected particle pair (*i*, *j*)–either

$$\boxed{P_{ij}\Psi(\xi_1, \ldots, \xi_N) = +\Psi(\xi_1, \ldots, \xi_N)} \tag{2.19}$$

or

$$\boxed{P_{ij}\Psi(\xi_1, \ldots, \xi_N) = -\Psi(\xi_1, \ldots, \xi_N).} \tag{2.20}$$

This requirement is self-consistent: if for any pair of particles (*i*, *j*) holds $+(-)$, then also for every other pair of particles in the system under consideration. If for (1, 2) we have

$$P_{12}\Psi = +\Psi \tag{2.21}$$

then we get

$$P_{ij} = P_{1j}P_{2i}P_{12}P_{1j}P_{2i}, \tag{2.22}$$

such that

$$P_{ij}\Psi = P_{12}\Psi = +\Psi \tag{2.23}$$

regardless of whether P_{1j} and P_{2i} in the state Ψ have eigenvalue $+1$ or –1, since these operators in (2.22) each appear twice.

2.4 Composite Particles

All elementary particles–known so far–can be classified as bosons or fermions. Without exception, bosons have an integer spin, fermions have half-integer spin.

Examples: Fermions, e.g. electrons, protons, neutrons, neutrinos are spin 1/2 particles, whereas photons, pions, phonons ($\equiv$ lattice oscillations in crystals) are bosons. Atomic nuclei are bosons for an even number of nucleons, fermions for an odd number of nucleons, provided that an 'atomic nucleus' can be treated as a particle. This is the case in molecular and solid state physics. To prove these properties of atomic nuclei we consider two identical nuclei with each *Z* protons and *N* neutrons,–i.e. in total $2Z + 2N = 2A$ particles. Exchanging the two nuclei then implies exchanging the nucleons of one nucleus with those of the other, which involves in total *A* exchanges. Since the wave function Ψ changes the sign for every single exchange of two fermions,

$$\tilde{\Pi}_{12}\Psi = (-)^A\Psi, \tag{2.24}$$

if $\tilde{\Pi}_{12}$ is the operator of exchanging the two identical nuclei. The extension to more than two identical nuclei is trivial; we thus get: nuclei with an even number of nucleons behave like bosons (e.g. ^4He); nuclei with an odd number of nucleons behave like fermions (e.g. ^3He). These properties of composite particles will be of importance e.g. in the calculation of the specific heat of an ideal gas of diatomic molecules.

Part II
Fundamentals of Statistical Physics

W. Cassing, *Theoretical Physics Compact IV*
https://doi.org/10.1007/978-3-031-95518-1_3

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3. Concept of the Statistical Ensemble

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In this chapter we will discuss the difference between micro- and macro-states and introduce the statistical operator in quantum mechanics. Observables then are defined by matrix elements within the micro-states and by a statistical average over the ensemble. The differences to the classical density function will be pointed out explicitly.

3.1 Micro and Macro-States

A system of N identical particles is completely described, if its wave function $\Psi(\xi_1 ... \xi_N;t)$ is known; in classical physics the coordinates $q_i(t)$ and momenta $p_i(t)$ give a complete description. Such a completely determined state we call a **micro-state** in the following. It describes–within the framework of quantum theory–a **pure ensemble** (cf. quantum theory). For macroscopic dimensions $(N \sim 10^{23})$ such a complete description is impossible in practice. We can characterizee a macroscopic system practically only by macroscopic measurements such as the total energy E, volume V, temperature T, pressure P etc. Such a state, that is characterized by a few macroscopic quantities, we denote by **macro-state**. The same macro-state can generally be realized by a large number of micro-states.

Example: For three independent, similar oscillators a state with a given total energy $E = \hbar\omega(3/2 + 3) = 9/2\hbar\omega$ can be realized in various ways (see Fig. 3.1):

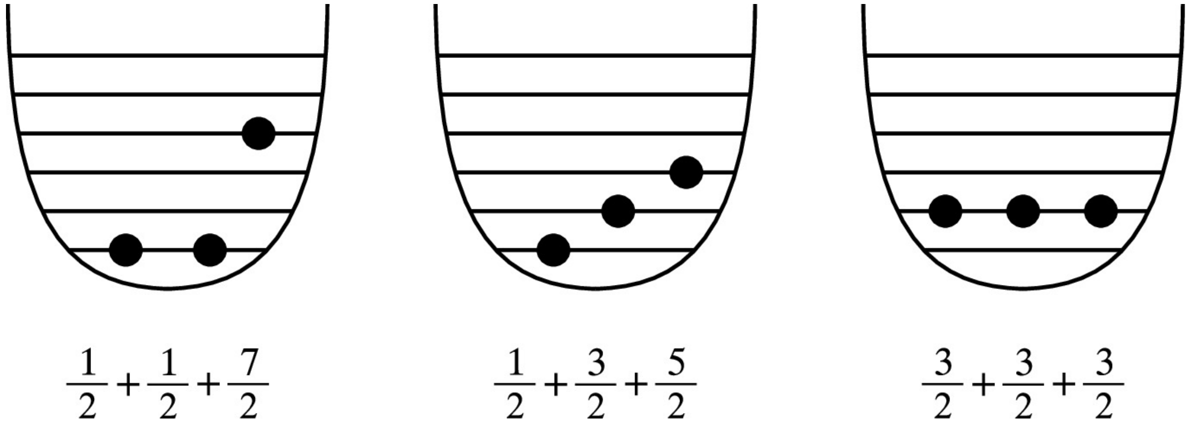

Fig. 3.1 Possible realizations for a macro-state with energy $9/2\hbar\omega$ and particle number 3 for identical oscillators

or:

three particles with spin 1/2 localized at different points in space (paramagnetic crystal); depending on the spin position $\vec{\sigma}$ relative to the direction of an external magnetic field $\mathbf{B}$, the magnetic moment can be $+\mu(-\mu)$. The state with total magnetic moment $-\mu$ can be realized in the following different ways (see Fig. 3.2). Obviously the number of possibilities increases drastically with N.

Fig. 3.2 Three particles with spin 1/2 localized at different points in space (paramagnetic crystal); depending on the spin position $\vec{\sigma}$ relative to the direction of an external magnetic field, the magnetic moment can be $+\mu(-\mu)$

To determine the macroscopic properties of a system of many identical particles one proceeds as follows in statistical mechanics: Instead of the actual system (e.g. a gas with N molecules), for which one wants to calculate certain macroscopic properties (e.g. the specific heat), one considers a large number of copies of this system, which all can be in different micro-states, that fulfill the macroscopically predetermined conditions (e.g. constant total energy for a closed system). Such a **statistical ensemble** is characterized by the distribution of the individual systems across the possible micro-states. In quantum theory one uses the **statistical operator** ρ (also the term **density operator** is common) (cf. quantum theory), in classical physics the density function $\rho_{cl.}$ is used to describe a statistical ensemble in the $6N$-dimensional phase space.

If one knows ρ or $\rho_{cl.}$, one can calculate macroscopic properties of the actual system by averaging over the statistical ensemble. As a measure for the reliability of such average values one can look for the corresponding mean-square fluctuations. It will be shown that the relative fluctuations decrease with increasing particle number N.

Note: The *N* particles of a system can interact with each other (e.g. the atoms or molecules of a real gas) or also not (ideal gas). In contrast, the concept of the statistical ensemble implies that the **individual systems** of the ensemble always are **independent** of each other.

3.2 The Statistical Operator

If $|\Psi_m\rangle$ are the possible micro-states and p_m the relative probabilities, that the entire system is in the state $|\Psi_m\rangle$, then the statistical operator ρ can be written as (cf. quantum theory)

$$\boxed{\rho = \sum_m p_m |\Psi_m\rangle\langle\Psi_m| \text{with } \sum_m p_m = 1. \qquad (3.1)}$$

In the Schrödinger picture $|\Psi_m\rangle$ and therefore ρ is time-dependent. Let us write the time evolution of $|\Psi_m\rangle$ as (with the time-evolution operator $U(t,t_0)$),

$$|\Psi_m(t)\rangle = U(t,t_0)|\Psi_m(t_0)\rangle, \tag{3.2}$$

then (cf. quantum theory)

$$\rho(t) = U(t,t_0)\rho(t_0)U^\dagger(t,t_0) \tag{3.3}$$

or, after differentiation with respect to time *t*,

$$\boxed{i\hbar\frac{\partial}{\partial t}\ \rho = [H,\rho]. \qquad (3.4)}$$

Important special cases:

1. Pure ensembles

If

$$\rho = |\Psi_m\rangle\langle\Psi_m| \tag{3.5}$$

for a single state $|\Psi_m\rangle$, we have a **pure ensemble** and the maximum possible information about the system. All systems of the ensemble are located definitely in the state $|\Psi_m\rangle$. In this case we get (with (3.5))

$$\rho^2 = \rho \tag{3.6}$$

if ρ–as assumed usually–is normalized,

$$Tr\{\rho\} = 1, \;\text{i. e.}\; \textstyle\sum_m p_m = 1. \tag{3.7}$$

2. Statistical equilibrium

Of particular interest in statistical mechanics is the case of **statistical equilibrium** defined by

$$\frac{\partial}{\partial t}\;\rho = 0. \tag{3.8}$$

It can be realized in two ways, i.e. by

$$\rho = \rho_0 \cdot 1 \tag{3.9}$$

or by

$$\boxed{\rho = \rho(Q)} \tag{3.10}$$

if Q is a conserved quantity; in particular

$$\boxed{\rho = \rho(H).} \tag{3.11}$$

With (3.4) the stationarity (3.8) follows from (3.9) or (3.10) directly. When discussing the practically important equilibrium ensembles we will come back to (3.9) or (3.10).

3.3 Statistical Averages

If we know the statistical operator ρ for a system for certain macroscopic conditions (e.g. fixed number of particles, constant pressure, ...), the average value of an observable A in the statistical ensemble is calculated as

$$\boxed{\begin{aligned}\langle A\rangle = Tr\{\rho A\} = \textstyle\sum_{i,m}\langle\Psi_i|\Psi_m\rangle\langle\Psi_m|A|\Psi_i\rangle p_m = \textstyle\sum_{i,m}\delta_{im}\; p_m\langle\Psi_m|A|\Psi_i\rangle \\ = \sum_m p_m\langle\Psi_m|A|\Psi_m\rangle = Tr\{A\rho\}.\end{aligned}} \tag{3.12}$$

Equation (3.12) shows that in the calculation of $\langle A\rangle$ except for the **statistical** averaging

(3.13)

$$\langle A \rangle = \sum_m p_m A_m$$

with

$$A_m = \langle \Psi_m | A | \Psi_m \rangle \tag{3.14}$$

another **quantum mechanical** averaging enters in the form of the expectation value (matrix element) (3.14).

To clarify the difference, let’s compare the statistical average (3.13) for the statistical ensemble described by (3.1) with the expectation value of A in the pure state

$$|\Psi(t)\rangle = \sum_m c_m(t) |\Phi_m\rangle, \tag{3.15}$$

i.e.

$$\langle \Psi | A | \Psi \rangle = \sum_{m,n} c_m^* c_n \langle \Phi_m | A | \Phi_n \rangle, \tag{3.16}$$

assuming that $|\Psi\rangle$ is normalized,

$$\sum_m |c_m|^2 = 1, \tag{3.17}$$

for orthonormal states $|\Phi_m\rangle$. In contrast to (3.13), where the p_m are real, positive numbers (as probabilities) the coefficients in (3.16) are complex in general; they depend on the phases of the coefficients $c_m(t)$.–The expectation value $\langle \Psi | A | \Psi \rangle$ of the observable A in total, of course, is real!–Only if the $|\Phi_m\rangle$ are eigenstates of A,

$$A|\Phi_m\rangle = a_m |\Phi_m\rangle, \tag{3.18}$$

Equation (3.16) achieves the form of a statistical average

$$\langle \Psi | A | \Psi \rangle = \sum_m |c_m|^2 a_m. \tag{3.19}$$

The form (3.19) for the expectation value of an observable A is the starting point for a statistical interpretation of quantum mechanics (see quantum theory).

In order to avoid misunderstandings, let’s stress again: a statistical (or mixed) ensemble ρ is described by the **real numbers** p_m, which are the specific probabilities, that the state $|\Psi_m\rangle$ is realized in the ensemble; on the other hand, a pure state $|\Psi\rangle$ is characterized by its **complex expansion coefficients** $c_m(t)$ in an orthonormal basis $|\Phi_m\rangle$. While in a pure state–due to phase relationships (given by the complex numbers $c_m(t)$)–an interference between the $|\Phi_m\rangle$ is possible (cf. (3.16)!), this is not possible for a **mixed ensemble** as shown by Eq. (3.12). In other words: a statistical ensemble is described by an **incoherent superposition** of states, a pure state by a **coherent superposition.**

The statistical average $\langle A\rangle$, of course, must be independent of the basis in which the trace (*Tr*) is taken. This is the case indeed: we expand $|\Psi_i\rangle$ in a complete orthonormal basis $|\Phi_\nu\rangle$,

$$|\Psi_i\rangle = \sum_\nu a_{i\nu}|\Phi_\nu\rangle, \tag{3.20}$$

and due to the unitarity of the matrix $a_{i\nu}$,

$$\boxed{\begin{aligned}\sum_i\langle\Psi_i|\rho A|\Psi_i\rangle &= \sum_{\mu\nu}\left(\sum_i a^*_{i\mu}a_{i\nu}\right)\langle\Phi_\mu|\rho A|\Phi_\nu\rangle \qquad (3.21)\\ &= \sum_{\mu\nu}\delta_{\mu\nu}\langle\Phi_\mu|\rho A|\Phi_\nu\rangle = \sum_\mu\langle\Phi_\mu|\rho A|\Phi_\mu\rangle.\end{aligned}}$$

For the stationary ensembles defined in (3.8) the statistical averages are (as expected) independent of time *t*, since–according to (3.8)–ρ does not depend on *t* in the statistical equilibrium. Observables are time-independent in the Schrödinger picture (see quantum mechanics) and the trace formation we can consider to be carried out in the basis of stationary states to the Hamilton operator *H* of the system.

3.4 The Classical Density Function ρ_{cl}

We now want to briefly describe the classical description of a statistical ensemble and clarify the analogy to quantum statistics.

A classical mechanical system is completely described by specifying the position and momentum coordinates of the particles as a function of time,

$$\{q_i(t), p_i(t)\};\ i = 1, \ldots, 3N. \tag{3.22}$$

In the 6*N*—dimensional space of the coordinates q_i, p_i (**phase space**) the *N* particle system for each point in time *t* is represented by a dot. The system moves in time–characterized by the point in phase space–according to the Hamilton equations of motion

$$\dot{p}_i = -\frac{\partial}{\partial q_i}\ H_{cl.};\dot{q}_i = \frac{\partial}{\partial p_i}\ H_{cl.} \tag{3.23}$$

with $H_{cl.} = H_{cl.}(q_i, p_i)$ as a Hamilton function, on a trajectory through the phase space (see Fig. 3.3).

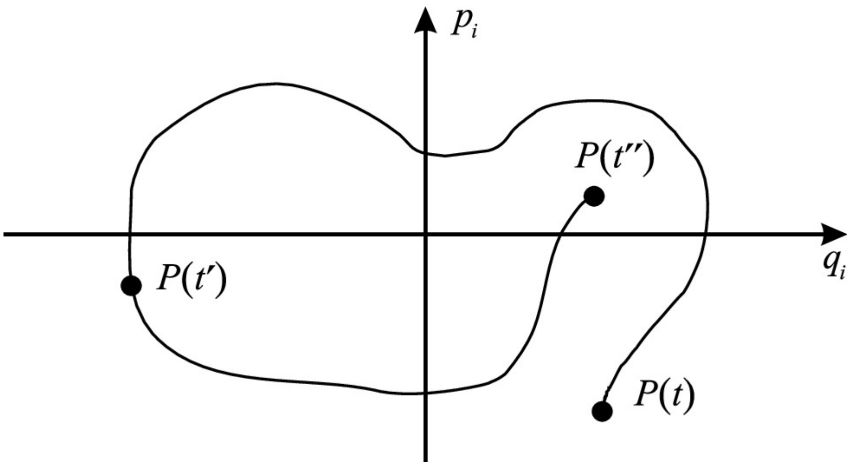

Fig. 3.3 Trajectory in phase space; $P(t) \equiv$ state of the system considered at time t

We then describe a statistical ensemble of systems using the density function $\rho_{cl.} = \rho_{cl.}(q_i, p_i; t)$ in phase space, which is the probability to find the phase point $\{q_i, p_i\}$ in the entire ensemble at time t (see Fig. 3.4).

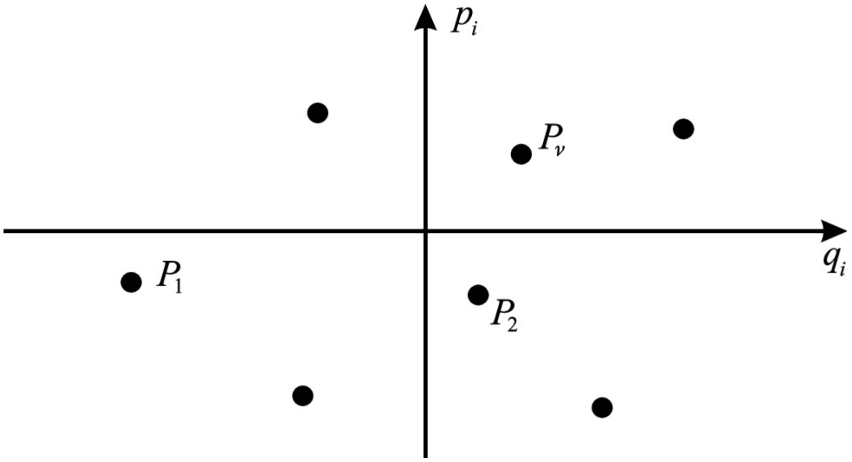

Fig. 3.4 Snapshot of an entire system in phase space for $M = 7$

Since the number of the systems in the ensemble M is fixed, we can normalize $\rho_{cl.}$ such that

$$\int \prod_{i=1}^{3N} dq_i dp_i \quad \rho_{cl.}(q_i, p_i; t) = 1. \tag{3.24}$$

We now examine the time evolution of $\rho_{cl.}$. Since the total number of systems of the ensemble is fixed, the number of phase points, that leave a certain volume in phase space per time, must be equal to the decrease in phase points in this volume. We formulate this **conservation law** (approximately in analogy to the conservation of charge) in the form of a continuity equation in $6N$ dimensions,

(3.25)

$$\frac{\partial}{\partial t}\ \rho_{cl.} + div(\rho_{cl.}\mathbf{v}_{cl.}) = 0,$$

with

$$\mathbf{v}_{cl.} =: (\dot{q}_i, \dot{p}_i), \tag{3.26}$$

$$div =: \left(\frac{\partial}{\partial q_i}, \frac{\partial}{\partial p_i}\right). \tag{3.27}$$

Equation (3.25) can be converted into a compact form, which clearly expresses the analogy between the classical distribution function $\rho_{cl.}$ and the statistical operator ρ. To this aim we transform to

$$div(\rho_{cl.}\mathbf{v}_{cl.}) = \sum_{i=1}^{3N}\left(\frac{\partial}{\partial q_i}\ (\rho_{cl.}\dot{q}_i) + \frac{\partial}{\partial p_i}\ (\rho_{cl.}\dot{p}_i)\right) \tag{3.28}$$

$$= \sum_i \left(\frac{\partial \rho_{cl.}}{\partial q_i}\dot{q}_i + \frac{\partial \rho_{cl.}}{\partial p_i}\dot{p}_i\right) + \sum_i \rho_{cl.}\left(\frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial \dot{q}_i}{\partial q_i}\right)$$

and note that the last term in (3.28) vanishes due to the Hamilton equations of motion. Equation (3.25) then reads

$$\frac{\partial}{\partial t}\rho_{cl.} + \sum_i \frac{\partial \rho_{cl.}}{\partial q_i}\dot{q}_i + \sum_i \frac{\partial \rho_{cl.}}{\partial p_i}\dot{p}_i = 0, \tag{3.29}$$

from which–with the help of (3.23) and the definition of the Poisson brackets–we obtain:

$$\frac{\partial}{\partial t}\rho_{cl.} = \{H_{cl.}, \rho_{cl.}\}. \tag{3.30}$$

Equation (3.30) corresponds to Eq. (3.4) and is denoted by the **Liouville equation**.

A classical statistical ensemble is in statistical equilibrium if

$$\frac{\partial}{\partial t}\rho_{cl.} = 0. \tag{3.31}$$

This case can be realized in two ways, i.e.:

(3.32)

$$\rho_{cl.}(q_i, p_i; t) = \text{const.}$$

or by

$$\boxed{\rho_{cl.} = \rho_{cl.}(Q_{cl.}), \tag{3.33}}$$

if $Q_{cl.}$ is a conserved quantity. In the case of (3.32) Eq. (3.31) is satisfied trivially; in case of (3.33) it follows for a conserved quantity $Q_{cl.}$

$$\tfrac{d}{dt} Q_{cl.} = \sum_i \left(\tfrac{\partial Q_{cl.}}{\partial q_i} \dot{q}_i + \tfrac{\partial Q_{cl.}}{\partial p_i} \dot{p}_i \right) = 0. \tag{3.34}$$

From (3.33) (together with (3.29)) we obtain:

$$\tfrac{\partial}{\partial t} \rho_{cl.} = -\tfrac{d\rho_{cl.}}{dQ_{cl.}} \sum_i \left(\tfrac{\partial Q_{cl.}}{\partial q_i} \dot{q}_i + \tfrac{\partial Q_{cl.}}{\partial p_i} \dot{p}_i \right) = 0, \;\; q.e.d. \tag{3.35}$$

With the normalization (3.24) we get as average value for an observable $A_{cl.}$ in an ensemble described by $\rho_{cl.}$

$$\boxed{\langle A_{cl.} \rangle = \int \prod_{i=1}^{3N} dq_i dp_i \quad \rho_{cl.}(q_i, p_i; t) A_{cl.}(q_i, p_i). \tag{3.36}}$$

3.5 Summary

The fundamental tasks of statistical mechanics are:

1. Determination of ρ or $\rho_{cl.}$ in dependence of the system considered with the respective macroscopic conditions. We will discuss this point for the case of statistical equilibrium in Chap. 5.

2. Calculation of macroscopic properties for known ρ or $\rho_{cl.}$.

For quantities that correspond to observables in quantum theory, represented by a self-adjoint operator, we use the method of averaging from Sect. 3.3. The internal energy U of a system e.g. we calculate as

$$U = Tr\{\rho H\}, \tag{3.37}$$

where H is the Hamiltonian of the system, or for the magnetization

$$\langle \overrightarrow{M} \rangle = Tr\{\rho \overrightarrow{\mu}\}. \tag{3.38}$$

The second class of macroscopic quantities are parameters such as volume, external fields (here we address macroscopic, classical fields), spatial position of the macroscopic system etc.; for such parameters we assume that they can be determined with arbitrary accuracy. The two most important parameters—volume, external fields—turn to parameters of the wave function; **examples**: normalization volume V, magnetic field $\mathbf{B}$. Finally, there are quantities in the context of thermodynamics, that are not found in classical mechanics but occur in quantum theory, e.g. **entropy** S, **temperature** T, **chemical potential** μ etc.

In summarizing this chapter we have discussed the difference between micro- and macro-states and introduced the statistical operator in quantum mechanics. Observables have been defined by matrix-elements within the micro-states and by a statistical average over the ensemble. The differences to the classical density function have been be pointed out and discussed in detail.

W. Cassing, *Theoretical Physics Compact IV*
https://doi.org/10.1007/978-3-031-95518-1_4

4. Statistical Definition of Entropy

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In this chapter we will introduce the entropy *S* as a measure for missing information. It will turn out that the entropy *S* can strictly be defined in quantum mechanics by the average of the negative logarithm of the statistical operator ρ. When restricting to the diagonal elements of the statistical operator in some approximate basis, it can be shown that the entropy increases in time, i.e. $S(t) \geq S(0)$ for $t > 0$. Furthermore, the difference between micro-reversibility and macro-irreversibility will be discussed and the general postulates of statistical mechanics be formulated.

4.1 Entropy as a Measure for Missing Information

Statistics are used when, despite incomplete information about a system of macroscopic dimension, one wants to make statements about macroscopic properties. It therefore makes sense to look for a quantitative measure for **information**.

About an object of our interest (e.g. the weather situation) we gain information in the form of **news** (wind strength, air temperature, etc.). If a message is less likely, the larger is the gain of information, if one actually receives this message. In particular a message, that is certainly expected, provides no information. If the probability to receive a message *i* is p_i $(0 \leq p_i \leq 1)$, then the information I (≥ 0), which we obtain by receiving the message *i*, will increase with decreasing p_i. **In formulae**:

$$I(p_i) = 0 \quad \text{if } \ p_i = 1 \tag{4.1}$$

and

$$I(p_i) \geq I(p_i') \quad \text{if } \ p_i \leq p_i'. \tag{4.2}$$

The concrete form of the function $I(p_i)$ results from the plausible assumption, that the **information is additive for independent messages**. If p_i, p_j are the probabilities of independent messages *i*, *j*, then the probability of receiving both messages is the product $p_i p_j$. The **additivity of information** then states

$$I(p_i p_j) = I(p_i) + I(p_j). \tag{4.3}$$

The solution of the Eqs. (4.1)–(4.3) is

$$I(p_i) = -C \ \ \ln \ \ p_i \tag{4.4}$$

with $C > 0$ as a constant and $0 \leq p_i \leq 1$.

After these preliminary remarks about the basics of information theory we consider a statistical ensemble, where the micro-states $|\Psi_i\rangle$ are realized with the probabilities p_i. If we perform a complete measurement on an arbitrarily selected system of the ensemble and find out that it is in the state $|\Psi_i\rangle$, then we gain an information proportional to $\ln \ \ p_i$; vice versa we can view $\ln \ \ p_i$ as a measure for our lack of information, if we do not carry out this measurement (which we neither can nor want to do in practice, see introduction). The **missing information** with respect to the system under consideration we then can **measure** by the statistical average

$$S = -k_B \sum_i p_i \ln \ \ p_i. \tag{4.5}$$

The quantity *S* introduced here will turn out to be the **entropy of the system**; k_B is the Boltzmann constant.

In the case of a pure ensemble in the state $|\Psi_m\rangle$,

$$p_i = 1 \ \text{if} \ i = m; \quad p_i = 0 \ \text{else}, \tag{4.6}$$

obviously $S = 0$. This is reasonable: if we already know for sure, that the system is in the state $|\Psi_m\rangle$, then a confirmation of this fact by a measurement gives no gain in information.

For the following considerations it is useful to express *S* by the statistical operator *ρ*. We claim that

$$S = -k_B Tr\{\rho \ \ \ln \ \ \rho\} = -k_B \ \langle \ln \ \ \rho \rangle. \tag{4.7}$$

Proof

$$Tr\{\rho \ \ \ln \ \ \rho\} = \sum_{i,m} \langle \Psi_i|\Psi_m\rangle\langle\Psi_m|\ln \ \ \rho|\Psi_i\rangle p_m = \sum_i p_i \langle\Psi_i|\ln \ \ \rho|\Psi_i\rangle = \sum_i p_i \ln \ \ p_i, \tag{4.8}$$

since the states $|\Psi_i\rangle$ are eigenstates to *ρ* with the eigenvalues p_i:

$$\rho|\Psi_i\rangle = \sum_m p_m |\Psi_m\rangle\langle\Psi_m|\Psi_i\rangle = \sum_m p_m |\Psi_m\rangle \delta_{mi} = p_i|\Psi_i\rangle. \tag{4.9}$$

According to (4.7) the **entropy** *S* **is the statistical average of the quantum operator** $-k_B \ln \ \ \rho$.

4.2 A Simple Example

Let three particles with spin $1/2\hbar$ be localized at different points in space; there is no interaction between the particles. Depending on the spin orientation there are magnetic moments $\pm\mu$ of a single particle in a constant homogeneous magnetic field B. Then $2^3 = 8$ micro-states are possible, whose properties are summarized in the table:

$$\begin{array}{ccc} \text{number of micro} - \text{states} & \text{total moment} & \text{total energy} \\ 1 & 3\mu & -3\mu B \\ 3 & \mu & -\mu B \\ 3 & -\mu & \mu B \\ 1 & -3\mu & 3\mu B \end{array} \quad . \tag{4.10}$$

We now want to calculate the entropy of the system according to (4.5) for the following cases:

1. If we have no further information about the system, all micro-states have the same probability (**least bias assumption**). Then

$$p_i = \tfrac{1}{8} \quad \forall i, \tag{4.11}$$

such that

$$S = -k_B \ln \ \tfrac{1}{8} = k_B \ln \ 8. \tag{4.12}$$

2. It is known that $E = \mu B$ for the total system; this can only be realized by 3 micro-states, which in turn have equal probability. Thus

$$p_i = \tfrac{1}{3};\ i = 1, 2, 3\ , \tag{4.13}$$

such that

$$S = -k_B \ln \ \tfrac{1}{3} = k_B \ln \ 3. \tag{4.14}$$

3. It is known that the total energy is $E = -3\ \mu B$; this situation can only be realized in a single way; thus we have a complete knowledge about the system. The entropy is

$$S = -k_B \ln \ 1 = 0 \tag{4.15}$$

as expected.

4.3 Temporal Change in Entropy

The definition of S by (4.5) shows that S is constant in time, since the numbers p_m (from the concept of a statistical ensemble) do not depend on t. If we want to interpret S as entropy, our theory so far is limited to reversible processes or the description of equilibrium states; **irreversible processes are associated with a change in entropy**. That we cannot describe irreversible processes within the framework of the previous theory is not surprising: the classical equations of motion for a closed system are invariant with respect to time reversal, i.e. for every solution $\{q_i(t), p_i(t)\}$ also $\{q_i(-t), -p_i(-t)\}$ are a possible solution of the equations of motion; a corresponding statement holds in quantum theory for the solutions of the Schrödinger equation (see Sect. 4.4). The Eqs. (3.4) and (3.30) for the temporal behavior of ρ or $\rho_{cl.}$ are a direct and exact consequence of the Schrödinger equation or the equations of motion, such that by the introduction of the statistical operator ρ (3.1) or the density function $\rho_{cl.}$ (3.24) the time reversal invariance is not destroyed! Our theory therefore has no place for irreversible processes in its current form.

We want to show in the following, how the previous concept **has to be extended to include irreversible processes.** If our identification of entropy and lack of information is correct, then the extended theory must include the possibility, that information is lost in time; this then will correspond to an **increase in entropy**. Thus we are looking for a **worse** theory than the previous one, which is based on the statistical operator ρ and in turn is **worse** than the exact description of a system by its wave function $|\Psi(\xi_1 \ldots \xi_N;t)\rangle$. If the knowledge of ρ–for building a statistical justification of thermodynamics–is too good, then it makes sense to assume, that only the **expectation value of the statistical operator in some basis** is known. To carry out this idea quantitatively we transform the spectral representation (cf. quantum theory) of the statistical operator (using the micro-states $|\Psi_i\rangle$),

$$\boxed{\rho = \textstyle\sum_i p_i |\Psi_i\rangle\langle\Psi_i|, \qquad (4.16)}$$

to a representation in a fixed, orthonormalized and complete basis $|\Phi_\alpha\rangle$, in which ρ is no longer diagonal:

$$\boxed{\rho = \textstyle\sum_{\alpha\beta} \rho_{\alpha\beta} |\Phi_\alpha\rangle\langle\Phi_\beta|. \qquad (4.17)}$$

The coefficients $\rho_{\alpha\beta}$ then are the matrix elements of ρ in the basis $|\Phi_\alpha\rangle$,

$$\rho_{\alpha\beta} = \langle\Phi_\alpha|\rho|\Phi_\beta\rangle. \qquad (4.18)$$

If we **only** have knowledge about the diagonal elements in the basis $|\Phi_\alpha\rangle$. i.e. $\rho_{\alpha\alpha}$, this is obviously less knowledge than that provided by (4.16).

We now want to investigate the time evolution of the coefficients $\rho_{\alpha\beta}$ which, in contrast to the p_i, generally depend on t. We go back to (3.4) and form the matrix elements in the basis $|\Phi_\alpha\rangle$:

$$i\hbar \frac{\partial}{\partial t}\ \rho_{\alpha\beta} = \textstyle\sum_\gamma (H_{\alpha\gamma}\rho_{\gamma\beta} - \rho_{\alpha\gamma}H_{\gamma\beta}) \qquad (4.19)$$

with

$$H_{\alpha\gamma} =: \langle\Phi_\alpha|H|\Phi_\gamma\rangle. \qquad (4.20)$$

Here the completeness relation was used:

$$\textstyle\sum_\gamma |\Phi_\gamma\rangle\langle\Phi_\gamma| = 1_{\mathscr{H}}, \qquad (4.21)$$

where $1_{\mathscr{H}}$ denotes the identity in the Hilbert space. Alternatively, we can use (3.3) and find the formal solution from (4.19)

$$\rho_{\alpha\beta}(t) = \sum_{\gamma\delta} U_{\alpha\gamma}(t)\rho_{\gamma\delta}(0)U^*_{\beta\delta}(t) \tag{4.22}$$

with

$$U_{\alpha\gamma}(t) =: \langle\Phi_\alpha|U(t,0)|\Phi_\gamma\rangle. \tag{4.23}$$

Since (4.19) and (4.22) are exact transformations of (3.3) and (3.4), we have lost no information compared to (3.3) or (3.4); the entropy S calculated with (4.22) is still constant in time.

Note: In general we have

$$\sum_\alpha (\rho \ \ \ln \ \ \rho)_{\alpha\alpha} \neq \sum_\alpha \rho_{\alpha\alpha} \ln \ \ (\rho_{\alpha\alpha}) \tag{4.24}$$

with the exception that ρ is diagonal in the basis $|\Phi_\alpha\rangle$.

We now want to consider the case, that the statistical ensemble is not defined by the eigenvalues p_i of ρ, but only by the diagonal elements of ρ in the basis $|\Phi_\alpha\rangle$. It will turn out that **this reduced information is not constant in time, but decreases with time** t. To calculate the time evolution of the diagonal elements we use (cf. (4.19) or (4.22))

$$i\hbar\frac{\partial}{\partial t}\rho_{\alpha\alpha}(t) = \sum_\gamma (H_{\alpha\gamma}\rho_{\gamma\alpha}(t) - \rho_{\alpha\gamma}(t)H_{\gamma\alpha}) \tag{4.25}$$

or

$$\rho_{\alpha\alpha}(t) = \sum_{\gamma\delta} U_{\alpha\gamma}(t)\rho_{\gamma\delta}(0)U^*_{\alpha\delta}(t) = \sum_\gamma |U_{\alpha\gamma}|^2 \rho_{\gamma\gamma}(0) + \sum_{\gamma\neq\delta} U_{\alpha\gamma}(t)\rho_{\gamma\delta}(0)U^*_{\alpha\delta}(t). \tag{4.26}$$

Obviously, the knowledge of $\rho_{\alpha\alpha}(0)$ is not sufficient as initial information to determine $\rho_{\alpha\alpha}(t)$ exactly in time. A theory that only employs the diagonal elements of ρ has to introduce approximations with respect to the off-diagonal elements.

In statistical mechanics, the assumption is made ad hoc that due to statistically distributed phases the effect of the off-diagonal elements is averaged out in (4.25) or (4.26).

This assumption has the character of a fundamental **postulate** and can only be confirmed by experiment or be refused. As starting information one uses the approximation

$$\rho_{\alpha\beta}(0) = P_\alpha(0)\delta_{\alpha\beta} \tag{4.27}$$

and then formally obtains $P_\alpha(t)$ from

$$P_\alpha(t) = \sum_\gamma |U_{\alpha\gamma}(t)|^2 P_\gamma(0). \tag{4.28}$$

The quantities $P_\alpha(t)$ determine approximately the probabilities to find the systems of the statistical ensemble in the states $|\Phi_\alpha\rangle$ at time *t*. This leads to the missing information

$$S(t) = -k_b \sum_\alpha P_\alpha(t) \ln \; P_\alpha(t), \tag{4.29}$$

which depends on time. We now want to show that–using the approximation (4.28)–that *S*(*t*) actually increases with *t*. To this aim we use the inequality

$$x \;\ln\; x - x \;\ln\; y - x + y \geq 0 \tag{4.30}$$

for real, non-negative *x*, *y*, which is based on the fact that ln x is a monotonically increasing function. For our problem we have

$$P_\gamma(0) \ln \; P_\gamma(0) - P_\gamma(0) \ln \; P_\alpha(t) - P_\gamma(0) + P_\alpha(t) \geq 0. \tag{4.31}$$

We multiply Eq. (4.31) by $|U_{\alpha\gamma}(t)|^2$, sum over α, γ and note

$$\sum_\alpha U^*_{\alpha\mu} U_{\alpha\nu} = \sum_\alpha U_{\mu\alpha} U_{\alpha\nu} = \delta_{\mu\nu} \tag{4.32}$$

as a result of the unitarity of the time evolution operator. Using in the 2. term of (4.31)–after carrying out the operations above in the fundamental Eq. (4.28)–we obtain directly:

$$\sum_\gamma P_\gamma(0) \ln \; P_\gamma(0) - \sum_\alpha P_\alpha(t) \ln \; P_\alpha(t) - \sum_\gamma P_\gamma(0) + \sum_\alpha P_\alpha(t) \geq 0. \tag{4.33}$$

Since the normalization of the probabilities requires

$$\sum_\gamma P_\gamma(0) = \sum_\alpha P_\alpha(t), \tag{4.34}$$

we get

$$\sum_\gamma P_\gamma(0) \ln \; P_\gamma(0) \geq \sum_\alpha P_\alpha(t) \ln \; P_\alpha(t); \tag{4.35}$$

thus with (4.29)

$$S(0) \leq S(t). \tag{4.36}$$

This provides the framework for the **statistical mechanics of irreversible processes**.

After having formally clarified the possibility of decreasing information in time (increase of entropy), the question about the physical background comes up. Why is our information so bad in practice such that irreversible processes can occur? We point out the following reasons:

1. Closed systems cannot be realised in practice in the strict sense, since some (albeit small) interaction W with the environment is unavoidable. Such an interaction is even necessary in the case of **thermal contact**! Although we never know this interaction exactly, we know the Hamiltonian of the system only approximate; that's why the micro-states are only defined approximately. **In the basis of the approximate micro-states the full statistical operator is not diagonal!** The knowledge of the probability distribution of the systems of the ensemble in the approximate micro-states at time $t = 0$–as proven above–gets lost in time.

2. Even with the complete knowledge of the Hamiltonian we must expect, that every measurement is subject to inaccuracies, such that we can never know the statistical operator ρ exactly. Apart from practical reasons (which we could eliminate in the thought experiment) fundamental principles of quantum theory are responsible for this: the fact that in quantum theory the detection device influences the measured object, and especially that the exact determination of the energy of a system would take a $\infty-$ long time according to the uncertainty principle. These errors due to inaccuracies of measurements–regarding the determination of ρ–grow according to the general considerations above in time: our information deteriorates, i.e. the entropy increases.

4.4 Micro-Reversibility and Macro-Irreversibility

First of all, the **micro-reversibility** mentioned above needs to be formulated more precisely. For closed systems the equations of motion

$$m_i \tfrac{d^2}{dt^2} \ \mathbf{q}_i = \mathbf{F}_i \tag{4.37}$$

are **invariant** with respect to the operation

$$t \to t' = -t. \tag{4.38}$$

Thus if $\mathbf{q}_i(t)$, $\mathbf{p}_i(t)$ is a solution of (4.37), then also the set $\mathbf{q}_i(-t)$, $-\mathbf{p}_i(-t)$, which emerge from the former by the operation (4.38). Time reversal means that the orbits are passed in opposite directions.

In quantum theory, the equations of motion (4.37) are replaced by the Schrödinger equation

$$i\hbar \tfrac{\partial}{\partial t} \ \Psi(\xi_1 \ldots \xi_N; t) = H \ \Psi(\xi_1 \ldots \xi_N; t). \tag{4.39}$$

For simplicity we assume particles without spin, such that the coordinates ξ_i correspond to the position coordinates of the particles. The correspondence between classical observables and observables in quantum theory now requires that, when reversing the time, the position coordinates $\mathbf{r}_i$ and the momenta $\mathbf{p}_i$ transform according to

$$\mathbf{r}_i \to \mathbf{r}_i; \quad \mathbf{p}_i \to -\mathbf{p}_i. \tag{4.40}$$

Since the Hamilton operator H for a closed system only depends on the $\mathbf{r}_i$ and the $\mathbf{p}_i$ (squared!), but not on t, H is invariant under time reversal. If we transform the Schrödinger Eq. (4.39) by the operation (4.38) we get

(4.41)

$$-i\hbar\frac{\partial}{\partial t'}\ \Psi(\mathbf{r}_1\ldots\mathbf{r}_N;t') = H\ \Psi(\mathbf{r}_1\ldots\mathbf{r}_N;t');$$

and obtain after complex conjugation,

$$i\hbar\frac{\partial}{\partial t'}\ \Psi^*(\mathbf{r}_1\ldots\mathbf{r}_N;t') = H\ \Psi^*(\mathbf{r}_1\ldots\mathbf{r}_N;t'), \tag{4.42}$$

the Schrödinger equation for the functions $\Psi^*(\mathbf{r}_1\ldots\mathbf{r}_N;t')$. Thus, if Ψ is a solution of (4.39) in the t system, then Ψ^* is a solution in the t' system.

Example: plane wave in $+\mathbf{k}$ or $-\mathbf{k}$ direction.

The statement proven above (which in analogy is valid for particles with spin), that for every motion sequence, that results from the equations of motion or the Schrödinger equation, the time-reversed motion sequence is also possible. This is called **micro-reversibility**. At first glance this seems to contradict the **macro-irreversibility** formulated in Eq. (4.36), by which a time direction is preferred. The apparent contradiction between micro-reversibility and macro-irreversibility, however, can be solved by considering the following points:

1. The quantity S was introduced as a statistical average. The statement (4.36) therefore only has the character of a **probability statement**: The most probable time evolution of a macroscopic system (in the absence of external fields) is characterized by an increase in $S(t)$; nevertheless, processes are possible in which $S(t)$ decreases, since S is subject to statistical fluctuations.

2. Micro-reversibility is a statement about pure states and requires the exact knowledge of the Hamilton operator and the initial conditions. Macro-irreversibility is a statement about the behavior of a system, which we only know incompletely and whose properties we use as average values of a statistical ensemble. Both statements are therefore related to different situations.

To illustrate points (1.) and (2.), we consider the following **example**: A given container is divides into two equal parts separated by a wall; there is a small hole in the wall (see Fig. 4.1), which can be closed with a slider. The initial situation is characterized by a gas with the pressure P_I in area I, while area II is empty. If the slider is opened, the pressure in area I decreases and increases in area II until statistical equilibrium has been established with $P_I = P_{II}$. The final situation is different from the initial situation because our information has become less precise, the entropy according to (4.36) has increased. This does not exclude that in the course of pressure equilibration–for a short time–more gas molecules fly from II back to I than vice versa due to statistical fluctuations! The reversed process, starting from $P_I = P_{II} \neq 0$ to $P_{II} = 0$, $P_I \neq 0$ is possible in principle, but extremely unlikely since it is practically impossible to determine the positions and momenta of N gas molecules—in the sense of an initial condition for solving the equations of motion—to be adjusted such that there is a pressure difference between areas I and II and in the final state area II is empty.

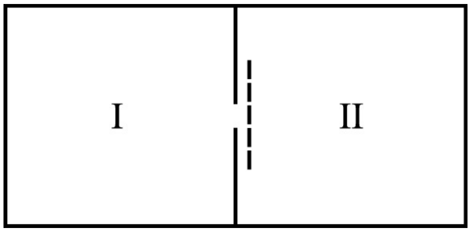

Fig. 4.1 Illustration of a container, which is divided into two equal parts by a wall with a small hole

This example shows that irreversibility is closely linked to the existence of many particles: For example, for $N = 2$ the process of **pressure equalization** is just as easy to prepare for both initial conditions (see Fig. 4.2).

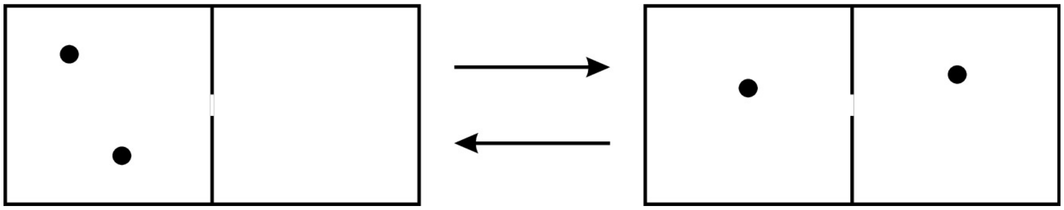

Fig. 4.2 For a few particles the process of pressure equilibration is just as easy to prepare as the reversed process

3. Finally, it should be noted that quantum theory—regardless of the time-reversal invariance of the Schrödinger equation—implicitly does not contain the equivalence of the two time directions. This non-equivalence can be shown in connection with the fundamental process of the interaction of a quantum mechanical system (e.g.. *H* atom) with a classical system (e.g. detector for excitation energies). If two such processes *A* and *B* take place one after the other (example: collisions of gas molecules with the walls of the container), the two time directions are no longer equivalent: the claim that the probability of a certain result for process *B*, which is influenced by the result of the process *A*, is only correct if *A* takes place before *B*. This is probably the key to a deeper understanding of the increase in entropy in the absence of external **organizing** fields.

4.5 The Postulates of Statistical Mechanics

The concept of a statistical ensemble and the definition of entropy (as lack of information) provide a sufficient basis for statistical mechanics, including the possibility of irreversible processes. However, this framework is only of practical use if (for a system of *N* particles with given macroscopic conditions) one can specify the probabilities, with which the members of the statistical ensemble are distributed with respect to the micro-states $|\Psi_m\rangle$. Since the knowledge of a few macroscopic data in general not clearly determines the statistical ensemble, we have to introduce **postulates** into the theory, that allow for a determination of the probabilities mentioned above. We will try to do this within the framework of the **principle of least bias** to exploit all available information about the system: **The whole truth, and nothing but the truth.** The available macroscopic information we can employ in the form of statistical averages

$$\langle R_i \rangle = r_i, \;\; i = 1, 2, 3, \ldots, n. \tag{4.43}$$

Here, Eq. (4.43) includes both the average values of observables $\langle A\rangle$ as well as their average quadratic fluctuations $\langle\Delta A^2\rangle$.

We now introduce the fundamental postulates of statistical mechanics:

Postulate I

All states $|\Phi_\alpha\rangle$ of a complete, orthonormalized basis have the same 'a priori' probability.

This implies that quantum theory has no tendency to **prefer** certain states (e.g. those that are energetically close to each other) compared to others (that are less energetically close). Differences in the probability distributions only emerge by macroscopic conditions imposed on the system. Postulate I in particular implies **total ignorance** about the state of the system; all micro-states are represented with equal probability in the ensemble.

In classical physics, postulate I can be formulated in such a way that the same volumes in phase space have the same 'a priori' probabilities.

Since the available macroscopic information in general does not determine the statistical operator ρ sufficiently, we need a criterion that distinguishes between different $\rho' s$, which all satisfy the macroscopic conditions, in order to make a selection. As a criterion we use the missing information S: If for two statistical operators $\rho_1 \neq \rho_2$, which both satisfy the macroscopic conditions, $S_1 > S_2$ holds, then ρ_2 contains additional information compared to ρ_1, which is not secured by measurement. Thus we favor ρ_1 for making the theory as good as possible by keeping it free from arbitrary (not controlled) assumptions. This results in

Postulate II

To the physical system under consideration we assign the statistical operator ρ, that satisfies the macroscopic conditions and maximizes the missing information (entropy).

In summarizing this chapter we have introduced the entropy S as a measure for missing information. The latter could strictly be defined in quantum mechanics by the average of the negative logarithm of the statistical operator. When restricting to the diagonal elements of the statistical operator in some approximate basis, it was shown that the entropy increases in time, i.e. $S(t) \geq S(0)$ for $t > 0$ or our information about a system decreases in time. Furthermore, the difference between micro-reversibility and macro-irreversibility has been discussed and the general postulates of statistical mechanics been formulated.

We now want to use postulates I and II to investigate the statistical ensembles in equilibrium for different macroscopic conditions.

W. Cassing, *Theoretical Physics Compact IV*
https://doi.org/10.1007/978-3-031-95518-1_5

5. Statistical Ensembles in Equilibrium

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In this chapter we will investigate different statistical ensembles, that are characterized by the knowledge of the energy E, the particle number N and the volume V. If these quantities are only known on average some Lagrange parameters have to be introduced, which later will be related to the temperature, the chemical potential and the pressure.

5.1 The Uniform Ensemble

It is defined by (ρ_0 = const.)

$$\rho = \rho_0 \cdot 1 \tag{5.1}$$

or

$$\rho_{\alpha\beta} = \rho_0 \delta_{\alpha\beta} \tag{5.2}$$

and according to Sect. 4.2 is in statistical equilibrium. Equations (5.1) or (5.2) correspond to the case of **total ignorance** (here **ignorance** refers to the state of the system, not the properties of the particles): all states are equally likely. Obviously

$$S = \text{ const;} \tag{5.3}$$

A total ignorance cannot increase in time. Fortunately this case is very rare; the following case is met more often.

5.2 The Microcanonical Ensemble

About an isolated system we know that it has sharp energy E, precise volume V and sharp particle number N; we denote the micro-states by $|\Psi_i\rangle;i = 1, 2, \ldots z_m$, that are compatible with E, V and N. Then the statistical operator has the form

$$\rho = \sum_{i=1}^{z_m} p_i |\Psi_i\rangle\langle\Psi_i| \tag{5.4}$$

and the task remains to find the coefficients p_i. To this aim we use the principle (see Sect. 4.5) that the missing information should be maximum. Therefore the variational problem

$$\delta S = 0 \tag{5.5}$$

with the constraint

$$Tr(\rho) - 1 = 0, \tag{5.6}$$

the normalization of ρ, has to be solved. Equations (5.5) and (5.6) are equivalent to

$$\boxed{\delta(S - \lambda[Tr(\rho) - 1]) = 0; \tag{5.7}}$$

one has vary with respect to the p_i while λ is a constant (Lagrange parameter) to be determined later. With ρ from (5.4) we get

$$Tr(\rho) = \sum_k \langle\Psi_k|\rho|\Psi_k\rangle = \sum_k \langle\Psi_k| \sum_{i=1}^{z_m} p_i|\Psi_i\rangle\langle\Psi_i|\Psi_k\rangle = \sum_{i=1}^{z_m} p_i \tag{5.8}$$

and

$$S = -k_B \sum_{i=1}^{z_m} p_i \ln \ p_i. \tag{5.9}$$

Then (5.7) reads:

$$\frac{\partial}{\partial p_j}(k_B \sum_i p_i \ln \ p_i + \lambda \sum_i p_i - \lambda) = k_B \ln \ p_j + k_B + \lambda = 0. \tag{5.10}$$

The solution is

$$\boxed{\ln \ p_j = -\frac{\lambda}{k_B} - 1 = \ \text{const} \tag{5.11}}$$

and the p_j itself is a constant.

The still free quantity λ now can be determined such that the normalization (5.6) is satisfied; this gives:

$$\boxed{p_j = \frac{1}{z_m} \ \rightarrow \sum_{j=1}^{z_m} p_j = 1. \tag{5.12}}$$

The result implies an equal distribution in the possible micro-states in accordance with the principle of equal ‘a priori’ probabilities (see Sect. 4.5). For the entropy S we get

$$\boxed{S = -k_B \sum_i^{z_m} \frac{1}{z_m} \ln \left(\frac{1}{z_m}\right) = k_B \ln \left(z_m\right) \sum_i^{z_m} \frac{1}{z_m} = k_B \ln \left(z_m\right). \tag{5.13}}$$

Equation (5.13) is often used as a definition of entropy, where z_m is nothing else than the number of possible realizations of the macro-state. However, it should have become clear that S from (5.13) refers to the case of statistical equilibrium; as a general definition for the entropy (5.13) is too narrow because it does not cover irreversible processes.

The quantity Z_m, defined by

$$Z_m = \sum_{j=1}^{z_m} 1 = Tr(\Pi(E,V,N)), \tag{5.14}$$

is also denoted as **microcanonical partition function**. In (5.14) $\Pi(E,V,N)$ denotes the projector on the subspace of states that have given sharp *E*, *V*, *N*. According to (5.13), *S* also becomes a function (via Z_m) of *E*, *V*, *N* :

$$S = S(E,V,N). \tag{5.15}$$

Since exact energy measurements are practically impossible within a finite time interval due to the uncertainty relation, it is useful to define a **softened** microcanonical ensemble. We replace (5.12) by

$$p_j = \frac{1}{z_m}\text{if } E-\delta E < E_j < E+\delta E \tag{5.16}$$

$$p_j = 0\text{else},$$

where z_m is the number of micro-states lying between $E-\delta E$ and $E+\delta E$. Here δE has to be chosen larger than the experimental energy uncertainty, but small compared to the total energy *E*.

5.3 The Canonical Ensemble

In contrast to Sect. 5.2 we no longer require, that all systems have the same constant energy *E*, but only prescribe the internal energy *U* as an average:

$$U = Tr(\rho H) = \text{ const.} \tag{5.17}$$

This corresponds to the situation that often occurs in practice, since the system under consideration has a weak interaction *W* with its environment. Then the energy of the system is no exact constant of motion; this comes about since by interactions with the environment the internal energy is subject to fluctuations. We can account for this situation by incorporating the condition (5.17) in the calculation of the statistical equilibrium. In the statistical equilibrium ρ has the general form

$$\rho = \sum_i p_i |\Psi_i\rangle\langle\Psi_i| \tag{5.18}$$

with

$$H|\Psi_i\rangle = E_i|\Psi_i\rangle. \tag{5.19}$$

Our task now is to calculate the numbers p_i in (5.18).

To this aim we use postulate II: We solve the variational problem

$$\delta S = 0 \tag{5.20}$$

with

$$S = -k_B \; Tr(\rho \;\; \ln \;\; \rho) \tag{5.21}$$

and the two constraints

$$Tr(\rho) - 1 = 0 \tag{5.22}$$

and

$$Tr(\rho H) - U = 0. \tag{5.23}$$

This leads to:

$$\delta(-k_B \sum_i p_i \ln \;\; p_i - k_B \beta(\sum_i p_i E_i - U) - \lambda(\sum_i p_i - 1)) = 0, \tag{5.24}$$

where β and λ are Lagrange parameters and $\sum_i$ is to extend over all states $|\Psi_i\rangle$ that have the same volume *V* and fixed particle number *N*. Variation of the p_i gives (in analogy to case 2):

$$\ln \;\; p_j = -\beta E_j - \frac{\lambda}{k_B} - 1, \tag{5.25}$$

such that

$$p_j = \text{const} \; \cdot \exp\,(-\beta \mathrm{E_j}). \tag{5.26}$$

The λ parameter has to be chosen such that $\sum_j p_j = 1$, i.e.

$$p_j = \frac{1}{Z_c} \exp\,(-\beta E_j), \tag{5.27}$$

where Z_c is the **canonical partition function**:

$$Z_c = \sum_i \exp\,(-\beta E_i). \tag{5.28}$$

With the help of Z_c we can now express *U* and *S*:

$$U = \sum_i p_i E_i = \frac{1}{Z_c} \sum_i E_i \exp\left(-\beta E_i\right) = -\frac{\partial}{\partial \beta} \ln Z_c \tag{5.29}$$

and (with $\ln p_m = -\ln Z_c - \beta E_m$)

$$S = -k_B \sum_m p_m \ln p_m = k_B \sum_m p_m (\ln Z_c + \beta E_m) = k_B \ln Z_c + k_B \beta \sum_m p_m E_m \tag{5.30}$$

$$= k_B(\ln Z_c + \beta U) = k_B\left(\ln Z_c - \beta \frac{\partial}{\partial \beta} \ln Z_c\right).$$

We will come back to these relationships in Chap. 7, where we will consider the connection between thermodynamics and statistical mechanics. This will show that β is directly connected with the temperature *T* via $T \sim 1/\beta$.

As another practically important equilibrium ensemble we discuss the grand-canonical ensemble.

5.4 Grand-Canonical Ensemble

We want to investigate a system, that not only exchanges energy with the environment (as in case 3), but also particles.

Example: Equilibrium of gas and liquid phases of a particular substance. We describe this case by prescribing in addition to the energy also the number of particles only as a statistical average, i.e.

$$Tr(\rho H) = U \tag{5.31}$$

as well as

$$Tr(\rho \hat{N}) = N, \tag{5.32}$$

where $\hat{N}$ is the particle number operator. The general formula for ρ is now to sum over all states, which belong to fixed volume *V*, i.e. over all possible energies and particle numbers.

In analogy to the procedure in Sect. 5.3 we get

$$p_i = \text{const}\cdot \exp\left(-\beta \mathrm{E_i} - \alpha \mathrm{N_i}\right) \tag{5.33}$$

where α is another Lagrange parameter and N_i is the particle number in the state $|\Psi_i\rangle$. The constant is again determined by $\sum_i p_i = 1$; with

$$Z_g = \sum_i \exp\left(-\beta E_i - \alpha N_i\right) \tag{5.34}$$

as the **grand-canonical partition function** the p_i become

$$p_i = \frac{1}{Z_g} \exp\left(-\beta E_i - \alpha N_i\right). \tag{5.35}$$

The fundamental quantities *U*, *S*, *N* can be calculated in analogy to chapter to 5.3 and be expressed by Z_g:

$$U = -\frac{\partial}{\partial \beta} \ \ln \ Z_g \tag{5.36}$$

$$N = -\frac{\partial}{\partial \alpha} \ \ln \ Z_g \tag{5.37}$$

as well as

$$S = k_B\left(\ln \ Z_g - \beta\frac{\partial}{\partial \beta} \ \ln \ Z_g - \alpha\frac{\partial}{\partial \alpha} \ \ln \ Z_g\right) = k_B(\ln \ Z_g + \beta U + \alpha N). \tag{5.38}$$

5.5 The General Case

In general *ρ* can depend on all conserved quantities of the system for the case of statistical equilibrium (see Sect. 3.2): energy, momentum, angular momentum and particle number; directly linked to the particle number is the total charge, which we thus do not have to list separately. Since the systems–we are interested in–all are spatially localized (example: gas in a macroscopic container), the momentum is omitted as a conserved quantity of the system (= gas without container). For a system in a perfectly spherical container the angular momentum is a constant of the motion. But in practice macroscopic containers never meet this requirement sufficiently well such that also the angular momentum is omitted as a conserved quantity. The remaining conserved quantities are energy and particle number; strictly speaking, they are in practice also no conserved quantities, since the interaction between the system and the environment never exactly disappears (e.g. interaction of the gas molecules with the walls of the container). Nevertheless, the microcanonical ensemble—the case of the isolated system—is a useful idealization. The canonical ensemble is more realistic, where only the conservation of the average value of the energy is required, and the grand canonical ensemble, where the energy and number of particles are only conserved on average. Other models are conceivable in which e.g. the mean-square fluctuation of energy and/or particle number is fixed.

5.6 Additions

Below we present some useful formulae for the practical use of the canonical and grand-canonical ensembles:

1. ρ as a function of H and $\hat{N}$

According to (5.18) and (5.27) we have

$$\rho_c = \sum_i p_i|\Psi_i\rangle\langle\Psi_i| = \frac{\exp(-\beta H)}{Tr(\exp(-\beta H))}, \tag{5.39}$$

since

$$\sum_i \exp\,(-\beta E_i)|\Psi_i\rangle\langle\Psi_i| = \exp\,(-\beta H)\sum_i |\Psi_i\rangle\langle\Psi_i|. \tag{5.40}$$

For the grand-canonical ensemble we get accordingly

$$\rho_g = \frac{\exp(-\beta H - \alpha\hat{N})}{Tr(\exp(-\beta H - \alpha\hat{N}))}. \tag{5.41}$$

2. Averages

In the canonical ensemble, a statistical average has the general form

$$\langle A\rangle_c = \frac{Tr(A\ \exp(-\beta H))}{Tr(\exp(-\beta H))}, \tag{5.42}$$

and the canonical partition function is

$$Z_c = Tr(\exp\,(-\beta H)). \tag{5.43}$$

When forming traces we have to use states with a fixed number of particles and fixed volume.

The corresponding expressions for the case of the grand canonical ensemble can be found from (5.42) and (5.43). First of all, since H and $\hat{N}$ commute:

$$Z_g = Tr(\exp\,(-\beta H - \alpha\hat{N})) = Tr(\exp\,(-\alpha\hat{N})\,\exp\,(-\beta H)) = \sum_{\nu=0}^{\infty} \exp\,(-\alpha\nu) Z_c^\nu, \tag{5.44}$$

where Z_c^ν is the canonical partition function for ν particles. The trace formation is therefore initially carried out in the subspace of the Fock space for a fixed particle number ν, then all of these subspaces are summed up. Likewise one finds

$$\langle A\rangle_g = \frac{\sum_{\nu=0}^{\infty} \exp(-\alpha\nu)\langle A\rangle_c^\nu}{\{\sum_\nu \exp(-\alpha\nu) Z_c^\nu\}}, \tag{5.45}$$

where $\langle A\rangle_c^\nu$ is the canonical average for ν particles. Alternatively:

$$\langle A\rangle_g = \frac{Tr(A\ \exp(-\alpha\hat{N} - \beta H))}{Tr(\exp(-\alpha\hat{N} - \beta H))}. \tag{5.46}$$

3. Systems with macroscopically specified volume

While in the microcanonical ensemble E, N and V have sharp values, in the canonical ensemble only N and V have sharp values and in the grand-canonical ensemble only V is sharp. From a formal point of view it makes sense to investigate the case, in which the volume V is specified only as an average. For the sake of simplicity, we limit ourselves to a single dimension: the volume is determined by the operator $\hat{x}$, i.e. the coordinate of a movable stamp in a cylinder, and the average value of this quantity is X. According to the procedure presented in Sects. 5.3 and 5.4 we obtain for the statistical operator

$$\rho = \frac{\exp(-\alpha\hat{N}-\beta H-\gamma\hat{x})}{Tr(\exp(-\alpha\hat{N}-\beta H-\gamma\hat{x}))}. \tag{5.47}$$

The additional (Lagrange) parameter γ will essentially be identified with the pressure P of the system under consideration. For the entropy S follows (in analogy to (5.38)):

$$S = k_B(\ln \quad Z + \alpha N + \beta U + \gamma X) \tag{5.48}$$

with Z as the partition function corresponding to (5.47). Equations (5.47) and (5.48) will prove useful, if we investigate the connection between statistical mechanics and thermodynamics, since with (5.47) and (5.48) also the case of **external work** can be included.

In summarizing this chapter we have investigated different statistical ensembles, that are characterized by the knowledge of the energy E, the particle number N and the volume V. In the microcanonical ensemble all these quantities are known precisely, whereas in the canonical ensemble the energy is only known on average, which lead to the introduction of a Lagrange parameter β, that is related to the temperature T. In the grand-canonical ensemble additionally the particle number is only known on average, which lead to the introduction of a Lagrange parameter α, which is related to the chemical potential μ. Furthermore, in the general case also the volume V is only known on average thus leading to another Lagrange parameter γ, which is related to the pressure P.

W. Cassing, *Theoretical Physics Compact IV*
https://doi.org/10.1007/978-3-031-95518-1_6

6. Independent Identical Particles

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In this chapter we will discuss the results for independent identical particles, i.e. separately for bosons and fermions, compute the equilibrium occupation numbers as well as characteristic observables. The limits of low density and/or high temperature will lead to the classical limit and the Boltzmann statistics.

6.1 Preliminary Remarks

As an example for the results of Chap. 5 we consider a system of independent identical particles, characterized by its Hamiltonian

$$H = \sum_{\nu=1}^{N} h(\xi_\nu), \tag{6.1}$$

where all single-particle operators $h(\xi_\nu)$ have the same form and consist of kinetic energy *t* and potential energy $u(\xi)$,

$$h = t + u. \tag{6.2}$$

The eigenstates of *H* can be specified immediately, most conveniently in particle number representation:

$$H|n_1 n_2 \ldots n_j \ldots\rangle = E|n_1 n_2 \ldots n_j \ldots\rangle \tag{6.3}$$

with

$$E = \sum_i \epsilon_i n_i \ , \tag{6.4}$$

if ϵ_i are the single-particle energies ($\equiv$ eigenvalues of *h*) and n_i indicates how many particles are occupied in the single-particle state *i*. For bosons the values 0, 1, 2,... are possible for n_i, for fermions only 0 or 1.

We now want to calculate the most important statistical variables of such a system of independent particles for the case of the grand-canonical ensemble. This case is closest to reality and is also computationally easier. For large particle numbers $\mathscr{N}$ we will show (Chap. 8), that for the microcanonical and the canonical ensemble we get the same results.

6.2 Average Occupation Numbers of the Single-Particle States

For the case of independent particles we expect that the statistical average values of the many-body system can be built up additively from the contributions of the single-particle states. We start with the average occupation numbers of the single-particle state

$$\boxed{\langle n_i \rangle = \frac{Tr(\hat{n}_i \exp[-\beta H - \alpha \hat{N}])}{Tr(\exp[-\beta H - \alpha \hat{N}])}. \qquad (6.5)}$$

We carry out the evaluation of (6.5) in the basis of the eigenstates (6.3) of *H*, in which $\hat{n}_i$, $\hat{N}$ and *H* are simultaneously diagonal. In this basis the partition function Z_g reads (with (5.44))

$$Z_g = \sum_{\nu=0}^{\infty} \exp\,(-\alpha\nu) \Big\{ \sum_{\{n_j\}} \exp\,\Big(-\beta \sum_j \epsilon_j n_j \Big) \Big\} \qquad (6.6)$$

with the boundary condition $\sum_j n_j = \nu$ and (5.45)

$$\boxed{\langle n_i \rangle = \frac{1}{Z_g} \sum_{\nu=0}^{\infty} \exp\,(-\alpha\nu) \Big\{ \sum_{\{n_j\}} n_i \exp\,\Big(-\beta \sum_j \epsilon_j n_j \Big) \Big\}. \qquad (6.7)}$$

Combination of (6.6) and (6.7) gives

$$\boxed{\langle n_i \rangle = -\beta^{-1} \ \frac{\partial}{\partial \epsilon_i} \ln \ \ Z_g \ ; \qquad (6.8)}$$

it is thus sufficient to calculate Z_g as a function of ϵ_i. To this aim we rewrite (6.6):

$$Z_g = \sum_{n_1} \sum_{n_2} \sum_{n_3} \cdots \sum_{n_j} \cdots \big[(\exp\,(-\beta\epsilon_1 - \alpha))^{n_1} \cdots (\exp\,(-\beta\epsilon_j - \alpha))^{n_j} \cdots \big]. \qquad (6.9)$$

Whereas in (6.6) we first consider the contributions from ν-particle states and then sum over all values $\nu = 0, 1, 2, \ldots$, in (6.9) the contributions of all single-particle states are summed up according to their occupation number. It is possible to rewrite Eq. (6.9) in product form:

$$Z_g = \prod_i \ \Big[\sum_{n_i} (\exp\,(-\beta\epsilon_i - \alpha))^{n_i} \Big], \qquad (6.10)$$

which now can be evaluated separately for bosons and fermions. For **fermions** $n_i = 0$, 1, thus:

$$Z_g^F = \prod_i \; \{1 + \exp\,(-\beta\epsilon_i - \alpha)\}. \tag{6.11}$$

For **bosons**, n_i contributes with all values $n_i = 0, 1, 2, \ldots \infty$. In order for Z_g to converge, (for positive ϵ_i) α and β must be positive, such that the geometric series in (6.10) can be summed up:

$$Z_g^B = \prod_i \; (1 - \exp\,(-\beta\epsilon_i - \alpha))^{-1}. \tag{6.12}$$

From (6.11) or (6.12) follows with (6.8)

$$\begin{aligned} \langle n_i \rangle &= -\beta^{-1} \tfrac{\partial}{\partial \epsilon_i} \ln \left(\prod_k \; \{1 + \exp\,(-\beta\epsilon_k - \alpha)\}\right) \\ &= -\beta^{-1} \sum_k \tfrac{\partial}{\partial \epsilon_i} \ln \left(\{1 + \exp\,(-\beta\epsilon_k - \alpha)\}\right) \\ &= \frac{\exp\,(-\beta\epsilon_k - \alpha)}{1 + \exp\,(-\beta\epsilon_k - \alpha)} = \frac{1}{\exp\,(+\beta\epsilon_i + \alpha) + 1} \end{aligned} \tag{6.13}$$

for fermions,

$$\begin{aligned} \langle n_i \rangle &= -\beta^{-1} \tfrac{\partial}{\partial \epsilon_i} \ln \left(\prod_k \; (1 - \exp\,(-\beta\epsilon_k - \alpha))^{-1}\right) \\ &= \beta^{-1} \sum_k \tfrac{\partial}{\partial \epsilon_i} \ln \left(\; (1 - \exp\,(-\beta\epsilon_k - \alpha))\right) \\ &= \frac{\exp\,(-\beta\epsilon_k - \alpha)}{1 - \exp\,(-\beta\epsilon_k - \alpha)} = \frac{1}{\exp\,(+\beta\epsilon_i + \alpha) - 1} \end{aligned} \tag{6.14}$$

for bosons. These are the well-known **Bose** and **Fermi distributions** for independent particles.

6.3 Averages

For average values such as the internal energy U or the average particle number $\mathscr{N}$ of the entire system one expects expressions of the form

$$U = \sum_i \langle n_i \rangle \epsilon_i, \tag{6.15}$$

$$\mathscr{N} = \sum_i \langle n_i \rangle. \tag{6.16}$$

This formally results from (5.36) and (5.37) when using (6.11) for fermions and (6.12) for bosons.

Equations (6.15) and (6.16) fix the Lagrange parameters α and β: U and $\mathscr{N}$ are macroscopically given quantities, the single-particle energies ϵ_i are determined by quantum theory (i.e. by the single-particle potential $u(\xi)$). Unfortunately, Eqs. (6.15) and (6.16) are too complicated to be solved directly for α and β.

The entropy can also be calculated additively from the contributions of the single-particle states as (5.38) directly shows: except from U and $\mathscr{N}$ only $\ln\ Z_g$ appears in the expression for S (5.38) ($S = k_B(\ln Z_g + \beta \sum_i \langle n_i \rangle \epsilon_i + \alpha \sum_i \langle n_i \rangle$), and results in

$$\boxed{\ln\ Z_g^F = \ln \prod_i (1 + \exp(-\beta\epsilon_i - \alpha)) = \sum_i \ln(1 + \exp(-\beta\epsilon_i - \alpha))} \tag{6.17}$$

for fermions and

$$\boxed{\ln\ Z_g^B = \ln \prod_i (1 - \exp(-\beta\epsilon_i - \alpha))^{-1} = -\sum_i \ln(1 - \exp(-\beta\epsilon_i - \alpha))} \tag{6.18}$$

for bosons.

6.4 The Classical Limit

There is no spin in classical physics. In the classical limit thus the difference between fermions and bosons should disappear. Let's consider as a typical quantity the average occupation numbers $\langle n_i \rangle$; the classical limit is achieved if

$$\exp(\alpha) \gg 1. \tag{6.19}$$

Then we get from (6.13) for bosons and fermions

$$\boxed{\langle n_i \rangle = \exp(-\alpha)\exp(-\beta\epsilon_i).} \tag{6.20}$$

This result is plausible: the Pauli principle (i.e. the question about the symmetry of wave functions) is used for problems in statistics (think of the number of possible realizations of a certain macro-state) and becomes insignificant, if the number of particles is much smaller than the number of available single-particle states, i.e. when $\langle n_i \rangle$ is small.

For the average occupation number (6.20) (**Boltzmann statistics**) the parameter α can be determined by:

$$\mathcal{N} = \sum_i \langle n_i \rangle = \exp\,(-\alpha) \sum_i \exp\,(-\beta\epsilon_i), \tag{6.21}$$

thus

$$\exp\,(-\alpha) = \frac{\mathcal{N}}{\sum_i \exp(-\beta\epsilon_i)}. \tag{6.22}$$

Then follows:

$$\langle n_i \rangle = \frac{\mathcal{N}}{\sum_j \exp(-\beta\epsilon_j)} \;\; \exp\,(-\beta\epsilon_i). \tag{6.23}$$

We can interpret the condition (6.19) physically by showing that for free particles $(u(\xi) = 0)$ the sum

$$\sum_i \exp\,(-\beta\epsilon_i) \sim V, \tag{6.24}$$

where *V* is the macroscopic volume. For free particles the single-particle states are plane waves with momentum $\mathbf{p} = \hbar\mathbf{k}$ and energy $\epsilon = \hbar^2 k^2/(2\,m)$. We thus replace the sum over states *i* by a sum over the discrete states $\mathbf{k}$ and account for the degeneracy of the spin *s* by a factor $(2s + 1)$:

$$\sum_i \cdots = (2\,s + 1) \sum_{\mathbf{k}} \cdots; \tag{6.25}$$

here $\mathbf{k}$ runs over all possible values in the normalization volume *V*. If *V* is large, then the $\mathbf{k}$-values are very close and we can replace the sum by an integral,

$$\sum_{\mathbf{k}} \to \frac{V}{(2\pi)^3} \int d^3k = \frac{V}{(2\pi\hbar)^3} \int d^3p \;. \tag{6.26}$$

Since the energy $\epsilon = p^2/(2m)$ in (6.24) we can rewrite

$$\int d^3k \cdots = \frac{1}{\hbar^3} \int d^3p \cdots = \frac{4\pi}{\hbar^3} \int_0^\infty p^2 dp \tag{6.27}$$

and finally get (with $h = 2\pi\hbar$ and $\int_0^\infty dx\;\, x^2 \,\exp\,(-x^2/b^2) = \sqrt{\pi} b^3/4$):

$$\begin{aligned}\sum_i \exp\,(-\beta\epsilon_i) \;&= \frac{4\pi V}{h^3}\;(2\,s+1)\;\int_0^\infty dp\;p^2\,\exp\,(-\beta p^2/(2\,m))\\ &= (2\,s+1)\frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}\\ &= \frac{V(2\,s+1)}{\lambda^3} = \mathscr{N}\,\exp\,(\alpha)\end{aligned} \tag{6.28}$$

with the abbreviation

$$\lambda = h\sqrt{\beta/(2\pi m)}. \tag{6.29}$$

The quantity λ is also called **thermal De Broglie wavelength**. Then (6.19) reads as follows:

$$V/\mathscr{N} \gg 1: \;\; \text{low} \;\; \text{density!} \tag{6.30}$$

Except for the case of low density one can also use the classical limit (6.20) if β is small. Then λ becomes small and thus–according to (6.28) and (6.22)–exp (α) large. If we antipate from Chap. 7 that β is related to the temperature T of the system by $\beta = 1/(k_B T)$, **the classical limit also holds for high temperatures**. The thermal de Broglie wavelength (6.29) then reads

$$\lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}}. \tag{6.31}$$

Result: For low density and/or high temperature Bose statistics and Fermi statistics, Eqs. (6.13) and (6.14), merge to the classical Boltzmann statistics.

It is also interesting to investigate the internal energy for free classical particles. It is

$$U = \sum_i \epsilon_i \langle n_i\rangle = \mathscr{N}\frac{\sum_i \epsilon_i \exp(-\beta\epsilon_i)}{\sum_i \exp(-\beta\epsilon_i)} = -\mathscr{N}\frac{\partial}{\partial\beta}\;\;\ln\,\left(\sum_i \exp\,(-\beta\epsilon_i)\right) \tag{6.32}$$

$$= -\mathscr{N}\frac{\partial}{\partial\beta}\;\;\ln\,(V(2\,s+1)/\lambda^3) = -\frac{N}{V}\,\frac{\lambda^3}{2\,s+1}\;\frac{\partial}{\partial\lambda}\left(\frac{V}{\lambda^3}(2\,s+1)\right)\;\frac{\partial\lambda}{\partial\beta}$$

$$= \frac{3\mathscr{N}}{\lambda}\;\frac{\partial\lambda}{\partial\beta} = \frac{3}{2}\;\frac{\mathscr{N}}{\beta} = \frac{3}{2}\mathscr{N}k_B T,$$

such that on average the energy for each particle is $3/(2\beta) = 3/2\ k_B T$ (**equipartition theorem**).

We will discuss Fermi and Bose statistics in detail in connection with concrete examples (conduction electrons in metals, lattice oscillations $\equiv$ phonons, photon gas) in Part III.

Warning: The Boltzmann factor exp $(-\beta\epsilon_i)$ should not be mixed up with the relative probabilities $p_j =$exp $(-\beta E_j)$ in the statistical operator of the canonical ensemble! Because:

1. ϵ_i is a single-particle energy, E_j is the energy of a many-body state;

2. the above expression for p_j holds in general for a canonical ensemble also for interacting particles in the system and

3. the form of the statistical operator (derived in Sect. 5.3) holds for fermions and bosons or classical particles!

In summarizing this chapter we have discussed the results for independent identical particles separately for bosons and fermions and computed the equilibrium occupation numbers, which are given by the Fermi and Bose distributions. Furthermore, we have calculated characteristic observables such as the internal energy and particle number. The limits of low density and/or high temperature have lead to the classical limit and the Boltzmann statistics.

W. Cassing, *Theoretical Physics Compact IV*
https://doi.org/10.1007/978-3-031-95518-1_7

7. Statistical Mechanics and Thermodynamics

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In this chapter we will establish the relation of the Lagrange parameters to the temperature, chemical potential and the pressure. Furthermore, thermodynamical potentials are introduced for the different ensembles, that are functions of the natural variables as well as their total differentials. The latter lead to various Maxwell relations between thermodynamic quantities. We will formulate (and prove) the main laws of thermodynamics and discuss in particular the specific heat and the thermal expansion coefficient. It will be shown, that the classical ideal gas violates in particular the 3rd law of thermodynamics. Finally, we will discuss different changes of state and compute the efficiency coefficient for the Carnot cycle and the Otto engine.

7.1 Temperature: Exchange of Heat

In the following we want to show that the Lagrange parameter β is linked to the phenomenological temperature T by the relation

$$\boxed{\beta = \frac{1}{k_B T}\,, \qquad (7.1)}$$

where k_B is the Boltzmann constant.

First we show that for two systems, which may exchange energy (**thermal contact**), in statistical equilibrium holds:

$$\beta_1 = \beta_2. \qquad (7.2)$$

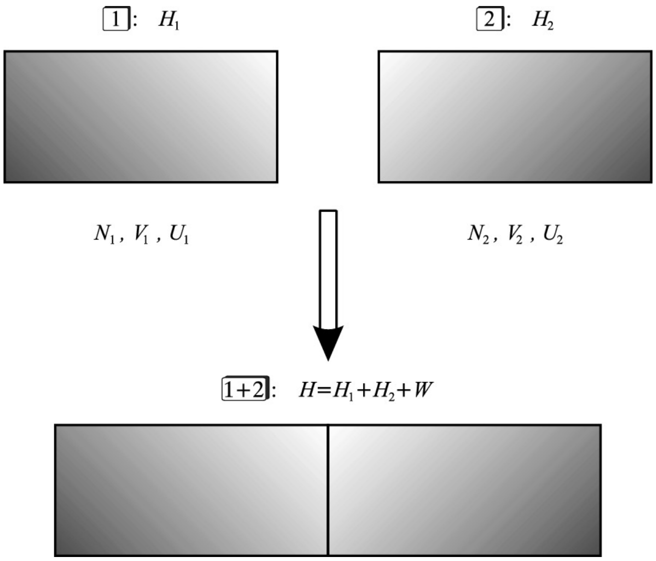

Fig. 7.1 Two systems H_1 and H_2 brought in thermal contact

The two separate systems 1 and 2 are characterized by their Hamiltonians H_1 and H_2. The given macroscopic data are particle numbers N_1, N_2 and the volumes V_1, V_2 as well as the average values of energy $U_1 = Tr(\rho_1 H_1)$, $U_2 = Tr(\rho_2 H_2)$, which correspond to the Lagrange parameters β_1 and β_2 (canonical ensembles). If we now bring the two systems into thermal contact, the resulting total system in general will not be in thermal equilibrium. Through exchange of energy by an interaction W between the systems 1 and 2 the equilibrium will be achieved after a long time, in which the entropy S of the entire system is maximum. We want to assume that the interaction W between the original systems is so weak, that it can be neglected in the energy balance, although it is crucial for establishing the equilibrium. With the requirement (see Fig. 7.1), that N_1, V_1, U_1 and N_2, V_2, U_2 are known, we also know the number of particles after the equilibrium is established

$$N = N_1 + N_2, \tag{7.3}$$

and the volume

$$V = V_1 + V_2 \tag{7.4}$$

sharp as well as the average value of the energy of the entire system:

$$\langle H \rangle = \langle H_1 + H_2 + W \rangle \approx \langle H_1 + H_2 \rangle = U; \tag{7.5}$$

We don't know the individual average values $\langle H_1 \rangle$ and $\langle H_2 \rangle$ because an energy exchange has taken place between the systems. The statistical operator in equilibrium—belonging to the conditions (7.3), (7.4) and (7.5)—is

$$\boxed{\rho = \frac{\exp\{-\beta(H_1+H_2)\}}{Tr(\exp\{-\beta(H_1+H_2)\})}. \qquad (7.6)}$$

Here the Lagrange parameter β is fixed by the condition

$$Tr(\rho H) = U. \tag{7.7}$$

Writing

$$\exp\{-\beta(H_1+H_2)\} = \exp(-\beta H_1)\exp(-\beta H_2), \tag{7.8}$$

we can also formulate the equilibrium condition for the entire system as

$$\boxed{\beta_1 = \beta_2 = \beta. \qquad (7.9)}$$

Starting from the separate systems with $\beta_1 \neq \beta_2$ energy exchange takes place until $\beta_1 = \beta_2 = \beta$ is reached. Exactly the same property holds for the temperature *T* introduced phenomenologically in thermodynamics: If we bring two systems with $T_1 \neq T_2$ into thermal contact, exchange of heat takes place until $T_1 = T_2 = T$.

From the considerations above it follows directly (the statement is often called **0th law of thermodynamics**): If two systems 1, 2 are in thermal equilibrium with a third system 3,

$$\beta_1 = \beta_3;\ \beta_2 = \beta_3, \tag{7.10}$$

then the two systems 1 and 2 are in thermal equilibrium with each other:

$$\beta_1 = \beta_2. \tag{7.11}$$

This provides the possibility of **temperature measurements**: With the help of a thermometer (system 3), the temperatures of two bodies (systems 1 and 2) can be compared. Any macroscopic system can be used as a thermometer that meets the following requirements:

(i) Bringing the thermometer into thermal contact with the system to be examined, a parameter of the thermometer (e.g. its length or its electrical resistance or ...) changes monotonically (due to the expected exchange of energy) until thermal equilibrium is reached.

(ii) The thermometer must be much **smaller** (i.e. have fewer degrees of freedom) as the system to be examined, such that the energy exchange and the perturbation of the system—to be examined—is as small as possible.

Of course, one always has to wait, when taking a temperature measurement, until thermal equilibrium between the thermometer and the system is achieved.

The considerations above show, that a relationship exists between the temperature *T* and the Lagrange parameter β,

$$\beta = \beta(T). \tag{7.12}$$

About the connection (7.12) we can prove the following general statement: β **must decrease with** *T*. Phenomenologically we know that higher temperature implies higher energy. On the other hand, for statistical mechanics (see Chap. 8) holds:

$$(\Delta H)^2 = \langle H^2\rangle - \langle H\rangle^2 = -\frac{\partial U}{\partial \beta} \ \geq 0. \tag{7.13}$$

To find the exact functional connection between β and *T*, we now consider an ideal gas. We found in Chap. 6, Eq. (6.32):

$$\boxed{U = \tfrac{3}{2}\mathscr{N}\beta^{-1}, \qquad (7.14)}$$

while in phenomenological thermodynamics we have

$$U = \tfrac{3}{2}\mathscr{N} k_B T. \tag{7.15}$$

We therefore identify

$$\beta = \tfrac{1}{k_B T}. \tag{7.16}$$

We have (tacitly) made use of the assumption, that the thermodynamically defined internal energy U can be identified with $Tr(\rho H)$. This identification follows inevitably, when we accept to describe a real macroscopic system by a statistical ensemble! In Sect. 7.5 we will confirm the relation (7.16) by the ideal gas equation $PV = Nk_B T$.

Note: The considerations above about the temperature of a system can also be employed within the framework of microcanonical ensembles, where at the beginning the systems 1 and 2 are considered to be isolated, as well as for the entire system after equilibration. If W is negligible within the energy balance (as assumed above), then the energy E (sharp value!) and entropy S of the entire system are additive with respect to the corresponding quantities of the individual systems (volume and number of particles are fixed!). The equilibrium state is characterized by

$$\delta S = \left(\frac{\partial S}{\partial E_1}\right)\delta E_1 + \left(\frac{\partial S}{\partial E_2}\right)\delta E_2 = 0 \tag{7.17}$$

with the additional condition

$$\delta E = 0 \rightarrow \delta E_1 = -\delta E_2. \tag{7.18}$$

A combination of (7.17) with (7.18) gives the equilibrium condition

$$\frac{\partial S}{\partial E_1} = \frac{\partial S}{\partial E_2}, \tag{7.19}$$

which corresponds to Eq. (7.2), or in the form

$$\frac{\partial S}{\partial U_1} = \frac{\partial S}{\partial U_2} = \beta. \tag{7.20}$$

The temperature for the **microcanonical ensemble**, defined by $\partial S/\partial E$, is not identical to the temperature defined by $\partial S/\partial U$ of the **canonical ensemble**; however, the difference disappears with increasing number of particles (see Chap. 8).

7.2 Chemical Potential: Particle Exchange

We next examine two systems that can exchange both energy and particles. The argumentation is in analogy to the heat exchange. The two separate systems are described by the grand-canonical ensemble:

(7.21)

$$\rho_i = \frac{\exp\{-\beta_i H_i - \alpha_i \hat{N}_i\}}{Tr(\exp\{-\beta_i H_i - \alpha_i \hat{N}_i\})}$$

for i = 1, 2, where in general

$$\beta_1 \neq \beta_2; \ \alpha_1 \neq \alpha_2. \tag{7.22}$$

Bringing the systems into contact, they exchange energy and particles until equilibrium is achieved for the entire system. The statistical operator of the entire system, for which holds

$$U = Tr(\rho H) \tag{7.23}$$

and

$$\mathscr{N} = Tr(\rho \hat{N}) \tag{7.24}$$

$$H = H_1 + H_2 (+W); \ \hat{N} = \hat{N}_1 + \hat{N}_2, \tag{7.25}$$

has the form:

$$\rho = \frac{\exp\{-\beta[H_1+H_2] - \alpha[\hat{N}_1+\hat{N}_2]\}}{Tr(\exp\{-\beta[H_1+H_2] - \alpha[\hat{N}_1+\hat{N}_2]\})}. \tag{7.26}$$

Since the exp-operator in (7.26) can be split into

$$\exp\{-\beta H_1 - \alpha \hat{N}_1\} \exp\{-\beta H_2 - \alpha \hat{N}_2\}, \tag{7.27}$$

the equilibrium conditions are:

$$\beta_1 = \beta_2; \quad \alpha_1 = \alpha_2. \tag{7.28}$$

Usually instead of α one uses the quantity

$$\mu = -\frac{\alpha}{\beta} = -\alpha k_B T, \tag{7.29}$$

such that (7.28) turns to

$$\beta_1 = \beta_2; \ \ \mu_1 = \mu_2. \tag{7.30}$$

Since the equilibrium parameter μ in chemical reactions (**example**: dissociation of atomic hydrogen: $H \leftrightarrow p + e$) plays an important role, it is generally denoted as **chemical potential**.

The equilibrium conditions can also be formulated for the case of isolated systems and the entire system, which are microcanonical ensembles. The equilibrium state of the entire system then is characterized by, since $V = V_1 + V_2$ is fixed,

(7.31)

$$\delta S = \left(\frac{\partial S}{\partial E_1}\right)\delta E_1 + \left(\frac{\partial S}{\partial E_2}\right)\delta E_2 + \left(\frac{\partial S}{\partial N_1}\right)\delta N_1 + \left(\frac{\partial S}{\partial N_2}\right)\delta N_2 = 0$$

at

$$\delta N = 0 \rightarrow \delta N_1 = -\delta N_2 \tag{7.32}$$

and

$$\delta E = 0 \rightarrow \delta E_1 = -\delta E_2. \tag{7.33}$$

This gives the equilibrium conditions

$$\boxed{\frac{\partial S}{\partial E_1} = \frac{\partial S}{\partial E_2}; \quad \frac{\partial S}{\partial N_1} = \frac{\partial S}{\partial N_2},} \tag{7.34}$$

which—in agreement with (7.20)—for the case of a grand-canonical ensemble are:

$$\boxed{\frac{\partial S}{\partial U_1} = \frac{\partial S}{\partial U_2}; \quad \frac{\partial S}{\partial \mathcal{N}_1} = \frac{\partial S}{\partial \mathcal{N}_2}.} \tag{7.35}$$

Note that in analogy to Sect. 7.1 only for large particle numbers $\partial S/\partial N = \partial S/\partial \mathcal{N}$ becomes valid.

7.3 Pressure: Volume Exchange, External Work

In the general case, where for the individual systems as well as for the entire system only the average values of energy, particle number and volumes are fixed, the statistical operator of the entire system—after equilibrium has been established—reads (cf. (5.47)):

$$\rho = \frac{\exp\{-\alpha\hat{N} - \beta H - \gamma\hat{x}\}}{Tr(\exp\{-\alpha\hat{N} - \beta H - \gamma\hat{x}\})}. \tag{7.36}$$

This corresponds to the situation where the two systems 1 and 2 are separated by a (freely) movable wall (in *x* direction), which is transparent for the exchange of energy and particles (see Fig. 7.2).

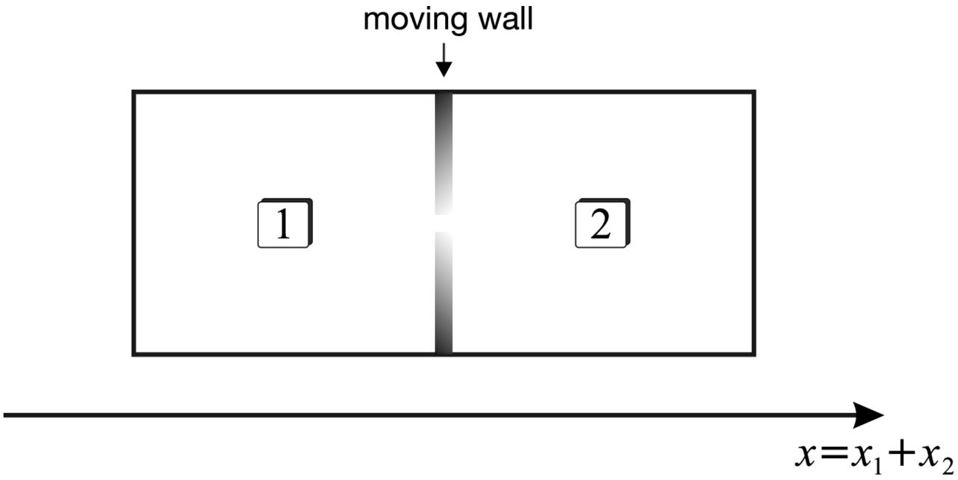

Fig. 7.2 Two systems H_1 and H_2 in thermal and mechanical contact also allowing for particle exchange

According to the considerations (1) and (2) we must have in equilibrium:

$$\beta_1 = \beta_2 \quad \text{(therm. equilibrium)} \tag{7.37}$$

$$\alpha_1 = \alpha_2 \quad \text{(chemical equilibrium)} \tag{7.38}$$

and

$$\gamma_1 = \gamma_2 \quad \text{(mechanical equilibrium).} \tag{7.39}$$

With (see eq. (5.48))

$$S = k_B(\ln Z + \alpha\mathcal{N} + \beta U + \gamma X) \tag{7.40}$$

we can also write (7.37), (7.38), (7.39) as in analogy to (7.35).

$$\frac{\partial S}{\partial U_1} = \frac{\partial S}{\partial U_2}; \quad \frac{\partial S}{\partial \mathcal{N}_1} = \frac{\partial S}{\partial \mathcal{N}_2}; \quad \frac{\partial S}{\partial X_1} = \frac{\partial S}{\partial X_2} \tag{7.41}$$

To associate the parameter γ with the pressure, we replace system 2 by an external force (e.g. weight in the gravitational field; see Fig. 7.3).

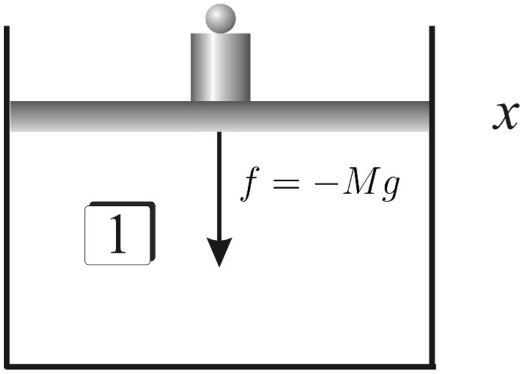

Fig. 7.3 Example of a system under the influence of an external force $f = -Mg$, where M denotes the mass of the weight

The statistical operator for the equilibrium then is obtained by adding to the Hamiltonian H of the system the potential energy $-f\hat{x} = Mg\hat{x}$ of the stamp, i.e.:

$$\rho = \rho(H - f\hat{x}, \hat{N}). \tag{7.42}$$

The comparison with (5.47) ($\rho = \rho(\beta H + \gamma\hat{x}, \hat{N})$) then leads to

$$\beta H + \gamma\hat{x} = \beta H - \beta f\hat{x}.$$

A comparison of the coefficients gives

$$\boxed{\gamma = -\beta\ f,} \tag{7.43}$$

where $f = -Mg$ is the constant external force. We thus can identify

$$\boxed{T\ \frac{\partial S}{\partial V} = \frac{T}{F}\ \frac{\partial S}{\partial X} = \frac{\gamma}{F\beta} =: P} \tag{7.44}$$

with the **pressure** P of the system on the stamp, where F denotes the area of the stamp. Transferring this result to our original example, we see that the equilibrium condition $\partial S/\partial V_1 = \partial S/\partial V_2$ implies $P_1 = P_2$; V and V_i denote the average values of the volumes, respectively.

Result: The formal Lagrange parameters α, β and γ we have linked with the temperature T, chemical potential μ and pressure P. Thus: a certain value of the internal energy U determines the temperature T, a given average particle number $\mathscr{N}$ determines the chemical potential μ and a given average volume V determines the pressure P. The statistical operator ρ (7.36) can thus also be written as

$$\rho = \frac{\exp\{-\beta(H - \mu\hat{N} + P\hat{V})\}}{Tr(\exp\{-\beta(H - \mu\hat{N} + P\hat{V})\})}. \tag{7.45}$$

For the entropy S we get (after multiplication by T)

$$TS = Tk_B \ln Z + U - \mu\mathscr{N} + PV. \tag{7.46}$$

7.4 Simple Examples

In this section we will cover some simple examples for the equilibrium conditions (7.41)

$$T_1 = T_2; \quad P_1 = P_2; \quad \mu_1 = \mu_2.$$

The condition $\mu_1 = \mu_2$ will be of priority, which represents the chemical equilibrium (equilibrium with respect to particle exchange). Systems 1 and 2, which are in equilibrium, we assume to be homogeneous ($\mathscr{N}/V$ = const). Then particle number and volume are not independent variables of the system, which implies that the three conditions (7.41) are not independent. One thus can consider e.g. μ as a function of P and T,

$$\mu = \mu(P, T),$$

where in (7.41) the third condition follows from the first two.

Example 1: Phase equilibria Experience has shown that one and the same substance, consisting of a specific type of atoms or molecules, can occur in various modifications (**phases**). Different phases have different physical properties such as density, compressibility, susceptibility etc. A first rough distinction is between **solid, liquid** and **gaseous** phases; solid and liquid phases in turn can occur in various phases, for example as different lattice structures of the same substance, or in **ferromagnetic, superconducting, superfluid** phases.

Phase equilibrium occurs when two or more phases are in contact with each other and the equilibrium conditions (7.41) are fulfilled. Overall it then is an inhomogeneous system; every individual phase can, however, be viewed as homogeneous.

For a two-phase system of a substance equation (7.41) reads

$$\mu_1(P, T) = \mu_2(P, T), \tag{7.47}$$

where P and T are the common pressure and temperature of the two phases. Equation (7.47) then describes a line $P = P(T)$ in the $P - T$ plane (see Fig. 7.4), where the two phases can coexist. On either side of this line, however, only a single phase can exist.

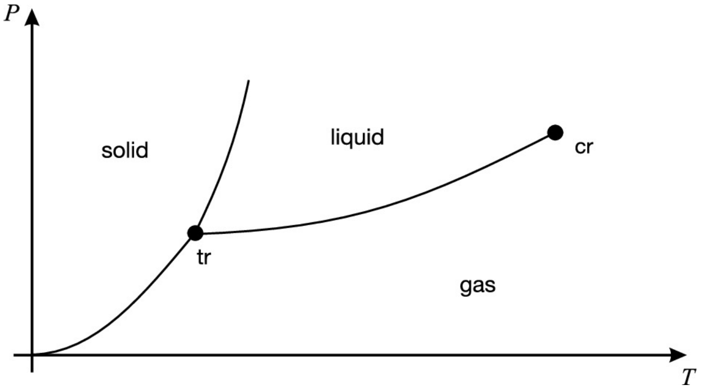

Fig. 7.4 Example of a *P*-*T* diagram

In the three-phase system of a substance the equilibrium conditions for particle exchange are:

$$\mu_1(P, T) = \mu_2(P, T) = \mu_3(P, T). \tag{7.48}$$

By (7.48) a point is defined in the $P-T$ diagram (*tr*), the so-called **triple point** in which all three phases can exist simultaneously. Obviously, no more than three phases of a substance can exist in equilibrium. Above a critical point (*cr*) no longer a clear distinction between liquid and gas is possible. The 'phase transition' then is called a **crossover**.

If we generalize the considerations above, we get the **Gibbs phase rule**.

For *n* different substances the chemical potentials μ_i^a $(i =$ phase, *a* = material) in each phase depend—apart from *P* and *T*—also on $(n-1)$ concentrations c_a of the substances. If *r* phases are in equilibrium, then we get as equilibrium conditions (in analogy to (7.48)) $n \cdot (r-1)$ equations. The variables, on which the μ_i^a depend, are *P* and *T* as well as $(n-1)$ concentrations c_a for each phase; these are $2 + r \cdot (n-1)$ variables. When considering the $n \cdot (r-1)$ equilibrium conditions we remain with

$$f = 2 + r \cdot (n-1) - (n \cdot (r-1)) = 2 + n - r \tag{7.49}$$

free independent variables. In (7.49) *f* indicates the number of variables that can be changed without destroying the equilibrium. If $f = 0$, i.e. $r = n + 2$, all variables are fixed due to the equilibrium conditions; one cannot change any of the variables without destroying the equilibrium.

> The maximum number of phases of a system with *n* components (substances), which simultaneously are in equilibrium, thus is $n + 2$.

Example 2: Chemical reactions Chemical reactions, that occur in a mixture of substances reacting with each other, ultimately lead to a state of equilibrium in which the amounts of the substances (involved in the reaction) no longer change: **chemical equilibrium**. Any chemical reaction generally occurs in both directions; before reaching the equilibrium, one direction of the reaction predominates, in equilibrium both reaction rates (forward and backward) become the same such that the total amount of each of the substances involved no longer changes. The **thermodynamics of chemical reactions** just deals with the investigation of the equilibrium, not with the processes leading to equilibrium!

During a chemical reaction the particle numbers of the different reaction partners cannot change arbitrarily. For example, in the reaction

$$H + D \Leftrightarrow HD \tag{7.50}$$

always

$$\delta N_H = \delta N_D = -\delta N_{HD}, \tag{7.51}$$

or for

$$2H_2 + O_2 \Leftrightarrow 2\ H_2O \tag{7.52}$$

must hold

$$2\delta N_{H_2} = -2\delta N_{H_2O} = \delta N_{O_2}. \tag{7.53}$$

Writing chemical reactions as

$$\textstyle\sum_i \nu_i A_i = 0, \tag{7.54}$$

where A_i is the chemical symbol of the $i-th$ particle type, then

$$\delta N_i = \nu_i \delta N, \tag{7.55}$$

if δN is the number of elementary reactions. In the example (7.53) ν_1 = 2 (for H_2), ν_2 =1 (for O_2) and $\nu_3 = -2$ (for H_2O). The equilibrium state of a closed system then has a maximum of the entropy S with respect to the changes in N_i following the constraints (7.55). Thus inserting

$$0 = \delta S = \sum_i \left(\frac{\partial S}{\partial N_i}\right)\delta N_i = -\beta \sum_i \mu_i \ \delta N_i = -\beta(\sum_i \mu_i \ \nu_i)\delta N = 0 \tag{7.56}$$

into equation (7.55), this results in the condition for chemical equilibrium:

$$\boxed{\sum_i \nu_i \mu_i = 0. \tag{7.57}}$$

If one knows the chemical potentials $\mu_i(P, T, c_i)$ of the reaction partners as a function of pressure P, temperature T and the concentrations $c_i = N_i/(\sum_i N_i)$, then Eq. (7.57) provides a relation between the concentrations c_i, P and T (**law of mass action**).

7.5 The Way to Equilibrium

Compared to the theory of statistical equilibrium the theory of thermodynamic processes—especially the way to equilibrium—is more complex. Therefore, this topic will be addressed only by a few qualitative statements here, which confirm the discussion made in Sects. 7.1–7.3 in connection of thermodynamic quantities (μ, T, P) with statistical mechanics (Lagrange parameters α, β, γ). For the treatment of processes out of equilibrium we refer to Part IV.

We first consider the case of approaching thermal equilibrium. The two systems 1, 2 are initially characterized by $\beta_1 > \beta_2 \ \ (T_1 < T_2)$. Bringing the systems in thermal contact, then the entropy for $1 + 2$ increases since we describe the internal energies U_1 and U_2 by only a single condition for the total internal energy U and thus lose information. After producing the thermal contact, S will increase such that for quasi-static processes (see below) from

$$\delta S > 0 \tag{7.58}$$

follows:

$$\left(\frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2}\right)\delta U_1 > 0, \tag{7.59}$$

using

$$\delta U_1 = -\delta U_2. \tag{7.60}$$

With $\beta_1 = \partial S_1/\partial U_1$, $\beta_2 = \partial S_2/\partial U_2$ we get

$$(\beta_1 - \beta_2)\delta U_1 > 0 \tag{7.61}$$

or, since $\beta_1 > \beta_2$ was assumed,

$$\delta U_1 > 0. \tag{7.62}$$

Equation (7.62) states that the energy of the system with the lower temperature increases until thermal equilibrium is reached.

We now consider 2 substances, which are in thermal equilibrium ($\beta_1 = \beta_2 = \beta = 1/(k_B T)$), but not yet in mechanical equilibrium: $\gamma_1 > \gamma_2 \ (P_1 > P_2)$. The entire system then develops in such a way that the entropy increases until mechanical equilibrium also is achieved. After bringing the systems into contact, then according to the considerations for case 1 we have:

$$\left(\frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2}\right)\delta V_1 = \frac{1}{T}(P_1 - P_2)\delta V_1 > 0. \tag{7.63}$$

Since $P_1 > P_2$ was assumed, it follows:

$$\delta V_1 > 0. \tag{7.64}$$

Thus the system with the higher pressure expands until mechanical equilibrium is achieved.

Using the same procedure, one proves that, when establishing the chemical equilibrium, the system with the higher chemical potential μ releases particles to the system with lower chemical potential.

7.6 Thermodynamic Potentials

In the phenomenological thermodynamics any equilibrium state can be described completely by exactly one function of the **natural** variables of the system. Such a function, where all other thermodynamic variables can be determined by differentiation, is called **thermodynamic potential**. The natural variables are the independent variables of the system specified experimentally; in the absence of external fields and for systems of identical particles there are—depending on the macroscopic conditions—3 such variables, e.g. *E*, *V*, *N* for an **isolated system** or *T*, *V*, *N* for a **system in thermal contact with a heat reservoir**. Depending on the choice of the natural variables there are different thermodynamic potentials. The **free energy** $F =: U - TS$ is the thermodynamic potential of the natural variables *T*, *V*, *N*, while for *T*, *P*, *N* the **free enthalpy** $G =: U - TS + PV$ is the thermodynamic potential.

The importance of natural variables becomes specially clear from the perspective of statistical mechanics: for every system of a statistical ensemble the natural variables have the same, fixed value, the other thermodynamic quantities are only to be taken as average values and subject to fluctuations. The phenomenological thermodynamics does not know this difference; statistical mechanics and phenomenological thermodynamics can only be merged fully with each other, if the fluctuations in the average values become vanishingly small, i.e. for very large particle numbers (see Chap. 8).

In table (7.65) the most important thermodynamic potentials and their natural variables are listed:

	thermodyn. potential	natural variables	total differential
I	S	E, V, N	$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$
II	$F = U - TS$	T, V, N	$dF = -SdT - PdV + \mu dN$
III	$G = U - TS + PV$	T, P, N	$dG = -SdT + VdP + \mu dN$
IV	$J =: E - TS - \mu N$	T, V, μ	$dJ = -SdT - PdV - Nd\mu$
V	U	S, V, N	$dU = TdS - PdV + \mu dN$
VI	$\epsilon := U + PV$	S, P, N	$d\epsilon = TdS + VdP + \mu dN$

(7.65)

with the **entropy** *S*, the **free energy** *F*, the **free enthalpy** *G*, the **grand-canonical potential** *J*, the **internal energy** *U* and the **enthalpy** $\epsilon = U + PV$.

The total differentials indicate how the thermodynamic potentials change in **quasi-static** processes due to infinitesimal changes of the natural variables. Quasi-static processes are those that are slow compared to the time needed to achieve equilibrium; thus there will be a chain of equilibrium states that are close to each other. Quasi-static processes can be both reversible and irreversible. A simple example is the heat exchange between 2 systems with a finite temperature difference through a very poor heat conduction contact. Such a process is quasi-static, but irreversible.

We begin by discussing case I, in which E, N, V are the natural variables. This is the case of a **closed system**, which we can describe by the **microcanonical ensemble** as found in Sect. 5.2:

$$S = k_B \ln \ Z_m, \tag{7.66}$$

where the number of possible realizations of the macro-states Z_m is a function of E, V, N,

$$Z_m = Z_m(E, V, N), \tag{7.67}$$

thus also

$$S = S(E, V, N). \tag{7.68}$$

S is in fact the desired **thermodynamic potential** (entropy). In addition we form the total differential

$$dS = \left(\frac{\partial S}{\partial E}\right) dE + \left(\frac{\partial S}{\partial V}\right) dV + \left(\frac{\partial S}{\partial N}\right) dN \tag{7.69}$$

and take into account the results from Sects. 7.1–7.3. For quasi-static processes $\partial S/\partial E$ is

$$\frac{\partial S}{\partial E} = k_B \beta = \frac{1}{T} \tag{7.70}$$

and linked to the temperature T (of the microcanonical ensemble); accordingly

$$\frac{\partial S}{\partial N} = -k_B \beta \mu = -\frac{\mu}{T} \tag{7.71}$$

and

$$\frac{\partial S}{\partial V} = k_B \beta P = \frac{P}{T}, \tag{7.72}$$

where P is the pressure and μ the chemical potential (of the microcanonical ensemble). With these we get (see table (7.65))

$$\boxed{TdS = dE + PdV - \mu dN;} \tag{7.73}$$

this relation will help again in the discussion of the first law of thermodynamics. However, it should be noted that the quantities introduced above (T, P and μ) only match the quantities discussed in Sects. 7.1–7.3, if the fluctuations of U, N and V become infinitesimal (see Chap. 8).

We now choose T, V, N as the natural variables. Since according to Sect. 7.1 $T = 1/(k_B \beta)$ and since β determines the internal energy U of a system (as an average!), we can also consider U, V, N as given, $-V$ and N as sharp values, U as an average.—This is exactly the situation, which we describe by the **canonical ensemble**. For the partition function Z_c we found (Chap. 5):

$$\tag{7.74}$$

$$Z_c = \sum_i \exp\{-\beta E_i\};$$

the sum is over all micro-states with a fixed number of particles *N* and fixed volume *V*; E_i are the associated energies of the system. Since the energies E_i depend on the parameters *N* and *V*,

$$Z_c = Z_c(\beta, N, V). \tag{7.75}$$

The associated thermodynamic potential is (with $S = k_B(\ln Z_c + \beta U) = k_B \ln Z_c + U/T$)

$$\boxed{F =: -k_B T \ \ \ln \ \ Z_c = U - TS,} \tag{7.76}$$

cf. (5.30), in accordance with the phenomenological thermodynamics. For the total differential we get

$$dF = dU - TdS - SdT, \tag{7.77}$$

or, if we neglect the fluctuations of *U* and use *dU* from the table (7.65):

$$dF = (TdS - PdV + \mu dN) - TdS - SdT = -SdT - PdV + \mu dN. \tag{7.78}$$

Corresponding considerations can be carried out for cases III and *V*. The general equilibrium condition $\delta S = 0$ transfers—for all cases II to VI—to corresponding conditions for *F*, *U*, *G* or *J*.

> **Note**: In the mathematical sense, the different thermodynamic potentials correspond to Legendre transformations with respect to the conjugate variables (*T*, *S*), (μ, N) and (*P*, *V*).

A set of useful relations (**Maxwell relations**) result from the integrability conditions for the total differentials for *S*, *F*, *G*, *U*, *J* and others (practically less important) thermodynamic potentials.

Example: For the total differential of $F = F(T, V, N)$ (7.78) must hold:

$$\boxed{\left(\frac{\partial^2 F}{\partial T \partial V}\right) = \left(\frac{\partial^2 F}{\partial V \partial T}\right) \quad \text{or} \quad \left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N},} \tag{7.79}$$

where the indices indicate, which quantities must be kept constant when forming the partial derivatives. It is useful to prepare a table of the various possible Maxwell relations for each thermodynamic potential in table (7.65).

7.7 The Main Laws of Thermodynamics

The first law is nothing else than the general energy theorem formulated in terms of thermodynamics:

> 1. The energy of an isolated system is constant in time.

This statement is also provided by statistical mechanics, because an isolated system is described by the microcanonical ensemble, where all systems of the ensemble have the same, constant energy.

> 2. The internal energy of a system changes, when energy is added to (or withdrawn from) the system.

The change ΔU is decomposed in thermodynamics in 2 parts: (i) the work done by the environment on the system ΔW and (ii) the heat absorbed (emitted) ΔQ,

$$\Delta U = \Delta Q + \Delta W. \tag{7.80}$$

This division is not determined by the initial and final state of the system, but depends on the character of the process; thus the quantities W and Q are no thermodynamic potentials. For the conceptual distinction between W and Q we consider the (external) parameters of the system such as volume, external fields, spatial position of the system etc.: ΔW originates from the change of external parameters, e.g. the volume, while $\Delta Q \neq 0$ can happen even if the external parameters do not change.

Example: Take a bottle of beer out of the fridge and put it on a table (of the same height). Then $\Delta W = 0$; no work is done. Nevertheless, the energy of the environment is transferred to the bottle of beer in the form of heat: $\Delta U = \Delta Q \neq 0$; the beer changes its condition; it heats up and becomes less tasty.

To prove the first law—in the form of the energy balance (7.80)—from statistical mechanics we transform the process of energy change into quasi-static steps. For each step the following differential applies according to the table (7.65)

$$dU = TdS - PdV + \mu dN, \tag{7.81}$$

or (as tacitly assumed in (7.80)) for fixed particle number ($dN = 0$)

$$dU = TdS - PdV = \delta Q + \delta W. \tag{7.82}$$

The 2nd term has to be identified with the work done

$$\delta W = -PdV \ ; \tag{7.83}$$

this leaves

$$\delta Q = TdS. \tag{7.84}$$

(**Note**: We rewrite δW and δQ to indicate that W and Q are not thermodynamic potentials.)

Equation (7.84) is consistent with the connection between entropy and heat, that is expressed in the second law, if we identify the missing information S with the entropy. Before we continue this line of arguments, let's once again briefly come back to the splitting of dU into the two parts heat and work.

Starting from the general formula for the average value of the internal energy

$$U = \textstyle\sum_i p_i E_i \tag{7.85}$$

we form

$$dU = \textstyle\sum_i E_i dp_i + \sum_i p_i dE_i = \delta Q + \delta W \ . \tag{7.86}$$

Since heat transfer occurs for fixed external parameters, and since for fixed external parameters (e.g. volume) the energy eigenvalues of the system are fixed, the first term in (7.86) represents the heat transfer,

(7.87)

$$\delta Q = \sum_i E_i dp_i,$$

originating from a change in the probabilities p_i describing the ensemble. Then it follows for the work done

$$\delta W = \sum_i p_i dE_i, \tag{7.88}$$

which stems from a change of external parameters (e.g. volume) leading to a change in the energy levels of the system.

The **2nd law of thermodynamics** states, that to a macroscopic system in equilibrium we can assign a quantity **entropy**, which has the following properties:

1. For quasi-static processes the heat absorbed by the system δQ is linked to an entropy change **dS** by

$$dS = \frac{\delta Q}{T}, \tag{7.89}$$

where *T* is the temperature of the system in equilibrium.

2. The entropy of an isolated system can never decrease $(\Delta S \geq 0)$.

The missing information *S*, that we have introduced according to equation (7.84) and (4.36), has exactly the properties required above and can therefore finally be identified with the entropy. Processes for which $S(0) = S(t)$ are called reversible, those with $S(0) < S(t)$ are called irreversible. Irreversible processes are therefore those that only run in a single direction; reversible processes are idealizations, that are necessary for the construction of the thermodynamics (example: **Carnot cycle**). Every real process contains irreversible parts and runs by itself until the entropy reaches a maximum: **statistical equilibrium**.

Notes:

(i) If one naively applies the above statements to the whole universe, then its entropy would have to increase continuously until total equilibrium is reached. However, this consideration is not conclusive, since we use statistical mechanics within the framework of a non-relativistic theory, which is certainly not applicable to the universe as a whole.

(ii) Note that (7.73) only applies to quasi-static processes. If this condition is not met, the inequality applies instead

$$TdS > dE + PdV - \mu dN. \tag{7.90}$$

3. Entropy is an **extensive** quantity.

This property of additivity also holds for the missing information *S*: Considering 2 independent systems 1, 2 with the statistical operators ρ_1, ρ_2 as a new, combined system $1+2$, its statistical operator is given by

$$\rho_{1+2} = \rho_1 \rho_2 = \rho_2 \rho_1; \tag{7.91}$$

note that the micro-states of the combined system are direct products of the micro-states of the individual systems. If one assumes ρ_1, ρ_2 to be normalized, we get:

$$S_{1+2} = -k_B Tr(\rho_1 \rho_2 \{\ln \ \rho_1 + \ln \ \rho_2\}) = S_1 + S_2 \tag{7.92}$$

as claimed above.

Note: In thermodynamics a distinction is made between **extensive** quantities (such as volume *V*, internal energy *U*, entropy *S*) and **intensive** quantities (such as temperature *T*, pressure *P*, density $\mathcal{N}/V$). Intensive quantities do not change if one divides a homogeneous system into smaller (but still large) systems, extensive quantities decrease in relation to the number of particles.

Example: A homogeneous system with a number of particles *N*, internal energy *U* and pressure *P* is divided into two equal parts: $N_1 = N_2 = 1/2N$; then $P_1 = P_2 = P$, but $U_1 = U_2 = 1/2\ U$.

The **3rd law of thermodynamics** provides a further statement about the entropy *S* :

> For every pure system, that contains only 1 type of particles, the following holds
>
> $$S(T = 0, \ldots) = 0 \tag{7.93}$$
>
> independent of the values of other variables (e.g. pressure or external magnetic field), on which *S* still depends.

For systems with several types of particles in the limit $T \to 0$ a nonzero **mixing entropy** remains.

The statement above can be derived as follows from statistical mechanics: The Hamilton operator has a discrete and limited spectrum from below,

$$E_0 < E_1 < E_2 < \cdots . \tag{7.94}$$

If *T* is small enough, i.e.

$$E_1 - E_0 \gg k_B T, \tag{7.95}$$

then follows (5.27)

$$p_i = \tfrac{1}{g_0} \tag{7.96}$$

for the states belonging to E_0,

$$p_i = 0 \quad \text{otherwise},$$

where g_0 is the degeneracy of the groundstate. Then

$$\lim_{T\to 0} S = k_B \ln \ g_0, \tag{7.97}$$

such that for systems with a non-degenerate ground state, $g_0 = 1$,

$$\lim_{T\to 0} S = 0. \tag{7.98}$$

Concrete examples are free fermions and free bosons, for which (7.98) can be proven directly (see Chaps. 9 and 10). On the other hand, for a classical ideal gas equation (7.98) is not fulfilled; the classical theory is no longer applicable at low temperatures (see Sect. 6.4).

The 3rd law of thermodynamics—in the formulation given above—cannot be tested experimentally since only entropy differences can be measured. However, it has a number of direct consequences, some of which are listed below.

7.8 Specific Heat

A heat transfer ΔQ increases the temperature of a system according to its heat capacity. The latter depends on both the nature of the system as well the type of heating. For a fixed number of particles—and without external fields—we have to distinguish between: heating at constant volume with the **heat capacity**

$$C_V =: \left(\frac{\partial U}{\partial T}\right)_V \tag{7.99}$$

and heating at constant pressure, where the heat capacity C_P is defined by

$$C_P =: \left(\frac{\partial [U+PV]}{\partial T}\right)_P = \left(\frac{\partial \epsilon}{\partial T}\right)_P; \tag{7.100}$$

here the quantity $\epsilon = U + PV$ is the **enthalpy**.

The definition (7.99) becomes immediately plausible, if one writes the total differential of U as

$$dU = \delta Q - PdV + \mu dN \tag{7.101}$$

and considers the case of constant particle number $(dN = 0)$ and constant volume $(dV = 0)$. To justify (7.100), we consider the total differential of $U + PV$,

$$d[U + PV] = \delta Q + VdP + \mu dN, \tag{7.102}$$

and takes the limit of constant pressure $(dP = 0)$ and constant particle number $(dN = 0)$.

We now want to show that the **specific heat** (heat capacity per unit mass) in both cases disappears at $T = 0$ as a consequence of the 3rd law of thermodynamics. We carry out the proof for C_V; for C_P it proceeds in analogy. For $dV = dN = 0$ we can write (7.101) with (7.89) as

$$dS = \left(\frac{\partial U}{\partial T}\right)_V \frac{dT}{T} = \frac{C_V}{T}\ dT \tag{7.103}$$

or in integral form

$$S(T) = \int_0^T \frac{C_V}{T'}\ dT', \tag{7.104}$$

since $S(T = 0) = 0$. In order to obtain a finite $S(T)$ the heat capacity C_V must disappear for $T' = 0$ to eliminate the singularity of $1/T'$.

This allows us to immediately prove that the model of the classical ideal gas at absolute zero temperature is wrong. We have found in Sect. 6.4 for the average value of the internal energy:

$$U = \frac{3}{2}\mathscr{N} k_B T, \tag{7.105}$$

such that:

$$C_V = \frac{3}{2}\ k_B \mathscr{N} \neq 0 \tag{7.106}$$

independent of T, thus contradicting the 3rd law. In Part III we will show that the ideal Fermi gas and the ideal Bose gas are consistent with the 3rd law.

7.9 Thermal Expansion Coefficient

The Maxwell relation, following from case III of the table (7.65) from the free energy G (for $dN = 0$), reads

$$\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial^2 G}{\partial P \partial T} \quad \rightarrow \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P. \tag{7.107}$$

Since $S(T, P) \rightarrow 0$ for $T \rightarrow 0$ for **all** values of P (or other parameters on which S may depend) follows i.e. the thermal expansion coefficient at constant pressure vanishes at absolute zero temperature. This can be illustrated using the example of an adiabatic change of pressure that the **absolute zero temperature** is inaccessible.

$$\boxed{\lim_{T\rightarrow 0} \left(\frac{\partial V}{\partial T}\right)_P = 0,} \tag{7.108}$$

To prove this, we first show that for an adiabatic change of pressure $(dS = 0)$ holds:

$$\boxed{dT = \left(\frac{\partial V}{\partial T}\right)_P \frac{T}{C_P} dP.} \tag{7.109}$$

Proof We rewrite the total differential

$$dS = \frac{1}{T}\ dU + \frac{P}{T}\ dV \tag{7.110}$$

in the variables U, V to the variables T, P by:

$$dS = \frac{1}{T}\left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP. \tag{7.111}$$

We replace in the first [..]:

$$\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial U + PV}{\partial T}\right)_P = C_P \tag{7.112}$$

and rewrite the second [..]—using the integrability condition $\partial^2 S/\partial T \partial P = \partial^2 S/\partial P \partial T$ in the form,

$$\frac{1}{T}\ \frac{\partial}{\partial P}\left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right]_T = \frac{\partial}{\partial T}\left(\frac{1}{T}\left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right]\right)_P. \tag{7.113}$$

This leads to the desired form:

$$\frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{T^2}\left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right]\ ; \tag{7.114}$$

all remaining terms in (7.113) cancel. Then for an adiabatic process $dS = 0$ follows from (7.111) with (7.112) and (7.113):

$$\frac{C_P}{T}\ dT = \left(\frac{\partial V}{\partial T}\right)_P dP, \quad q.e.d. \tag{7.115}$$

In a second step we prove that the quotient $(\partial V/\partial T)_P/C_P$ for $T \rightarrow 0$ remains finite. It then follows in (7.109) that with decreasing pressure the change in temperature becomes smaller and smaller. Since we know that $C_P \to 0$ for $T \to 0$, we can write for small temperatures

$$C_P = T^\nu (a + bT + \cdots) \tag{7.116}$$

where $\nu > 0$ and a, b are functions of P. We can connect $(\partial V / \partial T)_P$ with C_P as follows:

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T = -\frac{\partial}{\partial P}\int_0^T \frac{C_P}{T'}\ dT' = -\int_0^T \frac{\partial C_P}{\partial P}\ \frac{1}{T'}\ dT', \tag{7.117}$$

if we insert (7.114) into (7.111). With

$$\frac{\partial C_P}{\partial P} = T^\nu (a' + b'T + \cdots) \tag{7.118}$$

After carrying out the integral in (7.117):

$$\left(\frac{\partial V}{\partial T}\right)_P = -T^\nu \left(\frac{a'}{\nu} + \frac{b'T}{\nu+1} + \cdots\right), \tag{7.119}$$

then

$$\left(\frac{\partial V}{\partial P}\right)_P / C_P = -\frac{a'}{\nu a}\ :\ \text{finite.} \tag{7.120}$$

The result illustrates the (schematic) representation of $S = S(T, P)$ in Fig. 7.5 for $S(T)$. By a sequence of isothermal and adiabatic changes in pressure one can reduce the temperature; but since according to the 3rd law $S(T, P) = S(T, P')$ for $T = 0$ the absolute zero temperature cannot be reached within a finite number steps with a finite pressure difference. Analogy: **magnetic cooling** (see Part III).

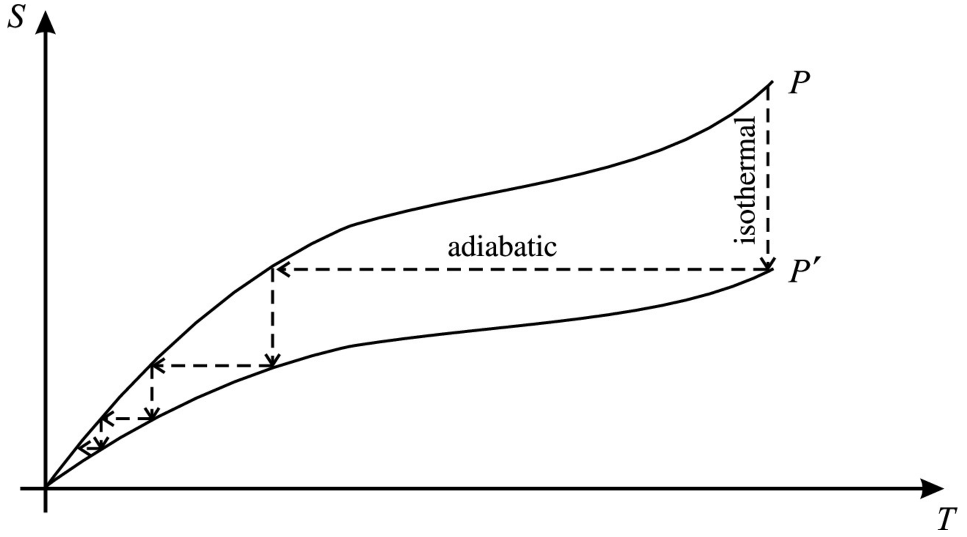

Fig. 7.5 Illustration of a sequence of isothermal and adiabatic changes in pressure for a reduction of the temperature

7.10 The Classical Ideal Gas

allows for a concrete evaluation of the previous considerations. First of all we want to look at the ideal gas equation. According to table (7.65) we can write P (in the case of the grand-canonical ensemble) as

(7.121)

$$P = -\left(\frac{\partial J}{\partial V}\right)_{T,\mu}$$

with

$$J = U - TS - \mu N = J(T, V, \mu). \tag{7.122}$$

This is just the case that fits the thermodynamic potential of the **grand-canonical** ensemble, i.e. (with $S = k_B(\ln Z_g + \beta U + \alpha N)$ or $TS = Tk_B \ln Z_g + U - \mu N$):

$$Tk_B \ln Z_g = \frac{1}{\beta} \ln Z_g = TS - U + \mu N = -J \tag{7.123}$$

according to equation (5.38). We can therefore obtain the pressure *P* from

$$P = \frac{1}{\beta} \left(\frac{\partial \ln Z_g}{\partial V}\right)_{T,\mu}. \tag{7.124}$$

We now calculate the quantity $\ln Z_g$ from (6.17) or (6.18) in the classical limit; with $\ln(1 \pm x) \approx \pm x \cdots$ for $|x| \ll 1$ we get immediately (with the $(+)$ sign for fermions and the (−) sign for bosons):

$$\ln Z_g = \pm \sum_i \ln\{1 \pm \exp(-\beta\epsilon_i - \alpha)\} \approx \sum_i \exp(-\beta\epsilon_i - \alpha) \tag{7.125}$$

$$= \exp(-\alpha) \sum_i \exp(-\beta\epsilon_i) = \exp(-\alpha) \frac{V}{\lambda^3}(2s+1) = \mathscr{N}.$$

Thus

$$P = -\left(\frac{\partial J}{\partial V}\right)_{T,\mu} = \frac{1}{\beta} \left(\frac{\partial \ln Z_g}{\partial V}\right)_{T,\mu} = \frac{1}{\beta} \exp(-\alpha) \frac{2s+1}{\lambda^3} = \frac{1}{\beta} \frac{\mathscr{N}}{V} = \frac{\mathscr{N}}{V} k_B T \tag{7.126}$$

or finally,

$$PV = \mathscr{N} k_B T. \tag{7.127}$$

From the internal energy $U = 3/2 \mathscr{N} k_B T$ (6.32) immediately follows:

$$C_V = \frac{3}{2} \mathscr{N} k_B, \tag{7.128}$$

in obvious contradiction to the 3rd law of thermodynamics: => the **classical approximation is not valid for low temperatures**! C_P follows from (7.100) with (6.32) and (7.127):

(7.129)

$$C_P = \frac{\partial(U+PV)}{\partial T} = C_V + \mathcal{N} k_B = \frac{5}{2}\mathcal{N} k_B.$$

For the ratio we get:

$$\kappa := \frac{C_P}{C_V} = \frac{5}{3}. \tag{7.130}$$

7.11 Special Changes of State

The following definitions hold in general and are illustrated for the example of the ideal gas (7.127) with fixed particle number N ($dN = 0$) to provide explicit results for the **work done** W_{12} and the **amount of heat absorbed** Q_{12}.

Isochoric changes: For isochoric changes of state the **volume** is constant ($dV = 0$), i.e. using the example of the ideal gas according to the equation of state (7.127)

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}; \qquad Q_{12} = U_2 - U_1 = C_V(T_2 - T_1). \tag{7.131}$$

Isobaric changes: For isobaric changes of state the **pressure** is constant ($dP = 0$), i.e. (using the example of the ideal gas) we get for the absorbed amount of heat Q_{12} and the work done on the system W_{12}

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}; \qquad W_{12} = \int_1^2 PdV = P(V_2 - V_1) = Nk_B(T_2 - T_1), \tag{7.132}$$

$$Q_{12} = \int_1^2 C_P \; dT = C_P \; (T_2 - T_1).$$

Isothermal changes: For isothermal changes of state the **temperature** (and therefore U, $dU = 0$) is constant, i.e. (using the example of the ideal gas) we get for the absorbed amount of heat Q_{12} and the work done on the system W_{12}

$$U_1 = U_2; \qquad \frac{P_1}{P_2} = \frac{V_2}{V_1}; \qquad PV = \text{const.}, \tag{7.133}$$

$$\delta W = -PdV = -Nk_B T \frac{dV}{V}$$

$$W_{12} = -\int_1^2 Nk_B T \frac{dV}{V} = -Nk_B T \ln\left(\frac{V_2}{V_1}\right) = -Nk_B T \ln\left(\frac{P_1}{P_2}\right),$$

$$\Delta U = 0 \;\; \rightarrow \;\; Q_{12} = -W_{12}.$$

Adiabatic changes: In this case the entropy is constant ($dS = 0$) and thus the absorbed heat $\delta Q = 0$;

$$dS = 0 \qquad \rightarrow \delta Q = 0. \tag{7.134}$$

The case of the ideal gas follows from $\ln Z_g = \text{const.}$ and $\lambda^2 \sim 1/T$ (6.31):

$$\frac{V}{\lambda^3} = \text{const.} \qquad \rightarrow VT^{3/2} = \text{const.} \qquad \rightarrow TV^{2/3} = TV^{\kappa-1} = \frac{T}{V}V^{\kappa} = \text{const.} \tag{7.135}$$

with $\kappa = 5/3 = C_P/C_V$. Since $T/V \sim P$ holds for the ideal gas, it follows

$$\boxed{PV^{\kappa} = \text{const.}} \tag{7.136}$$

For the ideal gas the following holds: $T/(PV) = \text{const.} \ \rightarrow (T/(PV))^{\kappa} = \text{const.}$ or $V^{\kappa} \sim T^{\kappa}P^{-\kappa}$ and it follows with (7.136)

$$\boxed{T^{\kappa}P^{-(\kappa-1)} = \text{const.} \qquad \rightarrow \left(\frac{T}{P^{(\kappa-1)/\kappa}}\right) = \text{const.}} \tag{7.137}$$

Together we get

$$\boxed{\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\kappa}; \qquad \frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{(\kappa-1)} = \left(\frac{P_1}{P_2}\right)^{(\kappa-1)/\kappa}.} \tag{7.138}$$

Since $\delta W = dU$ (for $\delta Q = 0$) we get for the work done on the system

$$\boxed{W_{12} = U_2 - U_1 = C_V(T_2 - T_1).} \tag{7.139}$$

7.12 The Carnot Cycle

A periodic machine, that converts thermal energy into mechanical energy, must have at least two heat reservoirs. The first heat bath provides energy to the system (heating phase) while the second heat bath absorbs energy from the system (cooling phase, e.g. in a cooling tower). We now want to discuss as an easy process the **Carnot cycle**. It consists of two isotherms ($dT = 0$) and two adiabates ($dS = 0$, δQ = 0) (see Fig. 7.6).

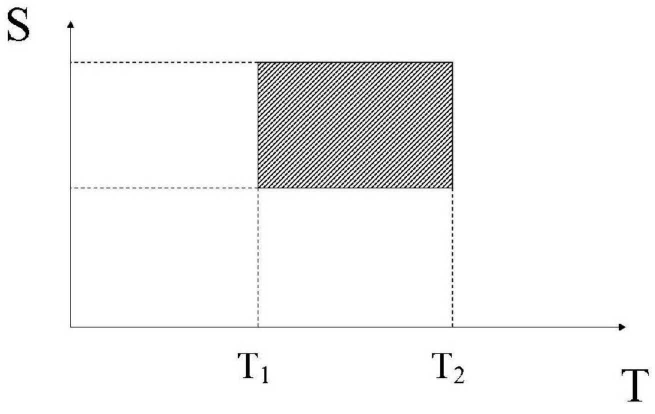

Fig. 7.6 Illustration of a Carnot cycle with two isotherms and two adiabates

Heat is only transferred when they come into contact with both of the heat reservoirs (of temperatures T_1, T_2). From

$$\oint dS = 0 \tag{7.140}$$

we get

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0; \qquad \rightarrow Q_2 = -\frac{T_2}{T_1} Q_1. \tag{7.141}$$

Since

$$\oint dU = 0 = \oint (\delta Q + \delta W) = Q_1 + Q_2 + W \tag{7.142}$$

the work absorbed by the system is

$$W = -(Q_1 + Q_2) = -Q_1 \; (1 - \frac{T_2}{T_1}). \tag{7.143}$$

Now let's assume $Q_1 > 0$, $Q_2 < 0$. The **efficiency coefficient** η is the ratio of the work done on the system ($-W$) to the amount of heat absorbed (Q_1). We get

$$\eta = -\frac{W}{Q_1} = 1 - \frac{T_2}{T_1} < 1, \tag{7.144}$$

which implies that the efficiency coefficient $\eta < 1$. For $T_1 > T_2$ the efficiency η becomes positive, i.e. the machine converts the absorbed heat (partially) into work. The efficiency increases with increasing temperature difference.

For $T_1 < T_2$ the efficiency η becomes negative, such that the machine does not produce work, but transforms mechanical work into heat. The heat bath with the higher temperature T_2 is supplied by heat and the heat bath 1 is cooled down. One can use this process (heat pump) to heat a house. This is technically interesting because we have to supply less mechanical energy for the heating than the gain in heat $-Q_2$ for the house. An electric heat pump is thus cheaper than a direct electric heating.

The second law of thermodynamics provides all of these statements without referring to a special system (gas, crystal etc.). The Carnot machine is therefore universal. The efficiency coefficient

$$\eta = 1 - \frac{T_2}{T_1} \tag{7.145}$$

is even the efficiency of all reversible machines with two heat reservoirs.

7.13 The Otto Engine

We now consider a circular process, which simulates the situation for an Otto engine, and consists of four sub-processes (see Fig. 7.7):

1→ 2 : Adiabatic compression ($dS = 0$) from volume $V_1 \to V_2$

2→ 3: At constant volume V_2 the amount of heat Q_{23} (due to the explosion of the gas mixture) is transferred

3→ 4 : Adiabatic expansion to volume V_1 (at $dS = 0$)

4→ 1: At constant volume V_1 the amount of heat $-Q_{41}$ is released.

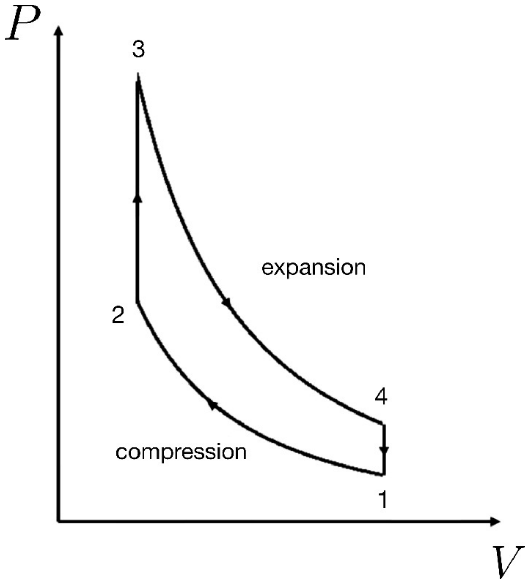

Fig. 7.7 Illustration of a circular process for the simulation of an Otto engine with 2 isochoric and 2 adiabatic processes

To calculate the efficiency, we first determine the entropy change of the two isochoric processes ($V = \text{const}$):

$$\Delta S_{23} = \int_2^3 dS = \int_2^3 \frac{\delta Q}{T} = C_V \int_2^3 \frac{dT}{T} = C_V \ln\left(\frac{T_3}{T_2}\right) = C_V \ln \frac{U_3}{U_2} = C_V \ln \frac{U_2+Q_{23}}{U_2}, \quad (7.146)$$

$$\Delta S_{14} = C_V \ln \frac{U_1 + Q_{14}}{U_1}.$$

Since

$$\Delta S_{23} = \Delta S_{14} \;\to \ln\left(\frac{U_2+Q_{23}}{U_2}\right) = \ln\left(\frac{U_1+Q_{14}}{U_1}\right); \quad (7.147)$$

we obtain

$$U_2(U_1 + Q_{14}) = U_1(U_2 + Q_{23}) \quad \to U_2 Q_{14} = U_1 Q_{23} \;\to T_2 Q_{14} = T_1 Q_{23}. \quad (7.148)$$

This results in the efficiency coefficient for the cycle process—using the adiabatic relations for an ideal classical gas—

$$\boxed{\eta = \frac{W_{1234}}{Q_{23}} = \frac{Q_{23}-Q_{14}}{Q_{23}} = 1 - \frac{T_1}{T_2} = 1 - \left(\frac{P_1}{P_2}\right)^{(\kappa-1)/\kappa} = 1 - \left(\frac{V_2}{V_1}\right)^{(\kappa-1)}. \quad (7.149)}$$

The efficiency coefficient η consequently increases with higher compression.

In summarizing this chapter we have established the relation of the Lagrange parameters to the temperature, chemical potential and the pressure. Furthermore, thermodynamical potentials have been introduced for the different ensembles, that are functions of the natural variables as well as their total differentials. The latter lead to various Maxwell relations between thermodynamic quantities. We have formulated (and proven) the main laws of thermodynamics and discussed in particular the specific heat and the thermal expansion coefficient. It was shown that the classical ideal gas violates in particular the 3rd law of thermodynamics. Finally, we have discussed different changes of state and computed the efficiency coefficient for the Carnot cycle and the Otto engine.

W. Cassing, *Theoretical Physics Compact IV*
https://doi.org/10.1007/978-3-031-95518-1_8

8. Small Deviations from Equilibrium

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In this chapter we want to examine the connection between **spontaneous fluctuations** of physical quantities around their average values in statistical equilibrium and **forced deviations** from the average values due to disturbances of the balance **by external perturbations**. It will show up, that these two phenomena are closely linked for **weak** external perturbations and find their expression in the **fluctuation-dissipation theorem**. To this aim we will introduce the thermodynamic perturbation theory and compute response functions for various examples.

8.1 Fluctuations

In Chap. 8 we have made the fundamental assumption, that macroscopic properties of a physical system can be calculated in the form of average values over the statistical ensemble representing the total system. As a measure of the quality of this approximation one can use the **relative quadratic fluctuation**

$$\frac{\Delta A}{\langle A\rangle} \tag{8.1}$$

with

$$(\Delta A)^2 = \langle A^2\rangle - \langle A\rangle^2 \tag{8.2}$$

of an observable A. Higher order fluctuations are required in rare cases. We consider as two important concrete cases **fluctuations in energy and particle number**.

For the internal energy U of a canonical ensemble we have found

$$U = \frac{Tr(H\ \exp(-\beta H))}{Tr(\exp(-\beta H))}\,. \tag{8.3}$$

We get the fluctuation by differentiating (8.3) with respect to β:

$$\boxed{\begin{aligned}\frac{\partial U}{\partial \beta} &= -\frac{Tr(H^2 \exp(-\beta H))}{Tr(\exp(-\beta H))} + \frac{[Tr(H\ \exp(-\beta H))]^2}{[Tr(\exp(-\beta H))]^2}\\ &= -\langle H^2\rangle + \langle H\rangle^2 = -(\Delta H)^2\end{aligned}} \tag{8.4}$$

therefore (with $\partial T/\partial\beta = -k_B T^2$)

$$\left(\Delta H\right)^2 = -\frac{\partial U}{\partial\beta} = -\frac{\partial U}{\partial T}\ \frac{\partial T}{\partial\beta} = k_B T^2\ \frac{\partial U}{\partial T} = k_B T^2\ C_V\ . \tag{8.5}$$

With (7.99) this leads to

$$\left(\frac{\Delta H}{\langle H\rangle}\right)^2 = \frac{k_B T^2 C_V}{U^2}. \tag{8.6}$$

Since U and C_V grow as extensive quantities—in contrast to T—linear with particle number N, the relative fluctuation depends on the number of particles as

$$\frac{\Delta H}{\langle H\rangle} \sim \frac{1}{\sqrt{N}}, \tag{8.7}$$

such that for large systems the energy fluctuations are negligible compared to the total energy, if one is not in the immediate vicinity of a phase transition, where C_V may become singular.

Example: For the ideal classical gas we have found

$$\langle H\rangle = U\ = \frac{3}{2}\ N\ k_B T, \tag{8.8}$$

such that

$$\frac{\Delta H}{\langle H\rangle} = \left(\frac{k_B T^2 C_V}{\left(3/2 N k_B T\right)^2}\right)^{1/2} = \left(\frac{k_B^2 T^2 3/2N}{\left(3/2 N k_B T\right)^2}\right)^{1/2} = \sqrt{\frac{2}{3}}\frac{1}{\sqrt{N}}. \tag{8.9}$$

The mean-square fluctuation of the particle number in the grand-canonical ensemble can be calculated in analogy from

$$\langle\hat N\rangle = \frac{Tr(\hat N \exp(-\alpha\hat N - \beta H))}{Tr(\exp(-\alpha\hat N - \beta H))}; \tag{8.10}$$

then we get in correspondence to (8.5):

$$\left(\Delta\hat N\right)^2 = -\frac{\partial\langle\hat N\rangle}{\partial\alpha}. \tag{8.11}$$

In analogy to (8.6) $\Delta\hat N$ can be written (with the **isothermal compressibility**)

$$\kappa_T := \; -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{8.12}$$

as (proof see below)

$$\left(\frac{\partial N}{\partial \mu}\right)_T = \frac{N^2}{V} \;\; \kappa_T \tag{8.13}$$

or with $\alpha = -\beta\mu$ ($\partial/\partial\alpha = -1/\beta \;\, \partial/\partial\mu$)

$$\boxed{\frac{(\Delta\hat{N})^2}{N^2} = \frac{k_B T}{N^2}\left(\frac{\partial N}{\partial \mu}\right) = \frac{k_B T \;\kappa_T}{V}.} \tag{8.14}$$

Since *V* is an extensive quantity, but *T* and κ_T are intensive quantities, the remaining result is ($\mathscr{N} =: \langle\hat{N}\rangle$)

$$\boxed{\frac{\Delta\hat{N}}{\langle\hat{N}\rangle} \sim \frac{1}{\sqrt{\mathscr{N}}}.} \tag{8.15}$$

Addition: (proof of equation (8.13))

For homogeneous systems we have for extensive quantities such as the average energy $U = U(S,V,N)$:

$$\nu U = U(\nu S, \nu V, \nu N), \tag{8.16}$$

since *S*, *V*, *N* are also extensive. Specifically, for $\nu = 1+\epsilon$, $|\epsilon| \ll 1$ follows by Taylor expansion in (8.16):

$$(1+\epsilon)U = U + \epsilon\Big(S\big[\tfrac{\partial U}{\partial S}\big]_{V,N} + V\big[\tfrac{\partial U}{\partial V}\big]_{S,N} + N\big[\tfrac{\partial U}{\partial N}\big]_{S,V}\Big). \tag{8.17}$$

A comparison of the factors in ϵ gives

$$U = TS - PV + \mu N, \tag{8.18}$$

if we consider case *V* from the table (7.65). Comparing the total differential of *U* according to (8.18) with the result of table (7.65), then the **Gibbs–Duhem relation** results:

$$SdT - \mathscr{V}dP + \mathscr{N}d\mu = 0. \tag{8.19}$$

Since in (8.19) T, P, μ are the natural variables, we have written volume and particle number as average values $\mathscr{V}$, $\mathscr{N}$. For **isothermal** ($dT = 0$), quasi-static processes follows:

(8.20)

$$\mathscr{V} dP = \mathscr{N} d\mu$$

or

$$\mathscr{V} \left(\frac{\partial P}{\partial \mathscr{N}} \right)_T = \mathscr{N} \left(\frac{\partial \mu}{\partial \mathscr{N}} \right)_T. \tag{8.21}$$

Since *P* in homogeneous systems, apart from *T*, only depends on the density $\mathscr{N}/\mathscr{V}$, we get

$$\mathscr{V} \left(\frac{\partial P}{\partial \mathscr{V}} \right)_T = -\mathscr{N} \left(\frac{\partial P}{\partial \mathscr{N}} \right)_T, \tag{8.22}$$

$$\kappa_T =: -\frac{1}{\mathscr{V}} \left(\frac{\partial \mathscr{V}}{\partial P} \right)_T = \frac{\mathscr{V}}{\mathscr{N}^2} \left(\frac{\partial \mathscr{N}}{\partial \mu} \right)_T. \tag{8.23}$$

As an example for formula (8.14) we consider an ideal classical gas with $\mathscr{V} = \mathscr{N}\ k_B T/P$. Then:

$$\kappa_T = -\frac{1}{\mathscr{V}} \left(\frac{\partial \mathscr{V}}{\partial P} \right)_T = \frac{\mathscr{N} k_B T}{P^2 \mathscr{V}} = \frac{1}{P}, \tag{8.24}$$

such that

$$\frac{\overline{(\Delta \hat{N})^2}}{\mathscr{N}^2} = \frac{k_B T}{P \mathscr{V}} = \frac{k_B T}{\mathscr{N} k_B T} = \frac{1}{\mathscr{N}}. \tag{8.25}$$

Result: For macroscopic systems the fluctuations of energy and particle number are negligible compared to the energy and particle number of the systems.

Therefore, for macroscopic systems it is practically meaningless whether one describes the system by the microcanonical, the canonical or the grand-canonical ensemble, as long as one is only interested in statements about the system in equilibrium. The choice of the ensemble—describing the system—then can be done from the point of view of simpler calculations. On the other hand, fluctuations are important when we consider small deviations from the equilibrium by external perturbations. Examples for this are Eqs. (8.6) and (8.14), in which the specific heat or the isothermal compressibility are linked with the fluctuations of energy and particle number. **Specific heat and compressibility characterize the response of the system to external perturbation in the form of heat supply or pressure.**

We now want to investigate the connection between fluctuations and the response of the system for (weak) external perturbations.

8.2 Thermodynamic Perturbation Theory

We first consider the case of a time-independent perturbation. Let's decompose the entire Hamiltonian as

$$H = H_0 + W, \tag{8.26}$$

where H_0 can be treated exactly and W is a small time-independent perturbation ($W \neq W(t)$). We describe the system by a canonical ensemble. Then it makes sense to separate the factor exp $(-\beta\ H_0)$ from the operator exp $(-\beta\ H)$, which can be treated exactly according to assumption:

$$\exp\{-\beta[H_0 + W]\} = \exp\{-\beta H_0\} \cdot \sigma(\beta). \tag{8.27}$$

To determine $\sigma(\beta)$ we differentiate (8.27) with respect to β and get:

$$\frac{\partial}{\partial\beta}\exp\{-\beta[H_0 + W]\} = \frac{\partial}{\partial\beta}\exp\{-\beta H_0\} \cdot \sigma(\beta)$$

$$= -[H_0 + W]\exp\{-\beta[H_0 + W]\} = -H_0\exp\{-\beta H_0\}\sigma(\beta) + \exp\{-\beta H_0\}\tfrac{\partial\sigma}{\partial\beta}. \tag{8.28}$$

After inserting (8.27) into (8.28) ($-W\ \exp\ (-\beta H_0)\sigma(\beta) = \exp\ (-\beta H_0)\partial\sigma/\partial\beta$) and multiplication by exp (βH_0) the **Bloch equation** results:

$$\tfrac{\partial\sigma}{\partial\beta} = -\exp\{\beta H_0\}\ W\ \ \exp\{-\beta H_0\}\sigma(\beta) = -W(\beta)\sigma(\beta) \tag{8.29}$$

with the abbreviation

$$W(\beta) = \exp\{\beta H_0\}\ W\ \ \exp\{-\beta H_0\}. \tag{8.30}$$

The Bloch equation is formally structured in analogy to the Dirac picture of quantum theory (see quantum mechanics). Consequently, one can formally transfer the **Dirac perturbation theory**: We transfer (8.29) with the boundary condition—following from (8.27)—

$$\sigma(\beta = 0) = 1 \tag{8.31}$$

into an integral equation

$$\sigma(\beta) = 1 - \textstyle\int_0^\beta\ W(\beta')\sigma(\beta')\ d\beta', \tag{8.32}$$

which can be solved by iteration:

$$\sigma(\beta) = 1 - \int_0^\beta \; W(\beta')d\beta' + \int_0^\beta W(\beta') \int_0^{\beta'} \; W(\beta'') \; d\beta'' d\beta' - \cdots \; . \tag{8.33}$$

To calculate the canonical partition function Z_c we use the basis of the eigenstates $|\Phi_i\rangle$ of H_0 with energies ϵ_i,

$$\begin{aligned} Z_c \; &= \sum_i \langle\Phi_i| \text{exp}\,\{-\beta H_0\}\sigma(\beta)|\Phi_i\rangle = \sum_i \text{ exp }(-\beta\epsilon_i)\langle\Phi_i|\sigma(\beta)|\Phi_i\rangle \\ &= \sum_i \text{ exp }(-\beta\epsilon_i)\sigma(\beta)_{ii}. \end{aligned} \tag{8.34}$$

Thus we need the diagonal elements of $\sigma(\beta)$ in the basis of the eigenstates of H_0. For these matrix elements we obtain from (8.33):

$$\begin{aligned} \sigma(\beta)_{ii} = \; & 1 - \beta W_{ii} + \tfrac{1}{2} \; \beta^2 |W_{ii}|^2 \\ & - \sum_{j\neq i} |W_{ij}|^2 \Big(\tfrac{\beta}{(\epsilon_i - \epsilon_j)} + \tfrac{1-\text{exp}\{\beta(\epsilon_i-\epsilon_j)\}}{(\epsilon_i-\epsilon_j)^2}\Big) \dots \end{aligned} \tag{8.35}$$

with

$$\langle\Phi_i| \int_0^\beta \text{ exp }\{\beta\epsilon_i\} W \text{ exp }\{-\beta\epsilon_i\} d\beta |\Phi_i\rangle = \beta W_{ii}.$$

Furthermore, the completeness of the intrinsic states has been exploited in the 2nd order contribution:

$$I_{ii} = (\int_0^\beta W(\beta') \int_0^{\beta'} W(\beta'') d\beta'' d\beta')_{ii} \tag{8.36}$$

$$\begin{aligned} = \quad & \sum_j \langle\Phi_i| \int_0^\beta \text{ exp }(\beta' H_0) W \text{ exp }(-\beta' H_0)|\Phi_j\rangle \\ & \langle\Phi_j| \int_0^{\beta'} \text{ exp }(\beta'' H_0) W \text{ exp }(-\beta'' H_0)|\Phi_i\rangle d\beta'' d\beta' \\ = \quad & |W_{ii}|^2 \int_0^\beta \int_0^{\beta'} d\beta'' d\beta' \\ & + \sum_{j\neq i} |W_{ij}|^2 \int_0^\beta \text{ exp }(\beta'(\epsilon_i - \epsilon_j)) \int_0^{\beta'} \text{ exp }(\beta''(\epsilon_j - \epsilon_i)) d\beta'' d\beta' \end{aligned}$$

with $W_{ij} = \langle\Phi_i|W|\Phi_j\rangle$. It is worth noting, furthermore, that the terms with $i = j$ and with $i \neq j$ had to be integrated separately. The remaining integrals give

$$I_{ii} = \tfrac{1}{2}|W_{ii}|^2\beta^2 + \sum_{j\neq i} |W_{ij}|^2 \int_0^\beta \text{ exp }(\beta'(\epsilon_i - \epsilon_j)) \tfrac{\text{exp}(\beta'(\epsilon_j-\epsilon_i))-1}{(\epsilon_j-\epsilon_i)} d\beta' \tag{8.37}$$

$$= \frac{1}{2}|W_{ii}|^2\beta^2 + \beta \sum_{j\neq i} \frac{|W_{ij}|^2}{\epsilon_j - \epsilon_i} + \sum_{j\neq i} |W_{ij}|^2 \frac{\text{exp }(\beta(\epsilon_i - \epsilon_j)) - 1}{(\epsilon_j - \epsilon_i)^2} \; .$$

When calculating Z_c with $\sigma(\beta)$ (8.35) the last term of (8.37) disappears exactly, since *i*, *j* run through the same values and $W = W^\dagger$,

$$\begin{aligned}&\sum\nolimits_{i\neq j} |W_{ij}|^2 \exp\left(-\beta\epsilon_i\right)\frac{[1-\exp\{\beta(\epsilon_i-\epsilon_j)\}]}{(\epsilon_i-\epsilon_j)^2}\\ &= \sum\nolimits_{i\neq j} |W_{ij}|^2\left(\frac{\exp(-\beta\epsilon_i)}{(\epsilon_j-\epsilon_i)^2} - \frac{\exp(-\beta\epsilon_j)}{(\epsilon_j-\epsilon_i)^2}\right) \equiv 0.\end{aligned} \tag{8.38}$$

It remains

$$Z_c = \sum\nolimits_i \exp\left(-\beta\epsilon_i\right)\left(1-\beta W_{ii} + \frac{1}{2}\ \beta^2|W_{ii}|^2 - \beta\sum\nolimits_{j\neq i}\frac{|W_{ij}|^2}{(\epsilon_i-\epsilon_j)}\dots\right)\ . \tag{8.39}$$

With the abbreviations

$$Z_c^0 = \sum\nolimits_i \exp\left(-\beta\epsilon_i\right); p_i = \frac{\exp(-\beta\epsilon_i)}{\sum_j \exp(-\beta\epsilon_j)} = \frac{\exp(-\beta\epsilon_i)}{Z_c^0} \tag{8.40}$$

we obtain a more suitable form for the further evaluation:

$$\boxed{Z_c = Z_c^0\left(1-\beta\sum\nolimits_i W_{ii}\ p_i + \frac{1}{2}\ \beta^2\sum\nolimits_i\{W_{ii}^2\ p_i - \sum\nolimits_{j\neq i}\frac{|W_{ij}|^2\cdot(p_i-p_j)}{\beta(\epsilon_i-\epsilon_j)}\}\right). \qquad (8.41)}$$

The explicit result for the last term in (8.41) is derived as

$$\begin{aligned}&\sum\nolimits_{j\neq i}\frac{p_i|W_{ij}|^2}{(\epsilon_i-\epsilon_j)} = \sum\nolimits_{j\neq i}\frac{(p_i-p_j)|W_{ij}|^2}{(\epsilon_i-\epsilon_j)} + \sum\nolimits_{j\neq i}\frac{p_j|W_{ij}|^2}{(\epsilon_i-\epsilon_j)}\\ &= \sum\nolimits_{j\neq i}\frac{(p_i-p_j)|W_{ij}|^2}{(\epsilon_i-\epsilon_j)} - \sum\nolimits_{j\neq i}\frac{p_j|W_{ij}|^2}{(\epsilon_j-\epsilon_i)},\end{aligned} \tag{8.42}$$

or

$$2\sum\nolimits_{j\neq i}\frac{p_i|W_{ij}|^2}{(\epsilon_i-\epsilon_j)} = \sum\nolimits_{j\neq i}\frac{(p_i-p_j)|W_{ij}|^2}{(\epsilon_i-\epsilon_j)}. \tag{8.43}$$

The term linear in *W* is just the average of *W* in the ensemble described by H_0,

$$\langle W\rangle_0 = \sum\nolimits_i p_i\ W_{ii}. \tag{8.44}$$

To evaluate the remaining terms in (8.41) we assume that[1] $\beta(\epsilon_i-\epsilon_j) \ll 1$ such that (in leading order in β)

$$p_i - p_j = \frac{\exp(-\beta\epsilon_i)-\exp(-\beta\epsilon_j)}{\sum_k\exp(-\beta\epsilon_k)} = \frac{\exp(-\beta\epsilon_i)(1-\exp(\beta(\epsilon_i-\epsilon_j))}{\sum_k\exp(-\beta\epsilon_k)} \tag{8.45}$$

$$= p_i(1-\ \exp\left[\beta(\epsilon_i-\epsilon_j)\right]) \approx -p_i\beta(\epsilon_i-\epsilon_j),$$

thus

$$\sum_{j\neq i}\frac{|W_{ij}|^2(p_i-p_j)}{[\beta(\epsilon_i-\epsilon_j)]}\approx -\sum_{j\neq i}p_i|W_{ij}|^2. \tag{8.46}$$

Due to the completeness of the eigenstates $|\Phi_i\rangle$ to H_0 we have:

$$\langle\Phi_i|W^2|\Phi_i\rangle=\sum_j\langle\Phi_i|W|\Phi_j\rangle\langle\Phi_j|W|\Phi_i\rangle=W_{ii}^2+\sum_{j\neq i}|W_{ij}|^2. \tag{8.47}$$

Thus (8.41) achieves the transparent form for Z_c:

$$\boxed{Z_c=Z_c^0\left(1-\beta\langle W\rangle_0+\tfrac{1}{2}\ \beta^2\langle W^2\rangle_0\dots\right) \tag{8.48}}$$

and the free energy $F=-k_BT\ \ \ln\ \ Z_c=-\beta^{-1}\ln\ \ Z_c$ takes the form

$$\boxed{F=-\tfrac{1}{\beta}\left(\ln\ \ Z_c^0+\ln\left[1-\beta\langle W\rangle_0+\tfrac{1}{2}\beta^2\langle W^2\rangle_0\dots\right]\right) \tag{8.49}}$$

With the expansion $\ln\ (1+x)=-\sum_{n=1}(-1)^nx^n/n\approx x-1/2x^2\cdots$ we obtain for $x=(-\beta\langle W\rangle_0+1/2\beta^2\langle W^2\rangle_0)$

$$F=F^0+\tfrac{1}{\beta}\left(-(-\beta\langle W\rangle_0+\tfrac{1}{2}\beta^2\langle W^2\rangle_0)+\tfrac{1}{2}(-\beta\langle W\rangle_0+\tfrac{1}{2}\beta^2\langle W^2\rangle_0)^2\dots\right) \tag{8.50}$$

$$\approx F^0+<W\rangle_0-\frac{1}{2}\ \beta\langle W^2\rangle_0+\frac{1}{2}\beta\langle W\rangle_0^2)\ \ \dots$$

$$=F^0+\langle W\rangle_0-\frac{1}{2}\ \beta(\langle W^2\rangle_0-\langle W\rangle_0^2)\ \ \dots=F^0+\langle W\rangle_0-\frac{1}{2}\ \beta\langle\Delta W^2\rangle_0\ \ \dots$$

in first order in β.

Thus we can express the corrections to the free energy *F*—caused by the perturbation *W*—by the average of *W* and its quadratic fluctuation in the undisturbed equilibrium, described by the statistical operator $\rho_0=\exp\ (-\beta H_0)/Tr(\exp\ (-\beta H_0))$.

We apply the formalism above to the case that an external force *f* (e.g. a homogeneous magnetic or electric field) acts on an observable *q* of the system (e.g. magnetic moment or electric current density), and ask how (small) changes of *f* affect the system. To this aim we write in (8.26)

$$H=H_0+W;\ W=-q\ \delta f, \tag{8.51}$$

where δf are the small changes which describe the external force. The associated thermodynamic potential is the free enthalpy $G = F + PV$, which differs from F by the potential energy due to the external force. According to (8.50) we get

$$\begin{aligned} G &= G^0 - \langle q\rangle_0 \delta f - \tfrac{1}{2}\ \beta \langle \Delta q^2\rangle_0\ (\delta f)^2 \cdots \\ &= G^0 - \langle q\rangle_0 \delta f - \tfrac{1}{2}\ \chi\ (\delta f)^2 \cdots, \end{aligned} \tag{8.52}$$

where χ is the **generalized susceptibility**,

$$\chi = \beta\langle (q - \langle q\rangle_0)^2\rangle_0 = \beta\langle \Delta q^2\rangle_0, \tag{8.53}$$

described by the product of β and the mean square fluctuation of q in the unperturbed equilibrium ensemble.

8.3 Linear Response

We now want to investigate the changes of the average value of an observable $\langle q\rangle$, if a time-dependent force $f(t)$ acts on q.

Examples: Current density under the influence of a time-dependent electric field; magnetic moment under the influence of a time-dependent magnetic field ($W = -\mathbf{d}\cdot\delta\mathbf{E}$ or $W = -\overrightarrow{\mu}\cdot\delta\overrightarrow{B}$).

Then in

$$\langle q(t)\rangle = Tr(q\ \rho(t)) \tag{8.54}$$

the statistical operator has to be determined from (see Eq. (3.4)):

$$\frac{\partial}{\partial t}\ \rho = -\frac{i}{\hbar}[H, \rho(t)] = -\frac{i}{\hbar}[H_0 + W, \rho(t)] = -\frac{i}{\hbar}[H_0 - q\ \ f(t), \rho(t)], \tag{8.55}$$

if H_0 is the complete Hamiltonian of the system without any external force.

For the approximate calculation of (8.54) we use the **Dirac picture of time-dependent perturbation theory** (see quantum mechanics):

$$q(t) = \exp\{\tfrac{i}{\hbar} H_0 t\}\ q\ \ \exp\{-\tfrac{i}{\hbar} H_0 t\}, \tag{8.56}$$

$$\sigma(t) := \exp\{\tfrac{i}{\hbar} H_0 t\}\ \rho(t)\ \ \exp\{-\tfrac{i}{\hbar} H_0 t\}, \tag{8.57}$$

and obtain

$$\langle q(t)\rangle = Tr\{q(t)\sigma(t)\}; \tag{8.58}$$

$\sigma(t)$ is easily found to obey the differential equation:

$$\boxed{\frac{\partial}{\partial t}\ \sigma(t) = \frac{i}{\hbar}[q(t),\sigma(t)]\ f(t), \tag{8.59}}$$

if we treat $f(t)$ as a classical function. As an initial condition we want to require, that the system is in thermal equilibrium at temperature T before switching on the perturbation $f(t)$,

$$\rho(-\infty) = \rho_0 = \frac{\exp(-\beta H_0)}{Tr(\exp(-\beta H_0))}. \tag{8.60}$$

For sufficiently weak forces $f(t)$ we can restrict to the first two terms of the perturbation theory,

$$\sigma(t) = \rho_0 + \frac{i}{\hbar}\int_{-\infty}^{t}[q(t'),\rho_0]\ f(t')\ dt'\ldots, \tag{8.61}$$

and obtain with

$$Tr\{q(t)[q(t'),\rho_0])\} = Tr\{q(t)q(t')\rho_0 - q(t)\rho_0 q(t')\} \tag{8.62}$$

$$= Tr\{q(t)q(t')\rho_0 - q(t')q(t)\rho_0\} = Tr\{[q(t),q(t')]\rho_0\}$$

(cyclic invariance of the trace) for the average value

$$\langle q(t)\rangle = Tr(q(t)\sigma(t)) = \langle q\rangle_0 + \frac{i}{\hbar}\int_{-\infty}^{t} Tr(q(t)[q(t'),\rho_0])\ f(t')\ dt' \tag{8.63}$$

$$= \langle q\rangle_0 + \frac{i}{\hbar}\int_{-\infty}^{t} Tr([q(t),q(t')]\rho_0)\ f(t')\ dt'$$

$$= \langle q\rangle_0 + \frac{i}{\hbar}\int_{-\infty}^{\infty} \Theta(t-t')\langle[q(t),q(t')]\rangle_0\ f(t')\ dt'.$$

In (8.63) Θ denotes the Theta-function:

$$\Theta(t-t') = 1 \text{ if } t \geq t'; \Theta(t-t') = 0 \text{ else}, \tag{8.64}$$

which allows to extend the upper integral limit in (8.63) to ∞.

We now take advantage of the fact that the undisturbed ensemble ρ_0 is stationary, i.e.

(8.65)

$$\langle[q(t), q(t')]\rangle_0 = \langle[q(t-t'), q(0)]\rangle_0,$$

and perform a Fourier transformation in (8.63). Introducing:

$$q_\omega = q(\omega) =: \int_{-\infty}^{\infty} (\langle q(t)\rangle - \langle q\rangle_0) \exp{(i\omega t)}\ dt, \tag{8.66}$$

$$f_\omega = f(\omega) =: \int_{-\infty}^{\infty} f(t) \exp{(i\omega t)}\ dt \tag{8.67}$$

$$r(\omega) =: \tfrac{i}{\hbar} \int_0^{\infty} \langle[q(t), q(0)]\rangle_0 \exp{(i\omega t)}\ dt \tag{8.68}$$

we get—after multiplying (8.63) by $\exp{(i\omega t)}$ and integration $[-\infty, \infty] \ldots dt$—the equivalent relationship

$$q(\omega) = \int_{-\infty}^{\infty} dt\ \ \exp{(i\omega t)}(\langle q(t)\rangle - \langle q\rangle_0) \tag{8.69}$$

$$= \tfrac{i}{\hbar} \int_{-\infty}^{\infty} dt\ \ \exp{(i\omega t)}\ \ \int_{-\infty}^{\infty} \Theta(t-t')\langle[q(t-t'), q(0)]\rangle_0\ f(t')\ dt'$$
$$= r(\omega)\ f(\omega).$$

In (8.69) the **response function** of the system $r(\omega)$ appears as a multiplicative function. For any external (small) perturbation $f(\omega)$, the response function $r(\omega)$ is a characteristic function of the system, which we will examine in more detail below.

Note: The transition (8.63) → (8.69) is denoted by **convolution theorem**.

Inserting (8.65) into (8.63) we obtain a convolution integral of the type:

$$a(t) = \int_{-\infty}^{\infty} b(t-t')\ c(t')\ dt'. \tag{8.70}$$

After Fourier transformation of the quantities $a(t)$, $b(t)$ and $c(t)$ we obtain for the Fourier transform $a(\omega)$, $b(\omega)$ and $c(\omega)$ the simple algebraic relation

$$a(\omega) = b(\omega)c(\omega), \tag{8.71}$$

which is easy to prove explicitly. This folding theorem has been used when passing from (8.63) to (8.69). It should be noted that with regards to the integration limits in (8.68) $(\tau =: t - t')$:

$$r(\omega) = \tfrac{i}{\hbar} \int_{-\infty}^{\infty} \langle[q(\tau), q(0)]\rangle_0 \exp{(i\omega\tau)}\Theta(\tau)\ d\tau \tag{8.72}$$

$$= \frac{i}{\hbar} \int_0^\infty \langle [q(\tau), q(0)] \rangle_0 \exp\left(i\omega\tau\right)\, d\tau.$$

8.4 Examples

To illustrate the role of the response function $r(\omega)$, let's look at some simple examples.

1. The equation of motion of a damped harmonic oscillator under the influence of an external force is:

$$m\left(\frac{d^2}{dt^2} q(t) + \omega_0^2 q(t)\right) + \gamma\ \frac{d}{dt}\ q(t) = f(t). \tag{8.73}$$

After Fourier transformation of $q(t)$ and $f(t)$ we obtain

$$\{m(\omega_0^2 - \omega^2) - i\gamma\omega\} q(\omega) = f(\omega), \tag{8.74}$$

or after comparison with (8.69),

$$\boxed{r(\omega) = \frac{1}{m(\omega_0^2 - \omega^2) - i\ \gamma\omega} = \frac{m(\omega_0^2 - \omega^2) + i\ \gamma\omega}{m^2 {(\omega_0^2 - \omega^2)}^2 + \gamma^2\omega^2},} \tag{8.75}$$

with the imaginary part

$$\boxed{\Im(r(\omega)) = \frac{\gamma\omega}{m{(\omega_0^2 - \omega^2)}^2 + \gamma^2\omega^2}.} \tag{8.76}$$

2. In **Brownian motion** we investigate the motion of macroscopic particles (e.g. dust particles) in a gas or liquid due to thermal motion of the molecules of the gas or liquid, that collide with the macroscopic particles. The force acting on a macroscopic particle is divided into a **friction force** and a **stochastic** force, whose temporal average value vanishes:

$$m\ \frac{d^2}{dt^2} q + \gamma\ \frac{d}{dt}\ q = f(t) \tag{8.77}$$

with the time average of $f(t)$

$$\bar{f} = 0. \tag{8.78}$$

For this case we obtain in analogy to example 1 ($\omega_0 = 0$):

$$\boxed{r(\omega) = \frac{1}{-m\omega^2 - i\ \gamma\omega}.} \tag{8.79}$$

3. In metals the **electrical conductivity** is traced back to the existence of **free** electrons. The equation of motion for a conduction electron *i* is:

$$M\frac{d\mathbf{v}_i}{dt} + \xi\mathbf{v}_i = e\mathbf{E}_i, \tag{8.80}$$

where $\mathbf{E}_i$ is the electric field acting on the electron *i* and the friction term ($\sim \mathbf{v}_i$) takes care of the fact, that the conduction electrons lose energy through collisions with the ions of the grid.

From (8.80) we obtain for the current density ($\mathbf{j}_f = en\mathbf{v}$):

$$\frac{d\mathbf{j}_f}{dt} + \frac{\xi}{M}\mathbf{j}_f = n\frac{e^2}{M}\mathscr{E}, \tag{8.81}$$

where we have identified the average over $\mathbf{E}_i$ with the macroscopic field $\mathscr{E}$, while *n* is the electron density. For static $\mathscr{E}$ fields (8.81) has the stationary solution ($d\mathbf{j}_f/dt = 0$):

$$\mathbf{j}_f = \frac{ne^2}{\xi}\mathscr{E} = \sigma_0\mathscr{E} \tag{8.82}$$

with the **DC conductivity**

$$\boxed{\sigma_0 = \frac{ne^2}{\xi}. \tag{8.83}}$$

For a time-periodic field

$$\mathscr{E} = \mathscr{E}_0 \exp\left(-i\omega t\right) \tag{8.84}$$

we get for the solution of (8.81)

$$\mathbf{j}_f = \mathbf{j}_0 \exp\left(-i\omega t\right). \tag{8.85}$$

Equation (8.81) then gives the relation

$$\mathbf{j}_f = \sigma(\omega)\mathscr{E} = r(\omega)\mathscr{E} \tag{8.86}$$

with the **frequency-dependent conductivity** (response function)

$$\boxed{\sigma(\omega) = \frac{\sigma_0}{1-i\omega\tau} = \frac{\sigma_0(1+i\omega\tau)}{1+\omega^2\tau^2}; \tag{8.87}}$$

here the attenuation constant τ is determined by

$$\boxed{\tau = \frac{M}{\xi}. \tag{8.88}}$$

For low frequencies ($\omega\tau \ll 1$) the conductivity $\sigma(\omega)$ becomes real, $\sigma(\omega) \approx \sigma_0$, while vice versa for high frequencies ($\omega\tau \gg 1$) $\sigma(\omega)$ becomes purely imaginary, such that $\mathbf{j}_f$ and $\mathscr{E}$ are out of phase with each other by $\pi/2$.

4. We continue to look at a simple example for the **resistance noise**:

A circuit contains a capacity C and an ohmic resistance R, which is kept at a temperature T by a heat bath (see Fig. 8.1).

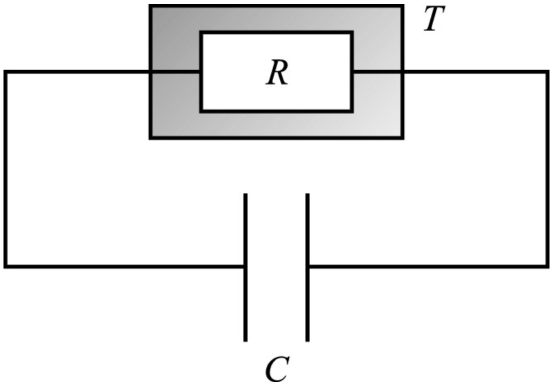

Fig. 8.1 Illustration of a circuit with a capacitor C and a resistance R kept on temperature T by a heat bath

If at the ends of the resistance R there is a voltage difference U, the average current in the circuit is $J = U/R$. Now the electrons—carrying the current—in addition to the thermal motion are subject to irregular scatterings with the atoms of the conductor. Hence the current fluctuates around the average U/R. In reality we expect the current

$$\tfrac{U}{R} = J + J_{th.}, \tag{8.89}$$

where $J_{th.}$ depends on the thermal motion of the electrons at temperature T; $J_{th.}$ therefore has nothing to do with the voltage U. With the connection of electric current change of the charge Q per unit time,

$$J = -\tfrac{d}{dt}\ Q = -C\ \tfrac{d}{dt}\ U, \tag{8.90}$$

we obtain (by multiplication with R)

$$U + RC\ \tfrac{d}{dt}\ U = U_{th.} \tag{8.91}$$

with the **fictitious** voltage

$$U_{th.} = R\ J_{th.} \tag{8.92}$$

After Fourier transformation of U and $U_{th.}$ we get

$$(1 - i\omega RC)U(\omega) = U_{th.}(\omega) \tag{8.93}$$

and by comparison with (8.69)

$$r(\omega)=\tfrac{1}{1-i\omega RC}=\tfrac{1+i\omega RC}{1+(\omega RC)^2}. \tag{8.94}$$

In all four examples the statistics only enter via the friction γ or the resistance *R*; that's why it's so easy to determine the response function $r(\omega)$.

8.5 Fluctuation-Dissipation Theorem

We now want to prove the connection between fluctuations in equilibrium—as stated at the beginning—with forced deviations from equilibrium due to time-dependent perturbations. The result will be a simple relationship between the **fluctuations of the observables**, on which the perturbation acts, and the **dissipative part of the response function** $r(\omega)$, which is responsible for the conversion of the work done by the external force on the system to internal energy.

For this purpose we introduce the **spectral functions**(ω) by

$$\begin{aligned} s(\omega) &= \tfrac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\langle q(t)q(0)\rangle_0 \exp\,(i\omega t)\;dt \\ &= \tfrac{1}{2\pi}\int_{-\infty}^{\infty} s(t)\;\;\exp\,(i\omega t)\;dt. \end{aligned} \tag{8.95}$$

$s(\omega)$ is a real function, i.e. $s(\omega)=s^{*}(\omega)$. To prove this, we form $\langle q(t)q(0)\rangle_0$ in the energy representation with $q(t)=\exp\,(i/\hbar H_0 t)q\,\exp\,(-i/\hbar H_0 t)$,

$$s(t)=\tfrac{1}{\hbar}\;\langle q(t)q(0)\rangle_0=\tfrac{1}{\hbar}\sum_i \tfrac{\exp\{-\beta\epsilon_i\}}{(\sum_k \exp(-\beta\epsilon_k))}\sum_j\langle\Phi_i|q(t)|\Phi_j\rangle\langle\Phi_j|q|\Phi_i\rangle \tag{8.96}$$

$$=\frac{1}{\hbar}\sum_{i,j}\frac{\exp\,\{-\beta\epsilon_i\}}{(\sum_k \exp\,(-\beta\epsilon_k))}|\langle\Phi_i|q|\Phi_j\rangle|^2\exp\left(\frac{i}{\hbar}[\epsilon_i-\epsilon_j]t\right).$$

The *t* integration in (8.95) then yields a δ-distribution in the argument $(\hbar\omega+\epsilon_i-\epsilon_j)$, i.e finally

$$s(\omega)=\sum_{i,j}|\langle\Phi_i|q|\Phi_j\rangle|^2\;\;\delta(\hbar\omega+\epsilon_i-\epsilon_j)\tfrac{\exp(-\beta\epsilon_i)}{\sum_k \exp(-\beta\epsilon_k)}\geq 0, \tag{8.97}$$

and is real as claimed. Another necessary relation—for the proof of the fluctuation-dissipation theorem—follows immediately by the substitution $\epsilon_i\to\epsilon_i=\epsilon_j+\hbar\omega$,

$$s(-\omega)=\exp\,(-\beta\hbar\omega)s(\omega). \tag{8.98}$$

For the proof, note that

$$\delta(-\hbar\omega + \epsilon_i - \epsilon_j) = \delta(\hbar\omega + \epsilon_j - \epsilon_i), \tag{8.99}$$

and that $|\langle\Phi_i|q|\Phi_j\rangle|^2$ is symmetric with respect to *i*, *j* and by virtue of the δ-distribution

$$\exp\,(-\beta\epsilon_i) \rightarrow \exp\,[-\beta(\epsilon_j + \hbar\omega)]. \tag{8.100}$$

We now need the connection of $s(\omega)$, $s(-\omega)$ with the complex response function $r(\omega)$. We separate the latter into real and imaginary parts

$$\boxed{r(\omega) = d(\omega) + i\pi\ a(\omega),} \tag{8.101}$$

where $d(\omega)$ is the **dispersive**, $a(\omega)$ the **dissipative** part (see explanation below). Using (8.68) we get

$$\tfrac{1}{\pi}\Im r(\omega) = a(\omega) = \tfrac{1}{2\pi i}(r(\omega) - r^*(\omega)) \tag{8.102}$$

$$= \frac{1}{2\pi i\hbar}\left(i\int_0^\infty \langle[q(t), q(0)]\rangle_0 \exp\,(i\omega t)dt + i\int_0^\infty \langle[q(t), q(0)]\rangle_0 \exp\,(-i\omega t)dt\right)$$

$$= \frac{1}{2\pi\hbar}\int_{-\infty}^\infty \langle[q(t)q(0) - q(0)q(t)]\rangle_0 \exp\,(i\omega t)dt$$

$$= \frac{1}{2\pi\hbar}\int_{-\infty}^\infty (\langle q(t)q(0)\rangle_0 \exp\,(i\omega t) - \langle q(0)q(-t)\rangle_0 \exp\,(-i\omega t))dt$$

$$= \tfrac{1}{2\pi\hbar}\int_{-\infty}^\infty (\langle q(t)q(0)\rangle_0 \exp\,(i\omega t) - \langle q(t)q(0)\rangle_0 \exp\,(-i\omega t))dt$$
$$= s(\omega) - s(-\omega).$$

In (8.102) we have used:

$$\langle q(t)q(0)\rangle_0 = \langle q(0)q(-t)\rangle_0 \tag{8.103}$$

due to the invariance with respect to time translation in the trace formation in the stationary ensemble ρ_0. From (8.101) and (8.98) we obtain

$$\boxed{a(\omega) = s(\omega)[1 - \exp\,(-\beta\hbar\omega)]} \tag{8.104}$$

and

$$s(\omega) + s(-\omega) = s(\omega)[1 + \exp\,(-\beta\hbar\omega)] = a(\omega)\tfrac{[1+\exp(-\beta\hbar\omega)]}{[1-\exp(-\beta\hbar\omega)]}. \tag{8.105}$$

With the identity

$$\frac{1+\exp(-x)}{1-\exp(-x)} = \frac{\exp(x)+1-1+1}{\exp(x)-1} = 1 + \frac{2}{\exp(x)-1} \tag{8.106}$$

we get the general **fluctuation-dissipation theorem**:

$$\boxed{\frac{\hbar}{2}\left[s(\omega)+s(-\omega)\right] = \frac{a(\omega)}{\omega}\left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{(\exp(\beta\hbar\omega)-1)}\right).} \tag{8.107}$$

On the left side of (8.107) we have the (negative) Fourier transform of the fluctuation for $\omega \neq 0$ (note that $q(0) \equiv q$ and $\langle f(q(t))\rangle_0 = \langle f(q)\rangle_0$))

$$\langle q(t)q + qq(t)\rangle_0 \equiv -\langle q(t)^2 - q(t)q - qq(t) + q^2\rangle_0 + \langle q(t)^2\rangle_0 + \langle q^2\rangle_0 \tag{8.108}$$

$$= 2\langle q^2\rangle_0 - \langle (q(t)-q)^2\rangle_0 = 2\langle q^2\rangle_0 - \langle \Delta q^2\rangle_0.$$

On the right side we have the dissipative part of the response function $r(\omega)$ (i.e. $a(\omega)$), apart from temperature and frequency-dependent terms.

We still want to convince ourselves that $a(\omega)$ can be identified with the dissipative part. To this aim we investigate the work done on the system by the external force $f(t)$, which is converted to internal energy of the system. We form with (8.55)

$$\frac{d}{dt}\langle H_0\rangle = Tr(\dot{\rho}H_0) = -\frac{i}{\hbar}Tr([H_0 - f(t)q, \rho]\ \ H_0) \tag{8.109}$$

$$= -\frac{i}{\hbar}Tr([H_0, H_0 - f(t)q]\rho) = \frac{i}{\hbar}Tr([H_0, q]f(t)\rho(t)) = \langle \dot{q}\rangle f(t).$$

The total energy delivered to the system—after t integration—is:

$$\langle H_0(\infty)\rangle - \langle H_0(-\infty)\rangle = \int_{-\infty}^{\infty}\langle \dot{q}\rangle f(t)\ dt \tag{8.110}$$

$$\begin{aligned}
&= -\tfrac{i}{2\pi}\int_{-\infty}^{\infty}\ \omega\ q(\omega)\Big(\int_{-\infty}^{\infty}\exp\ (-i\omega t)f(t)\ dt\Big)\ d\omega \\
&= -\tfrac{i}{2\pi}\int_{-\infty}^{\infty}\omega\ q(\omega)\ \ f(-\omega)\ d\omega \\
&= -\tfrac{i}{2\pi}\int_{-\infty}^{\infty}\omega\ q(\omega)f^*(\omega)\ d\omega = -\tfrac{i}{2\pi}\int_{-\infty}^{\infty}\omega|f(\omega)|^2\ r(\omega)\ d\omega \\
&= \int_0^{\infty}\omega|f(\omega)|^2\ a(\omega)\ d\omega > 0,
\end{aligned}$$

considering

(8.111)

$$f^*(\omega) = f(-\omega),$$

since $f(t)$ is real, as well as the fact (which follows directly from (8.68) and (8.103)), since

$$r^*(\omega) = r(-\omega). \tag{8.112}$$

Because of

$$\boxed{d(\omega) = d(-\omega); a(\omega) = -a(-\omega)} \tag{8.113}$$

only $a(\omega)$ contributes to the integral (8.110); the even function—after multiplication by $\omega |f_\omega|^2$—gives no contribution (odd integrand).

As an instructive **example** for the real and imaginary part of the response function $r(\omega)$ we consider the **refractive index of a substance**: The real part of the refractive index indicates how a light beam is refracted when passing a boundary between the vacuum and a substance; this refraction is generally frequency dependent: the substance shows **dispersion**. Therefore, the real part of $r(\omega)$ is generally referred to as the **dispersive** part. When passing through the substance the light beam is also weakened in its intensity, the substance absorbs radiation energy. This **absorption** is also frequency dependent and is described by the **imaginary component of the refractive index**.

In the **classical limit** $\hbar\omega \ll k_B T$ or $\beta\hbar\omega \ll 1$ we obtain

$$s(\omega) + s(-\omega) = a(\omega)\frac{(1+\exp(-\beta\hbar\omega))}{(1-\exp(-\beta\hbar\omega))} \approx a(\omega)\frac{2}{\beta\hbar\omega} = a(\omega)\frac{2\ k_B T}{\hbar\omega}, \tag{8.114}$$

such that (8.107) takes the form

$$\boxed{\frac{\hbar}{2}(s(\omega) + s(-\omega)) = \frac{a(\omega)}{\omega}\ \ k_B T.} \tag{8.115}$$

8.6 Generalization of the Classical Equipartition Theorem

From the fluctuation-dissipation theorem (8.107) follows by integration over ω

$$2\int_0^\infty \frac{a(\omega)}{\omega}\left\{\frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp(\beta\hbar\omega)-1}\right\}d\omega \tag{8.116}$$

$$= \hbar\int_0^\infty \{s(\omega) + s(-\omega)\}d\omega = \hbar\int_{-\infty}^\infty s(\omega)d\omega$$

$$= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \langle q(t)q(0)\rangle_0 \exp\,(i\omega t) \frac{d\omega}{2\pi} dt$$

(according to (8.95))

$$= \int_{-\infty}^{\infty} \langle q(t)q(0)\rangle_0 \delta(t)\ dt = \langle q(0)^2\rangle_0 = \langle q^2\rangle_0.$$

A corresponding relation is obtained for the average value of the canonically conjugate variable *p* to *q*. For the derivation we use:

$$\langle \Phi_i|\dot{q}(t)|\Phi_j\rangle = \tfrac{i}{\hbar}\langle \Phi_i|[H_0, q(t)]|\Phi_j\rangle = \tfrac{i}{\hbar}(\epsilon_i - \epsilon_j)\langle \Phi_i|q(t)|\Phi_j\rangle, \qquad (8.117)$$

from which follows by iteration

$$\langle \Phi_i|\tfrac{d}{dt}\dot{q}(t)|\Phi_j\rangle = -\tfrac{(\epsilon_i-\epsilon_j)^2}{\hbar^2}\langle \Phi_i|q(t)|\Phi_j\rangle. \qquad (8.118)$$

With (8.96) we get

$$\tfrac{d^2}{dt^2}s(t) = -\tfrac{1}{\hbar}\tfrac{\sum_{i,j}\exp(-\beta\epsilon_i)}{(\sum_k \exp(-\beta\epsilon_k))}|\langle \Phi_i|q|\Phi_j\rangle|^2 \tfrac{(\epsilon_i-\epsilon_j)^2}{\hbar^2}\ \exp\{\tfrac{i}{\hbar}(\epsilon_i - \epsilon_j)t\} \qquad (8.119)$$

$$= -\frac{1}{\hbar}\frac{\sum_{i,j}\exp\,(-\beta\epsilon_i)}{(\sum_k \exp\,(-\beta\epsilon_k))}|\langle \Phi_i|\dot{q}|\Phi_j\rangle|^2 \exp\{\frac{i}{\hbar}(\epsilon_i - \epsilon_j)t\} = -\frac{1}{\hbar}\langle \dot{q}(t)\dot{q}(0)\rangle_0$$

$$= \frac{1}{\hbar}\frac{\sum_{i,j}\exp\,(-\beta\epsilon_i)}{(\sum_k \exp\,(-\beta\epsilon_k))}\langle \Phi_i|\frac{d}{dt}\dot{q}|\Phi_j\rangle\langle \Phi_j|q|\Phi_i\rangle \exp\{\frac{i}{\hbar}(\epsilon_i - \epsilon_j)t\}$$

$$= \frac{1}{\hbar}\frac{\sum_{i}\exp\,(-\beta\epsilon_i)}{(\sum_k \exp\,(-\beta\epsilon_k))}\langle \Phi_i|\frac{d}{dt}\dot{q}(t)q|\Phi_i\rangle = \frac{1}{\hbar}\Big\langle \frac{d}{dt}\dot{q}(t)q(0)\Big\rangle_0$$

and (8.95) (after partial integration)

$$\omega^2 s(\omega) = -\tfrac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\langle\big(\tfrac{d}{dt}\dot{q}(t)\big)q(0)\rangle_0 \exp\,(i\omega t)dt. \qquad (8.120)$$

By integrating over *ω* (according to (8.116)) we get

$$\hbar\int_{-\infty}^{\infty}\omega^2 s(\omega)d\omega = 2\int_0^{\infty}\omega\ a(\omega)\{\tfrac{\hbar\omega}{2} + \tfrac{\hbar\omega}{\exp(\beta\hbar\omega)-1}\}d\omega \qquad (8.121)$$

$$= \langle \dot{q}^2\rangle_0 =: \langle p^2\rangle_0/m^2,$$

if we follow (8.119),

$$\lim_{t\to 0} \left\langle \left(\tfrac{d}{dt}\dot{q}(t)\right) q(0)\right\rangle_0 = -\langle \dot{q}^2\rangle_0. \tag{8.122}$$

The relations

$$\langle q^2\rangle_0 = \hbar \int_{-\infty}^{\infty} s(\omega)\ d\omega = 2\int_0^{\infty} \frac{a(\omega)}{\omega}\left\{\frac{\hbar\omega}{2} + \frac{\hbar\omega}{(\exp(\beta\hbar\omega)-1)}\right\}\ d\omega \tag{8.123}$$

and

$$\frac{\langle p^2\rangle_0}{m^2} = \hbar \int_{-\infty}^{\infty} \omega^2 s(\omega)\ d\omega = 2\int_0^{\infty} \omega\ a(\omega)\left\{\frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp(\beta\hbar\omega)-1}\right\}\ d\omega \tag{8.124}$$

can be interpreted as **quantum mechanical generalizations of the equipartition theorem**.

To convince ourselves we use (for $\hbar\omega \ll k_B T$)

$$a(\omega) \approx s(\omega)\frac{\hbar\omega}{k_B T} = s(\omega)\beta\hbar\omega \tag{8.125}$$

from (8.104) as well as

$$\left\{\frac{\hbar\omega}{2} + \frac{\hbar\omega}{(\exp(\beta\hbar\omega)-1}\right\} \approx k_B T = \beta^{-1} \tag{8.126}$$

according to (8.114). This gives

$$\begin{aligned} &\hbar \int_{-\infty}^{\infty} \omega^2 s(\omega)\ d\omega \approx 2\ k_B T \int_0^{\infty} \omega\ a(\omega) d\omega \\ &= 2\ k_B T \int_0^{\infty} \omega(s(\omega) - s(-\omega))\ d\omega \end{aligned} \tag{8.127}$$

$$= 2\ k_B T \int_{-\infty}^{\infty} \omega\ s(\omega)\ d\omega,$$

when inserting (8.102). Additionally—in line with the calculations above for (8.124)—we find

$$\int_{-\infty}^{\infty} \omega\ s(\omega) d\omega = \frac{i}{\hbar}\frac{\langle [p,q]\rangle_0}{2m} = \frac{1}{2m} \tag{8.128}$$

for canonically conjugate variables. Thus,

$$\frac{\langle p^2\rangle_0}{2m} = \frac{1}{2}\ k_B T, \tag{8.129}$$

as claimed by the equipartition theorem. The proof of the corresponding statement for $\langle q^2\rangle_0$ is more complex and is not given here explicitly.

8.7 Examples

To illustrate the fluctuation-dissipation theorem let's go back to the resistance noise. From (8.94) ($r(\omega) = 1/(1 - i\omega CR)$) immediately follows

$$\frac{1}{\pi}\Im(r(\omega)) = a(\omega) = \frac{1}{\pi}\ \frac{\omega RC}{(1+\omega^2R^2C^2)}, \tag{8.130}$$

such that in the classical approximation $\hbar\omega \ll k_BT$ according to (8.115) we get

$$\boxed{\frac{\hbar}{2}[s(\omega) + s(-\omega)] = \frac{a(\omega)}{\omega}k_BT = \frac{1}{\pi}\ \frac{k_BT\ RC}{(1+\omega^2R^2C^2)}. \qquad (8.131)}$$

When interpreting the left side of (8.131) we note that $q\ \ f(t)$ must be an energy and $f(t)$ a time-dependent classical quantity. Since equation (8.94) implies an identification of $f(t)$ and $U_{th.}(t)$, q corresponds to the charge $Q(t) = C\ \ U(t)$. On the left side of the **Nyquist formula** (8.131) then we have the Fourier transform of the fluctuation of the charge. If we want to go over to the voltage, then $r(\omega)$ in (8.94) has to be multiplied by $1/C$ and in (8.130) and (8.131) the factor C in the numerator drops out on the right side. The resulting Eq. (8.131) is integrated in analogy to (8.116) over ω, giving

$$\boxed{\begin{aligned}\langle U(t)^2\rangle_0 &= \frac{2}{\pi}\int_0^\infty \frac{k_BT\ R}{(1+\omega^2R^2C^2)}d\omega \\ &= \frac{2\ k_BT}{\pi C}\int_0^\infty \frac{1}{1+x^2}dx = \frac{k_BT}{C}\end{aligned} \qquad (8.132)}$$

for $x = \omega RC$, since the integral over dx gives $\pi/2$. $\langle U(t)^2\rangle_0$ is therefore independent of R; For smaller R values, the contribution of smaller frequencies decreases in (8.132), however, higher frequencies contribute to the integral.

In summarizing this chapter we have examined the connection between **spontaneous fluctuations** of physical quantities around their average values in statistical equilibrium and **forced deviations** from the average values due to disturbances of the balance **by external perturbations**. It was shown that these two phenomena are closely linked for **weak** external perturbations and find their expression in the **fluctuation-dissipation theorem**. To this aim we have introduced the thermodynamic perturbation theory and computed response functions for various examples like the electric conductivity and the resistance noise.

Footnotes

[1] This assumption is fulfilled in many practical cases.

Part III
Applications of Statistical Mechanics

W. Cassing, *Theoretical Physics Compact IV*
https://doi.org/10.1007/978-3-031-95518-1_9

9. The Ideal Fermi Gas

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In this chapter we will investigate the ideal Fermi gas in particular at low temperatures and calculate the equation of state and the fluctuations in the average occupation number. As examples the specific heat of metal electrons at low temperatures as well as the glow emission of electrons from metals at finite temperature will be calculated.

9.1 Fermi Distribution

For the average occupation number of the single-particle level *i* we have found

$$\boxed{\langle n_i \rangle = \frac{1}{\exp(\beta[\epsilon_i - \mu]) + 1} \ , \qquad (9.1)}$$

where $\beta = 1/(k_B T)$ and μ is the chemical potential. For the limiting case of high temperatures (or low density) we have found in Sect. 6.4, that $\langle n_i \rangle$ decays exponentially with energy,

$$\langle n_i \rangle \approx \exp\left(-\beta[\epsilon_i - \mu]\right) \qquad (9.2)$$

for $V/\mathscr{N}(2\pi m k_B T/h^2)^{3/2} \gg 1$. In the other limiting case of low temperatures $(T \to 0, \beta \to \infty)$ we have to distinguish $\epsilon_i > \mu$ and $\epsilon_i < \mu$. For $\epsilon_i > \mu$ and $\beta \to \infty$ obviously we obtain $\langle n_i \rangle \to 0$ exponentially, but $\langle n_i \rangle \to 1$ for $\epsilon_i < \mu$ and $\beta \to \infty$. For $\epsilon_i = \mu$ the occupation number $\langle n_i \rangle$ takes the value 1/2; this provides a clear interpretation of μ: $\mu_{T=0}$ indicates the energy up to which the single-particle levels at absolute zero temperature are fully occupied; for energies above $\mu(T=0)$ all states are empty. $\mu(T=0) =: \epsilon_F$ is called the **Fermi energy**; it is determined by the requirement

$$\sum_i \langle n_i \rangle = \mathscr{N}, \qquad (9.3)$$

where $\mathscr{N}$ is the given average particle number of the system. The Fermi energy therefore depends on the particle number of the system. The **sharp** Fermi distribution at $T = 0$ **softens** for $T > 0$ (see Fig. 9.1).

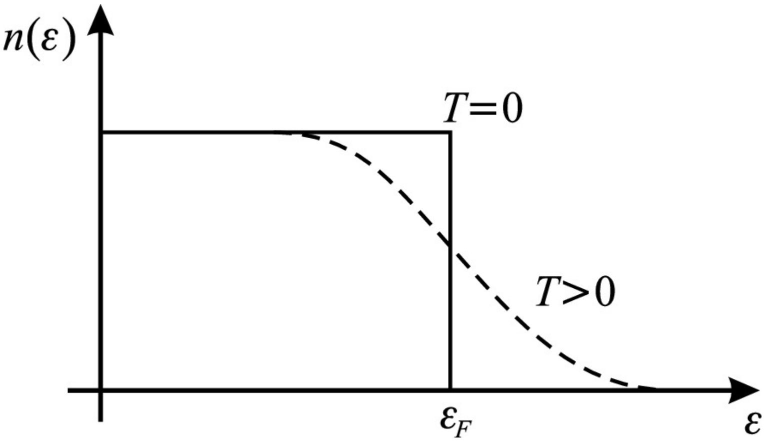

Fig. 9.1 Fermi distribution as a function of the single-particle energy ϵ for $T = 0$ and $T > 0$

9.2 Internal Energy and Particle Number at Low Temperatures $T \neq 0$

When calculating

$$\mathscr{N} = \sum_i \langle n_i \rangle \tag{9.4}$$

and

$$U = \sum_i \epsilon_i \langle n_i \rangle \tag{9.5}$$

we replace (see Sect. 6.4)

$$\sum_i \dots \to \frac{(2s+1)V}{(2\pi)^3} \int d^3k \dots . \tag{9.6}$$

Since the quantities we are interested in (9.4) and (9.5) in the non-relativistic limit only depend on

$$\epsilon = \frac{\hbar^2 k^2}{2m}, \tag{9.7}$$

we convert ($k^2 = 2m\epsilon/\hbar^2, d\epsilon = \hbar^2 k/m \ dk$)

$$\int_{-\infty}^{\infty} d^3k \dots = 4\pi \ \int_0^{\infty} \ k^2 dk \dots = 2\pi \left(\frac{2m}{\hbar^2}\right)^{3/2} \int \ \epsilon^{1/2} d\epsilon \dots \tag{9.8}$$

The integrals—we are interested in—then are of the form

$$I = C\int_0^\infty \frac{f(\epsilon)}{\exp\{(\epsilon-\mu)/k_BT\}+1}\ d\epsilon \tag{9.9}$$

with the prefactor (s denotes the spin of the particles)

$$C = \frac{V(2s+1)}{(2\pi)^3}\ 2\pi\left(\frac{2m}{\hbar^2}\right)^{3/2} = V(2s+1)2\pi\left(\frac{2m}{h^2}\right)^{3/2}. \tag{9.10}$$

For the calculation of $\mathcal{N}$ the function $f(\epsilon) = \epsilon^{1/2}$, for U accordingly $f(\epsilon) = \epsilon^{3/2}$. To calculate the integrals (9.9) for **low temperatures** we substitute

$$\epsilon - \mu = k_BT\ z, \tag{9.11}$$

such that (constant C from (9.9) omitted)

$$k_BT\int_{-\mu/k_BT}^{\infty} \frac{f(\mu+k_BTz)}{\exp(z)+1}dz = k_BT\left(\int_{-\mu/k_BT}^{0} \frac{f(\mu+k_BTz)}{\exp(z)+1}\ dz + \int_0^\infty \frac{f(\mu+k_BTz)}{\exp(z)+1}\ dz\right) \tag{9.12}$$

$$= k_BT\left(\int_0^{\mu/(k_BT)} \frac{f(\mu-k_BTz)}{\exp\ (-z)+1}dz + \int_0^\infty \frac{f(\mu+k_BTz)}{\exp\ (z)+1}dz\right).$$

With the identity

$$\frac{1}{\exp(-z)+1} = \frac{\exp(z)+1-1}{\exp(z)+1} = 1 - \frac{1}{\exp(z)+1} \tag{9.13}$$

we can convert (9.12) into a $T = 0$ contribution and split a correction for $T \neq 0$:

$$\int_0^\mu f(\bar{\epsilon})\ d\bar{\epsilon} + k_BT\int_0^\infty \frac{[f(\mu+k_BTz)-f(\mu-k_BTz)]}{\exp(z)+1}dz, \tag{9.14}$$

where in the 2nd term for $\mu/(k_BT) \gg 1$ the upper integration limit can be moved to ∞. In the second term we expand the numerator in the integrand in powers of k_BTz,

$$f(\mu \pm k_BTz) = f(\mu) \pm k_BTzf'(\mu) + \frac{z^2}{2}(k_BT)^2 f''(\mu) \pm \frac{z^3}{6}(k_BT)^3 f'''(\mu)\ldots \tag{9.15}$$

leading to

$$I = C\left(\int_0^\mu f(\bar{\epsilon})\ d\bar{\epsilon} + 2(k_BT)^2 f'(\mu)\int_0^\infty \frac{z}{\exp(z)+1}dz\right) \tag{9.16}$$

$$+\frac{C}{3}(k_BT)^4 f'''(\mu)\int_0^\infty \frac{z^3}{\exp\ (z)+1}dz + \cdots\ ;$$

all even derivatives of $f(\mu)$ cancel out. Inserting the values of the integrals from tables we get the final result

$$\boxed{I = C\Big(\int_0^\mu f(\bar\epsilon)\ d\bar\epsilon + \tfrac{\pi^2}{6}(k_BT)^2\ f'(\mu)\ldots\Big). \qquad (9.17)}$$

With (9.17) and (9.6) formula (9.4) (with $f(\epsilon) = \sqrt{\epsilon}$, $f' = 1/(2\sqrt{\epsilon})$) becomes

$$\boxed{\begin{aligned} \mathscr{N} &= \tfrac{2}{3}\ C\ \mu^{3/2} + C\tfrac{\pi^2}{6}(k_BT)^2\tfrac{1}{2\sqrt{\mu}} + \cdots \\ &= \tfrac{2}{3}\ C\ \mu^{3/2}\Bigg(1 + \tfrac{\pi^2}{8}\left(\tfrac{k_BT}{\mu}\right)^2 + \cdots\Bigg), \end{aligned} \qquad (9.18)}$$

or solved for $\mu^{3/2}$,

$$\begin{aligned} \mu^{3/2} &= \tfrac{3\mathscr{N}}{2C}\Bigg(1 + \tfrac{\pi^2}{8}\left(\tfrac{k_BT}{\mu}\right)^2 + \cdots\Bigg)^{-1}, \\ &\to\ \mu = \left(\tfrac{3\mathscr{N}}{2C}\right)^{2/3}\Bigg(1 + \tfrac{\pi^2}{8}\left(\tfrac{k_BT}{\mu}\right)^2 + \cdots\Bigg)^{-2/3}. \end{aligned}$$

Using for $T = 0$

$$\mu(T=0) = \epsilon_F = \left(\tfrac{3\mathscr{N}}{2C}\right)^{2/3}\ , \qquad (9.19)$$

then $\mu(T)$ emerges as—for low temperatures $T \neq 0$—after an expansion of the denominator

$$\boxed{\mu(T) = \epsilon_F\Bigg(1 + \tfrac{\pi^2}{8}\left(\tfrac{k_BT}{\epsilon_F}\right)^2\ldots\Bigg)^{-2/3} \approx \epsilon_F\Bigg(1 - \tfrac{\pi^2}{12}\left(\tfrac{k_BT}{\epsilon_F}\right)^2\ldots\Bigg). \qquad (9.20)}$$

Similarly, for $f(\epsilon) = \epsilon^{3/2}$ we get

$$\boxed{U \approx \tfrac{3}{5}\mathscr{N}\epsilon_F|_{T=0}\Bigg(1 + \tfrac{5\pi^2}{12}\left(\tfrac{k_BT}{\epsilon_F}\right)^2\ldots\Bigg). \qquad (9.21)}$$

It is important to note in context with Eq. (9.21), that the corrections to $T = 0$ start with T^2, and not with T. The correct behavior of C_V for low temperatures follows from (9.21) directly,

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V = \text{const.} \cdot T + \cdots , \tag{9.22}$$

such that $C_V \to 0$ for $T \to 0$ in agreement with the 3rd law of thermodynamics.

A practical example is provided by the **specific heat of metals**. For C_V/T it is found at low temperatures

$$\frac{C_V}{T} = a_1 + a_2 T^2 + \ldots \tag{9.23}$$

The quadratic term stems from lattice vibrations (cf. Chap. 10), while the a_1 contribution stems from the (almost free motion) of the conduction electrons. The experimental value of a_1 for many metals is in agreement with (9.22). The specific heat of metals at low temperatures clearly shows the failure of the classical theory (according to which the specific heat per degree of freedom is $1/2\ k_B$, thus $3/2\ k_B$ for free electrons) and gives a clear confirmation of quantum statistics.

The qualitative reason for the low contribution of free electrons to the specific heat at low temperatures is clear: the single-particle states far below the Fermi energy ϵ_F are fully occupied ($\langle n(\epsilon)\rangle = 1$) and add to the internal energy (9.5) a temperature-independent contribution. For the specific heat C_V only the electrons from states in the vicinity of the Fermi energy contribute, i.e. less and less with decreasing temperature of the electrons, since the Fermi energy distribution becomes increasingly **sharper**.

9.3 Degeneracy of the Fermi Gas

The term **low temperatures** still needs to be specified. This is achieved using formulas such as (9.18), (9.20) or (9.21), where $k_B T/\epsilon_F$ appears as an expansion parameter. Defining the Fermi temperature T_F by

$$k_B T_F =: \epsilon_F \tag{9.24}$$

(for metals $T_F \sim 10^5 K$, that is large compared to room temperature $\approx 300K$), which according to (9.19) is density-dependent, then high density and low temperature implies

$$T \ll T_F. \tag{9.25}$$

In this range a Fermi gas is called **degenerate**.

9.4 Equation of State

For the grand-canonical ensemble we have (see table (7.65))

$$J = J(T, V, \mu) = U - TS - \mu N \tag{9.26}$$

for the thermodynamic potential. Using the relation (8.18) ($U = TS - PV + \mu N$), which is valid for homogeneous systems, we obtain

$$PV = -J = k_B T \ \ln \ Z_g, \tag{9.27}$$

employing (5.38). With (6.11)

$$\boxed{\begin{aligned} PV &= k_B T \ln \left(\prod_i \{1 + \exp\left(-\beta(\epsilon_i - \mu)\right)\}\right) \\ &= k_B T \sum_i \ln \left\{1 + \exp\left(-\beta(\epsilon_i - \mu)\right)\right\} \end{aligned} \quad (9.28)}$$

we obtain the equation of state of the ideal Fermi gas. This expression contains deviations from the classical equation (7.127), which can be traced back to the Pauli principle. The calculation of $\sum_i \ln \{..\}$ in (9.28) can be converted to an energy integration in analogy to Sect. 9.2:

$$PV = k_B T \ C \int_0^\infty \sqrt{\epsilon} \ \ln \left(1 + \exp\left(-\beta(\epsilon - \mu)\right)\right) \ d\epsilon \tag{9.29}$$

$$= k_B T \ C \int_0^\infty \frac{2}{3} \epsilon^{3/2} \frac{\beta \exp\left(-\beta(\epsilon - \mu)\right)}{1 + \exp\left(-\beta(\epsilon - \mu)\right)} \ d\epsilon = \frac{2}{3} C \int_0^\infty \frac{\epsilon^{3/2}}{1 + \exp\left(\beta(\epsilon - \mu)\right)} \ d\epsilon$$

after partial integration. We thus get *PV* to be exactly 2/3 of the integral for the internal energy *U*. With (9.21) the result is

$$\boxed{PV = \tfrac{2}{3} U = \tfrac{2}{5} \mathscr{N} \epsilon_F \left(1 + \tfrac{5\pi^2}{12} \left(\tfrac{k_B T}{\epsilon_F}\right)^2 \ldots\right) . \quad (9.30)}$$

Equation (9.30) shows that for $T = 0$ still $PV \neq 0$ in contrast to the classical ideal gas. The **zero point pressure**—remaining at $T = 0$—is a direct consequence of the Pauli principle, according to which only two particles with spin 1/2 can have the momentum $\hbar \mathbf{k} = 0$; all other particles must have a higher momentum and generate the zero-point pressure.

9.5 Fluctuations in the Average Occupation Number

According to Sect. 8.2, Eq. (8.11), we get

$$\begin{aligned}(\Delta n_i)^2 &= k_B T\left(\frac{\partial\langle n_i\rangle}{\partial\mu}\right) = \beta^{-1}\left(\frac{\partial(\exp(\beta(\epsilon_i-\mu))+1)^{-1}}{\partial\mu}\right)\\ &= \frac{\exp(\beta(\epsilon_i-\mu))+1-1}{(\exp(\beta(\epsilon_i-\mu))+1)^2}\end{aligned} \tag{9.31}$$

and we obtain

$$\boxed{(\Delta n_i)^2 = \langle n_i\rangle(1-\langle n_i\rangle).} \tag{9.32}$$

The fluctuations disappear for energies far below the Fermi energy, where $\langle n_i\rangle \approx 1$ and far above, where $\langle n_i\rangle \approx 0$. With decreasing temperature the fluctuations become increasingly stronger and concentrate near the Fermi energy.

9.6 Glow Emission

We want to calculate the electron current emerging from a (flat) metal surface at finite temperature T. For this we assume that the emerging electrons have to pass a potential difference χ to leave the metal (see Fig. 9.2).

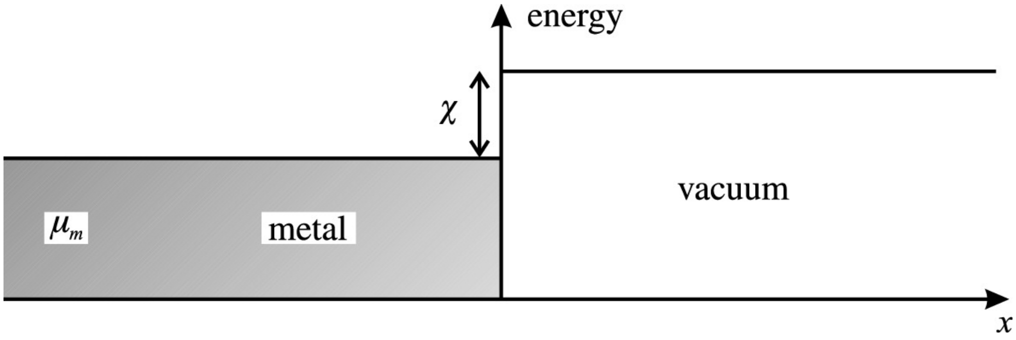

Fig. 9.2 Potential at the interface between metal and vacuum

The balance between electrons in the metal and electrons in the vacuum are characterized by the fact, that the chemical potentials (index m : metal, index v : vacuum) are the same,

$$\mu_m = \mu_v. \tag{9.33}$$

For room temperatures $(T \approx 300^0 K)$ we can neglect the temperature dependence of μ such that

$$\mu_m = \mu_v = \epsilon_F. \tag{9.34}$$

For the particle densities in the vacuum we then obtain $(2s+1=2)$

$$\frac{N}{V} = n_v = \frac{C}{V}\int_0^\infty \frac{\epsilon^{1/2}}{\exp\{\beta(\epsilon+\chi-\epsilon_F)\}+1}d\epsilon \tag{9.35}$$

and in the metal

$$n_m = \frac{C}{V}\int_0^\infty \frac{\epsilon^{1/2}}{\exp\{\beta(\epsilon-\epsilon_F)\}+1}d\epsilon. \tag{9.36}$$

In order to hold all conduction electrons in the metal, χ must be well above ϵ_F, such that for room temperatures (i.e. $\beta\epsilon_F \gg 1$) we can assume

$$\beta(\chi-\epsilon_F) \gg 1. \tag{9.37}$$

Then in n_v (9.35) we can neglect the 1 in the denominator of the integrand;

$$n_v = \frac{C}{V}\int_0^\infty \frac{\epsilon^{1/2}}{\exp\{\beta(\epsilon+\chi-\epsilon_F)\}}d\epsilon = \frac{C}{V}\ \exp\left(-\beta(\chi-\epsilon_F)\right)\ \int_0^\infty \frac{\epsilon^{1/2}}{\exp\{\beta\epsilon\}}d\epsilon\ . \tag{9.38}$$

The remaining integral of the form (with the substitution $x^2=\epsilon, d\epsilon = 2xdx$)

$$\int_0^\infty \frac{\epsilon^{1/2}}{\exp(\beta\epsilon)}d\epsilon = 2\int_0^\infty \frac{x^2}{\exp(\beta x^2)}dx = \int_{-\infty}^\infty x^2\ \ \exp\left(-\beta x^2\right)\ dx = \frac{\sqrt{\pi}}{2\beta^{3/2}} \tag{9.39}$$

is solvable in closed form and we obtain (with $\frac{C}{V} = 4\pi\left(\frac{2m}{h^2}\right)^{3/2}$) for n_v :

$$\boxed{\begin{aligned} n_v\ &= 2\pi\left(\frac{2m}{h^2}\right)^{3/2}\ \exp\left(-\frac{(\chi-\epsilon_F)}{k_BT}\right)\cdot(k_BT)^{3/2}\sqrt{\pi} \\ &= \frac{2\pi}{h^3}(2mk_BT)^{3/2}\ \exp\left(-\frac{(\chi-\epsilon_F)}{k_BT}\right)\ \sqrt{\pi}\ . \end{aligned} \tag{9.40}}$$

Now we can calculate the current density j_m of the **glow electrons** emitted by the metal, since in equilibrium the number of electrons emerging from the metal is equal to the number of **steam electrons** hitting the surface of the metal and return to the metal phase; thus:

$$\boxed{j_m = e\ n_v\frac{1}{2}\langle|v_x|\rangle\ . \tag{9.41}}$$

Since the density of electrons in the vapor phase is small, we can calculate $\langle|v_x|\rangle$ classically, i.e.

$$\langle|v_x|\rangle = \sqrt{\langle v_x^2\rangle} = \sqrt{\langle v^2\rangle/3} = \sqrt{\frac{2\langle\epsilon\rangle}{3m}} = \sqrt{\frac{2k_BT}{\pi m}}, \tag{9.42}$$

if $\langle\epsilon\rangle$ is calculated in analogy to (9.39). The final result is the **Richardson formula**,

$$\boxed{j_m = e\ \frac{4\pi m}{h^3}(k_BT)^2 \exp\left(-\frac{[\chi-\epsilon_F]}{k_BT}\right).} \tag{9.43}$$

In summarizing this chapter we have investigated the ideal Fermi gas in particular at low temperatures and calculated the internal energy and the equation of state as well as the fluctuations in the average occupation number. As examples the specific heat of metal electrons at low temperatures as well as the glow emission of electrons from metals at finite temperature has been calculated.

W. Cassing, *Theoretical Physics Compact IV*
https://doi.org/10.1007/978-3-031-95518-1_10

10. The Ideal Bose Gas

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In this chapter we will investigate the ideal Bose gas in particular at low temperatures and compute the properties of the Bose condensate. We will compute the internal energy and specific heat and show that the results are consistent with the 3rd law of thermodynamics. As examples we will study the properties of a photon gas in a large cavity and the phonons in solids.

10.1 Bose Distribution

The average occupation number of a single-particle level for bosons according to (6.13) is

$$\langle n_i \rangle = \frac{1}{\exp(\beta[\epsilon_i - \mu]) - 1}. \tag{10.1}$$

Since always $\langle n_i \rangle \geq 0$, it follows

$$\exp\left(\beta[\epsilon_i - \mu]\right) \geq 1. \tag{10.2}$$

If we normalize the scale of the single-particle energies such that the lowest state has $\epsilon_o = 0$, then must hold

$$\mu \leq 0. \tag{10.3}$$

We have discussed the shape of $\langle n_i \rangle$ for high temperatures (or low density) already in Sect. 6.4: we get an exponentially decreasing Boltzmann distribution $\exp\left(-\beta[\epsilon_i - \mu]\right)$. In general, $\langle n(\epsilon) \rangle$ has the shape shown in Fig. 10.1. With decreasing temperature the occupation number of energetically higher states decreases in favor of the energetically lower ones. For $T \to 0$ all Bose particles go to the lowest state $\epsilon_0 = 0$. The chemical potential μ must change in such a way that the given number of particles N is preserved. For $T \to 0$ the chemical potential μ always moves more towards its limit $\mu = 0$. Due to the singularity of $\langle n(\epsilon)\rangle$ for $\mu = \epsilon_0, T \neq 0$, which we find from (10.1) or Fig. 10.1, the discussion of low temperatures $T \to 0$ has to be treated with caution. We'll shift this analysis to Sect. 10.3, where we focus on the phenomenon of the **Bose-Einstein condensation**.

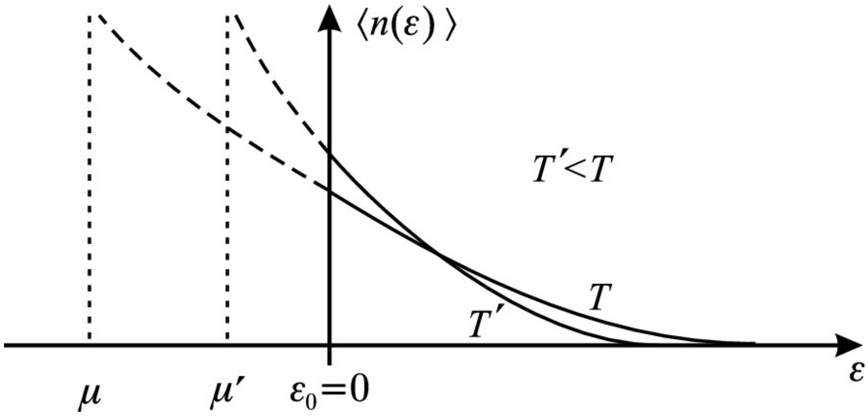

Fig. 10.1 Bose distribution $n(\epsilon)$ for two temperatures

10.2 Fluctuations in the Average Occupation Number

As in (9.31) we form

$$(\Delta n_i)^2 = \beta^{-1}\left(\frac{\partial\langle n_i\rangle}{\partial\mu}\right) = \frac{\exp(\beta(\epsilon_i-\mu))-1+1}{(\exp(\beta(\epsilon_i-\mu))-1)^2} \quad ; \qquad (10.4)$$

with (10.1) we get directly

$$\boxed{(\Delta n_i)^2 = \langle n_i\rangle(1+\langle n_i\rangle). \qquad (10.5)}$$

The difference to the Fermi gas (9.32) and to the classical limiting case, which results from (9.2) to be given by

$$(\Delta n_i)^2 = \langle n_i \rangle \tag{10.6}$$

is particularly clear, if we consider the relative fluctuation

$$\frac{(\Delta n_i)^2}{\langle n_i \rangle^2} = 1 + \frac{1}{\langle n_i \rangle}. \tag{10.7}$$

The remarkable point in (10.7) is that for large values of $\langle n_i \rangle$ the relative fluctuation does not vanish but remains of order 1!

10.3 Bose-Einstein Condensation

We now come to the behavior of Bose systems at low temperatures. To determine the temperature dependence of the chemical potential μ we go back to

$$\mathscr{N} = \sum_i \langle n_i \rangle = \sum_i \frac{1}{\exp(\beta[\epsilon_i - \mu]) - 1}, \tag{10.8}$$

which determines μ for given $\mathscr{N}$ and T. To evaluate (10.8) we use the same procedure as for Fermi statistics and classical statistics; we replace (spin $s = 0$)

$$\sum_k \dots \to \frac{V}{(2\pi)^3} \int d^3k \dots. \tag{10.9}$$

As long as only scalar quantities are of interest, the momentum integration can be replaced by an energy integration. We get e.g.

$$\mathscr{N} = C \int_0^\infty \frac{\epsilon^{1/2}}{\exp\{\beta[\epsilon - \mu]\} - 1} d\epsilon \tag{10.10}$$

with the constant $C = 2\pi(2m/\hbar^2)^{3/2} V/(2\pi)^3$ from (9.10). If we decrease the temperature at constant density $\mathscr{N}/V$, the (negative) quantity μ must increase, such that the value of the integral in (10.10) remains constant. The limit $\mu = 0$ then defines a critical temperature T_c by

$$\mathscr{N} = C \int_0^\infty \frac{\epsilon^{1/2}}{\exp\{\epsilon/(k_B T_c)\} - 1} d\epsilon. \tag{10.11}$$

To determine T_c we introduce the dimensionless variable $z = \epsilon/(k_B T_c)$,

$$\frac{\mathcal{N}}{V} = (k_B T_c)^{3/2} \frac{C}{V} \int_0^\infty \frac{z^{1/2}}{\exp(z)-1} dz \sim T_c^{3/2}. \tag{10.12}$$

The integral in (10.12) has a finite value $\neq 0$, such that

$$\boxed{T_c = \text{const.} \cdot \left(\frac{\mathcal{N}}{V}\right)^{2/3}.} \tag{10.13}$$

At first glance one is attempted to interpret the result above that one cannot cool down a Bose gas at constant density $\mathcal{N}/V$ to temperatures $T < T_c$. This consideration, however, is not valid since the formula (10.10)—obtained by (10.9)—is only valid for $T > T_c$: The divergent term with $\epsilon_0 = \mu = 0$ in the original formula (10.8) is suppressed in (10.10) by the factor $\epsilon^{1/2}$. For high temperatures all energies ϵ are weakly occupied, such that the suppression of the contribution of $\epsilon_0 = 0$ in the calculation of the total particle number $\mathcal{N}$ is permited by (10.10). In contrast, at low temperatures almost all particles remain in the state with $\epsilon_0 = 0$, such that this state—in the transition (10.9)—must be treated separately. Thus:

$$\boxed{\mathcal{N} = \frac{1}{\exp(-\beta\mu)-1} + C \int_0^\infty \frac{\epsilon^{1/2}}{\exp(\beta[\epsilon-\mu])-1} d\epsilon = \mathcal{N}_0 + \mathcal{N}_G} \tag{10.14}$$

for $T < T_c$. Since at low temperatures $T < T_c$ there are a lot of particles in the state $\epsilon_0 = 0$, -$\beta\mu \approx 0$ must be fulfilled. Then one can approximate $\mathcal{N}_G$ by

$$\mathcal{N}_G \approx C \int_0^\infty \frac{\epsilon^{1/2}}{\exp(\beta\epsilon)-1} d\epsilon = C (k_B T)^{3/2} \int_0^\infty \frac{z^{1/2}}{\exp(z)-1} dz = C' V T^{3/2} \tag{10.15}$$

with $z := \beta\epsilon$. Using (10.12) or (10.13) we get

(10.16)

$$\frac{\mathcal{N}_G}{\mathcal{N}} = \left(\frac{T}{T_c}\right)^{3/2} .$$

Accordingly we obtain ($\mathcal{N}_0 = \mathcal{N} - \mathcal{N}_G$)

$$\boxed{\frac{\tilde{\mathcal{N}_0}}{\tilde{\mathcal{N}}} = \frac{\mathcal{N}_0}{\mathcal{N}} = 1 - \left(\frac{T}{T_c}\right)^{3/2}. \qquad (10.17)}$$

In total, the following picture emerges (see Fig. 10.2).

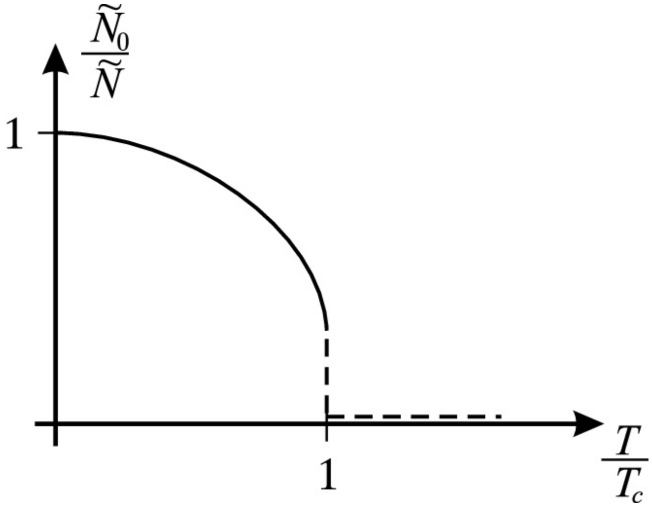

Fig. 10.2 The relative number of particles in the Bose-Einstein condensate as a function of temperature in units of T_c (10.17)

Above T_c the number of particles in the state $\epsilon_0 = 0$ is negligible relative to $\mathcal{N}$; below T_c the particle number in the condensate $\mathcal{N}_0$ increases rapidly and for $T = 0$ the occupation number $\mathcal{N}_0 = \mathcal{N}$. This process of gathering many (eventually all) particles in the state $\epsilon_0 = 0$ is called **Bose-Einstein condensation**; T_c is called the **condensation-temperature**. N_G gives the number of particles in the **gas phase**, N_0 that of the **condensate**. When using the term **condensation** one must point out, that for the Bose-Einstein condensation the particles are separated **in momentum space**, whereas in ordinary condensation (gas-liquid) a separation of the phases occurs **in space**.

A concrete **example** for Bose-Einstein condensation offers the ^4He system, which at $T_c = 2.18\,^\circ$K shows a clear phase transition (see Sect. 10.4). If we calculate T_c from (10.13), we get $3.14\,^\circ$K. The agreement is surprisingly good if one considers that the theory above neglects all intermolecular forces!

Note: The splitting made in (10.14) for $\mathscr{N}$ offers the question whether – apart from the state with $\epsilon_0 = 0$—also some higher states with energy $\epsilon_1, \epsilon_2, \ldots \neq 0$ have to be treated separately in the same way. This is not the case for $V \to \infty$, as the following consideration shows. As a typical example, we consider the term

$$\frac{\langle n_1 \rangle}{V} = \frac{1}{V} \frac{g(\epsilon)}{\exp(\beta[\epsilon - \mu]) - 1} \tag{10.18}$$

with

$$\epsilon_1 = \frac{\hbar^2 k_1^2}{2m} = \frac{\pi^2 \hbar^2}{2mL^2} = \frac{\pi^2 \hbar^2}{2m} V^{-2/3} \tag{10.19}$$

(generally: $\epsilon_i = \pi^2\hbar^2/(2mV^{2/3})(n_x^2 + n_y^2 + n_z^2)$; $V = L^3$; $n_x, n_y, n_z = 0$, 1, 2, ..).

and

$$g(\epsilon_1) = (2s+1) \cdot 3 \tag{10.20}$$

as a degeneracy factor of the ϵ_1 state. Since $e^{-\beta\mu} \geq 1$, it follows for $V \to \infty$ (i.e. $\epsilon_1 \to 0$)

$$\frac{\langle n_1 \rangle}{V} \leq \frac{1}{V} \frac{g(\epsilon_1)}{[\exp(\beta\epsilon_1) - 1]} \approx \frac{1}{V} \frac{g(\epsilon_1)}{\beta\epsilon_1} \tag{10.21}$$

$$= 3(2s+1) \frac{2mV^{-1/3}}{(\pi^2\hbar^2\beta)} \to 0$$

for $\beta \to \infty$ $(T \to 0)$. For macroscopic volumes V it is thus enough to just consider the $\epsilon_0 = 0$ term separately.

10.4 Internal Energy and Specific Heat

When calculating the internal energy U, a distinction must be made between $T > T_c$ and $T < T_c$:

(10.22)

$$U = C\int_0^\infty \frac{\epsilon^{3/2}}{\exp(\beta[\epsilon-\mu])-1} d\epsilon \,\text{for T} > \text{T}_\text{c}$$

and

$$U = C\int_0^\infty \frac{\epsilon^{3/2}}{\exp\,(\beta\epsilon)-1} d\epsilon \,\text{for T} < \text{T}_\text{c}.$$

For $T < T_c$ we can (as in Sect. 10.3) set $-\beta\mu \approx 0$, while for $T > T_c$ it should be noted that $\mu = \mu(T) \neq 0$. For temperatures T far above T_c we can use the classical approximation with the result already known from Sect. 4.4:

$$U = \tfrac{3}{2}\mathscr{N} k_B T. \tag{10.23}$$

For $T < T_c$ we can do the integration; with the substitution $z = \epsilon/k_BT$ we see immediately that $U \sim T^{5/2}$. The more precise result is

$$\boxed{U \approx 0.77\ \mathscr{N} k_B \frac{T^{5/2}}{T_c^{3/2}},} \tag{10.24}$$

from which follows

$$\boxed{C_V = \frac{\partial U}{\partial T} \approx 1.93\ \mathscr{N} k_B \left(\frac{T}{T_c}\right)^{3/2}.} \tag{10.25}$$

U and C_V arise only from the particles with $k \neq 0$. For C_V we get the following picture (see Fig. 10.3).

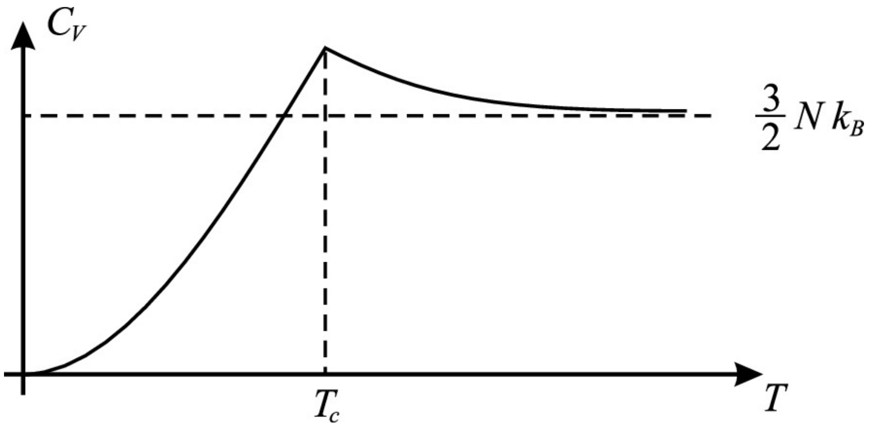

Fig. 10.3 Specific heat $C_V(T)$ for an ideal boson gas as a function of temperature

Such a peak also shows the specific heat of ^4He at $2.18\,^\circ$K, but in the form of a singularity. It is obvious that the ideal Bose gas is a too simple model to describe ^4He at low temperatures. Nevertheless, there is no doubt that during the phase transition in ^4He at $2.18\,^\circ$K the Bose statistics play an important role.

10.5 Photons

At temperatures $T \neq 0$ every body emits and absorbs electromagnetic radiation. In an evacuated cavity—whose walls are kept at a fixed temperature *T*—there will be a balance between the radiation in the cavity and the walls. For large cavities the special geometry shouldn't matter. For the sake of simplicity we choose a cube $V = L^3$.

We can describe the electromagnetic radiation in such a cavity by a photon gas. The main points for the following considerations are briefly summarized again:

1. Photons are characterized by their momentum $\hbar\mathbf{k}_\mu$, their energy $\hbar\omega_\mu$ and the polarization state *j*. The connection between energy and momentum follows from the theory of relativity for particles with rest mass 0,

$$E = p \cdot c \tag{10.26}$$

or

$$\omega_\mu = |\mathbf{k}_\mu| \cdot c. \tag{10.27}$$

The possible values $\mathbf{k}_\mu$ are

$$\mathbf{k}_\mu = \tfrac{2\pi}{L}(\mu_1, \mu_2, \mu_3); \mu_i \ = \pm 1, \pm 2, \pm 3 \ldots . \tag{10.28}$$

2. Photons have spin 1 $\hbar$ (since they are described by a vector field), and thus are bosons, which is reflected in the commutation rules for annihilation and production operators $b_{\mu j}, b^\dagger_{\mu' j'}$,

$$\boxed{[b_{\mu j,} b^\dagger_{\mu' j'}] = \delta_{\mu\mu'}\delta_{jj'} \ ; \qquad (10.29)}$$

all remaining commutators vanish. In (10.29) the indices $j, j' = 1, 2$ stand for the two polarization degrees of freedom of the photons (perpendicular to the direction of motion **k**).

3. The eigenstates of the radiation field are characterized by indicating the number of photons present of each species (μ, j) (see quantum mechanics),

$$|\ldots n_{\mu j} \ldots\rangle. \tag{10.30}$$

A direct photon-photon interaction (in lowest order) does not exist; photons are independent particles. The total energy E of the radiation field is composed additively from the contributions of the individual photons,

$$E = \textstyle\sum_{\mu,j} \hbar\omega_\mu \ n_{\mu j}, \tag{10.31}$$

if we consider E relative to the energy of the photon vacuum.

We can now describe the radiation in the cavity as a statistical ensemble of independent bosons (**photons**), from which we know the temperature T and the volume V. In contrast to an ordinary gas, we know the photon number neither sharp nor on average. This means that the statistical operator has the form

$$\rho = \exp\left(-\beta H_r\right), \tag{10.32}$$

where H_r is the Hamiltonian of the radiation field; by trace formation we have to sum over all basis states of the Fock-space with fixed volume. This results in e.g. for the average occupation number of the mode (μ, j) :

$$\langle n_{\mu j}\rangle = \frac{1}{\exp(\beta\hbar\omega_\mu)-1}. \tag{10.33}$$

To calculate the average energy we substitute—since there are two transversal polarization states ($j = 1.2$),

$$\sum_{\mu,j} \hbar\omega_j \ldots \to \frac{2V}{(2\pi)^3}\frac{4\pi}{c^3}\int_0^\infty \omega^2 d\omega\ \hbar\omega \ldots . \tag{10.34}$$

In contrast to the considerations in Sect. 10.3 the value $\omega = 0$ (or $k = 0$) does not need any special treatment, since it makes no sense to talk about photons with $\hbar\omega = 0$ and $\hbar\mathbf{k} = 0$. For the energy follows:

$$\boxed{U = V\int_0^\infty u(\omega, T)\ d\omega \qquad (10.35)}$$

with the energy density per frequency unit

$$\boxed{u(\omega, T) = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{\exp(\beta\hbar\omega)-1}. \qquad (10.36)}$$

Equation (10.36) is **Planck's radiation law**. For $\hbar\omega \ll k_B T$ ($\beta\hbar\omega \ll 1$) Eq. (10.36) leads to

$$\boxed{u(\omega, T) \approx \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{\beta\hbar\omega} = k_B T\ \frac{\omega^2}{\pi^2 c^3}; \qquad (10.37)}$$

this is the classical law derived by **Rayleigh** from the equipartition theorem. In (10.35) it leads to the divergence known as **ultraviolet catastrophe**. In the other extreme case $\hbar\omega \gg k_B T$ we get **Wien's law** (found empirically),

(10.38)

$$u(\omega, T) = \frac{\hbar\omega^3}{\pi^2 c^3} \exp\left(-\beta\hbar\omega\right).$$

The shape of $u(\omega, T)$ according to (10.36) is displayed in Fig. 10.4 for two different temperatures and reflects **Wien's displacement law**. The maximum in the energy density follows from

$$\frac{\partial u(\omega,T)}{\partial\omega} = \frac{\hbar\omega^2(3-\hbar\omega\beta)\exp(-\beta\hbar\omega)}{\pi^2c^3} = 0 \ , \tag{10.39}$$

i.e. $3k_BT = \hbar\omega_{max}$.

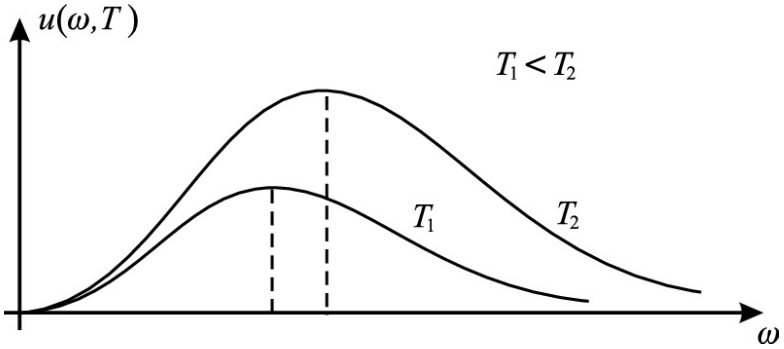

Fig. 10.4 Wien's displacement law for two temperatures

The total energy density reads (with $x = \beta\hbar\omega$)

$$\begin{aligned} \frac{U}{V} &= \frac{\hbar}{\pi^2c^3}\int_0^\infty \frac{\omega^3}{\exp(\beta\hbar\omega)-1}d\omega \\ &= \frac{(k_BT)^4}{\pi^2c^3\hbar^3}\int_0^\infty \frac{x^3}{\exp(x)-1}dx = \frac{\pi^2k_B^4}{15c^3\hbar^3}\ T^4 \equiv \frac{d}{30}\pi^2T^4 \end{aligned} \tag{10.40}$$

with $d = 2$ for two polarization degrees of freedom (in natural units). Equation (10.40) is denoted by the **Stefan-Boltzmann law**.

For the specific heat per unit volume we get

$$C_V \sim T^3. \tag{10.41}$$

The difference to (10.25) can be explained by the fact, that different energy-momentum relations exist: $\epsilon = pc$ for photons, but $\epsilon = p^2/(2m)$ for non-relativistic particles of mass m.

10.6 Detailed Balance

We want to examine more closely the processes, that lead to the equilibrium between the cavity radiation and its environment. It is sufficient to consider only the emission and absorption of photons of a certain frequency ω. It corresponds to the difference between two energies of the atoms of the walls delimiting the cavity:

$$\hbar\omega = E_2 - E_1. \tag{10.42}$$

The number of absorption processes ν_{12} per unit of time is

$$\boxed{\frac{d\nu_{12}}{dt} = B_{12} N_1 u(\omega, T), \qquad (10.43)}$$

where N_1 the number of atoms in state 1, $u(\omega, T)$ is the energy density of the photons of frequency ω, and B_{12} the probability for the elementary process of absorption.

For the number of emission processes ν_{21} one has to take into account that in addition to the induced emission (inverse of the absorption described by B_{12}) also spontaneous emission (due to quantization, see quantum mechanics) has to be considered. Thus:

$$\boxed{\frac{d\nu_{21}}{dt} = B_{21} N_2 u(\omega, T) + A_{21} N_2, \qquad (10.44)}$$

where B_{21} and N_2 are given according to (10.43) and A_{21} is the probability of the elementary process of **spontaneous emission**. As long as the Hamilton operator is time reversal invariant, we have according to micro-reversibility

$$B_{12} = B_{21}. \tag{10.45}$$

These equations are generally referred to as **detailed balance**. This statement also follows directly from the following considerations.

In thermal equilibrium we must have

(10.46)

$$\frac{d\nu_{12}}{dt} = \frac{d\nu_{21}}{dt}$$

or

$$B_{12}N_1u(\omega, T) = B_{12}N_2u(\omega, T) + A_{21}N_2 \qquad (10.47)$$

or

$$\frac{N_1}{N_2}u(\omega, T) - u(\omega, T) = \frac{A_{21}}{B_{12}}.$$

Furthermore,

$$\frac{N_1}{N_2} = \frac{\exp(-\beta E_1)}{\exp(-\beta E_2)} = \exp\left(-\beta(E_1 - E_2)\right) = \exp\left(\beta\hbar\omega\right), \qquad (10.48)$$

since the atoms at temperature *T* are described by the statistical operator $\exp\left(-\beta\ H_0\right)$, where H_0 is the Hamiltonian of atoms. This leads to

$$\boxed{u(\omega, T) = \frac{A_{21}}{B_{21}}\frac{1}{\exp(\beta\hbar\omega)-1} \quad . \qquad (10.49)}$$

Using Wien's law (10.38), which is valid for high frequencies, we obtain for A_{21}/B_{21} (by comparing the prefactors),

$$\boxed{\frac{A_{21}}{B_{21}} = \frac{\hbar\omega^3}{\pi^2c^3} \quad , \qquad (10.50)}$$

and (10.49) turns into Planck's law (10.36).

At first glance it seems like having derived Planck's radiation law without the concept of photons, i.e. within the framework of the classical radiation theory. The apparent contradiction is resolved, if we recall that the **spontaneous emission** used above is a direct consequence of the quantization of the radiation field (see quantum mechanics).

Equation (10.49) shows that Planck's law holds regardless of the material considered. The separate transition probabilities A_{21} and

$B_{21} = B_{12}$ depend on the type of the atom; however, the ratio A_{21}/B_{21} is independent of the atom type.

10.7 Phonons in Solids

The lattice building blocks of a solid body can oscillate around their equilibrium positions. For moderate temperatures these oscillations are small, such that anharmonic effects can be neglected. The Hamilton function of the crystal then has a quadratic form,

$$\boxed{H_{cl.} = \sum_{\nu=1}^{N} \frac{p_\nu^2}{2m_\nu} + \frac{1}{2} \sum_{\mu,\nu=1}^{N} K_{\mu\nu}\; q_\mu q_\nu. \qquad (10.51)}$$

Here p_ν, q_ν are the momenta and deflections of the particles, m_ν their masses, and $K_{\mu\nu}$ the force constants while *N* is the number of grid building blocks. By a linear transformation of the p_ν, q_ν it is always possible to decouple the oscillations. We then get 3N **normal oscillations** with frequencies ω_i (more precisely: 3N-6 after subtracting the degrees of freedom of translation and rotation; however, this correction is negligible for macroscopic systems). Each lattice building block therefore has three degrees of freedom of oscillation.

The quantization of such a system of decoupled harmonic oscillators proceeds as in the case of a single harmonic oscillator. The possible energies of the crystal during vibrational excitations (per direction) then is given by (see quantum mechanics)

$$\boxed{E = E_0 + \sum_{i=1}^{3N} \hbar\omega_i (n_i + \tfrac{1}{2}). \qquad (10.52)}$$

The vibration quanta are called **phonons**; they are characterized by their energy $\hbar\omega_i$, the propagation vector $\mathbf{k}_i$, which is linked to ω_i by a **dispersion relation** $\omega(k)$, and their polarization, corresponding to longitudinal and transverse oscillations. In the harmonic approximation the phonons are independent particles, which obey the Bose statistics.

We now consider a crystal with volume *V* at temperature *T*. As in case of a photon gas we do not know the total number of phonons (not to be confused with the number of grid building blocks *N*; it determines the number of possible frequencies ω_i!). So we know the average occupation number for a vibration *i* with excitation energy $\hbar\omega_i$,

$$\langle n_i \rangle = \frac{1}{\exp(\beta\hbar\omega_i)-1} \tag{10.53}$$

at a given temperature $k_B T = 1/\beta$ and given volume *V*, which determines the phonon frequencies ω_i.

We now want to calculate the **specific heat** of the crystal. To this aim we need the internal energy

$$\boxed{U = \sum_i \hbar\omega_i \langle n_i \rangle = \sum_i \frac{\hbar\omega_i}{\exp(\beta\hbar\omega_i)-1}.} \tag{10.54}$$

The calculation of the frequencies $\omega_i = \omega_i(k_i)$ is a complicated problem (to be solved numerically), which depends on the atomic structure of the crystal. The results of such a calculation cannot be specified in the form of simple functions $\omega = \omega(k)$. We therefore consider a model that is simple enough, but allows to calculate expressions like (10.54) and on the other hand remains sufficiently realistic. This **Debye model** is based on two approximations:

(1.) Since for macroscopic systems the frequencies ω_i lie close together, the sums are replaced by an integration

$$\sum_i \cdots = (2s+1)\sum_k \cdots = (2s+1)\frac{V}{(2\pi)^3}\int d^3k \cdots . \tag{10.55}$$

The integration must be **limited** such that the number of the degrees of freedom (3N) is kept constant!

(2.) For the connection between *ω* and *k* one assumes a simple dispersion relation,

$$\boxed{\omega = c_0 k,} \tag{10.56}$$

with c_0 as the speed of propagation of the vibrations in the crystal. This approximation corresponds to (10.27) for photons and is suitable for long wavelengths acoustic oscillations in an isotropic medium; c_0 then is the usual **speed of sound**.

The relation (10.56)—valid for small k values—is used in the Debeye model for all frequencies up to the maximum frequency ω_m, which is determined by the fixed number of degrees of freedom (with $(2s+1)=3$):

$$3\ N = \sum_i\ 1 = \frac{3V}{(2\pi)^3} 4\pi \int_0^{k_m} k^2 dk = \frac{V}{(2\pi^2)} k_m^3, \tag{10.57}$$

thus

$$k_m = \left(\frac{3\ N\ 2\pi^2}{V}\right)^{1/3} = (6\pi^2)^{1/3}\ \left(\frac{N}{V}\right)^{1/3} \tag{10.58}$$

or

$$\omega_m = c_0 \left(6\pi^2 \frac{N}{V}\right)^{1/3}. \tag{10.59}$$

This gives for U,

$$U = \frac{3V}{(2\pi^2 c_0^3)} \int_0^{\omega_m} \omega^2 \frac{\hbar\omega}{\exp(\beta\hbar\omega)-1} d\omega \tag{10.60}$$

or for the internal energy per lattice building block (with $t = \beta\hbar\omega$)

$$\frac{U}{N} = \frac{9(k_B T)^4}{(\hbar\omega_m)^3} \int_0^{\beta\hbar\omega_m} \frac{t^3}{\exp(t)-1} dt. \tag{10.61}$$

Defining the **Debeye function** by

$$D(x) = \frac{1}{x^3} \int_0^x \frac{t^3}{\exp(t)-1} dt, \tag{10.62}$$

we get

$$\frac{U}{N} = 9\ k_B T\ D\left(\frac{T_D}{T}\right) \tag{10.63}$$

with the **Debeye temperature** T_D defined by

$$k_B T_D =: \hbar\omega_m. \tag{10.64}$$

For the limiting cases $T \to 0, T \to \infty$ the explicit values of $D(T_D/T)$ are

$$\frac{U}{N} = \ 3\ k_B T \,\text{for}\ \ \mathrm{T \gg T_D}, \tag{10.65}$$

$$\frac{U}{N} \ = \ \frac{3}{5}\ \pi^4 k_B T\left(\frac{T}{T_D}\right)^3 \text{for}\ \ \mathrm{T \ll T_D}. \tag{10.66}$$

Then the specific heat per grid building block is

$$C_V = \ 3\ k_B \,\text{for}\ \ \mathrm{T \gg T_D} \tag{10.67}$$

$$C_V = \ \frac{12}{5}\pi^4 k_B\left(\frac{T}{T_D}\right)^3 \text{for}\ \ \mathrm{T \ll T_D}. \tag{10.68}$$

In practice $T_D \sim 10^2$ K. At low temperatures C_V vanishes with T^3 in agreement with the 3rd law of thermodynamics and the experimental findings.

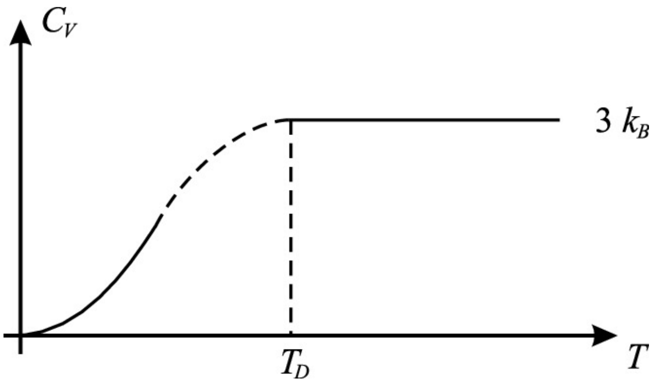

Fig. 10.5 Specific heat $C_V(T)$ as a function of temperature *T* for mono-atomic crystals

At high temperatures the classic result (**rule of Dulong-Petit**) is confirmed with $C_V = 3k_B$ (see Fig. 10.5).

The Debye model has been proven useful in the description of mono-atomic crystals when avoiding very high temperatures (close to the melting point), where the harmonic approximation fails.—Weak anharmonicities can be taken into account using the thermodynamic perturbation theory (Sect. 8.3).—In polyatomic lattices the simple model fails because there are in addition **optical** (dipole) oscillations.

Example: Oscillations of the Na^+ ions against the Cl^- ions in a *NaCl* crystal.

In summary of this chapter we have discussed the properties of ideal Bose systems in particular at low temperatures, where a Bose condensation occurs. Furthermore, we have calculated the specific heat and internal energy and confirmed the 3rd law of thermodynamics. As important example we have calculated the photon radiation in a large cavity and derived Planck's radiation law. As another example we have discussed phonons in solids as quantized harmonic vibrations of the building blocks.

W. Cassing, *Theoretical Physics Compact IV*
https://doi.org/10.1007/978-3-031-95518-1_11

11. Real Interacting Gases

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So far we have considered highly dilute (ideal) gases in which the interaction between the particles could be neglected. In the following we will consider moderately diluted and interacting gases; for the sake of simplicity we consider gas particles without spin, i.e. $(2s+1)=1$. As important example we will investigate the properties of a classical Van der Waals gas as well as ‘nuclear matter’ in thermal equilibrium as an example for an interacting Fermi system.

11.1 Virial Expansion

In order to deal with the effects of particle interactions we perform the following expansion of the grand-canonical partition function Z_g (with $PV=-J=k_BT\ \ln\ Z_g$),

$$\boxed{\ln\ Z_g=\frac{PV}{k_BT}=Z(1)\ \exp\left(\frac{\mu}{k_BT}\right)+\left(Z(2)-\frac{1}{2}Z(1)^2\right)\ \exp\left(\frac{2\mu}{k_BT}\right), \qquad (11.1)}$$

where $Z(1)=V/\lambda^3$ (6.28) is the partition function of a particle for a non-interacting ideal gas ($\lambda=h/\sqrt{2\pi mk_BT}$). The second contribution takes into account the interaction between two particles or exchange symmetries of the particles (via $Z(2)$). By differentiating with respect to μ we get the average number of particles

$$\boxed{\mathcal{N}=\frac{1}{\beta}\frac{\partial}{\partial\mu}\ \ln\ Z_g=Z(1)\ \exp\left(\frac{\mu}{k_BT}\right)+2\left(Z(2)-\frac{1}{2}Z(1)^2\right)\ \exp\left(\frac{2\mu}{k_BT}\right). \qquad (11.2)}$$

For the iterative solution of (11.2) we set (in agreement with (6.20))

$$\exp\ (-\alpha)=\exp\left(\frac{\mu}{k_BT}\right)=\frac{\mathcal{N}}{Z(1)} \tag{11.3}$$

in the correction part and get (after rearrangement)

$$Z(1)\,\exp\left(\tfrac{\mu}{k_BT}\right)=\mathscr{N}-2\Big(Z(2)-\tfrac{1}{2}Z(1)^2\Big)\Big(\tfrac{\mathscr{N}}{Z(1)}\Big)^2 \tag{11.4}$$

or, inserted into (11.1)

$$\ln Z_g=\tfrac{PV}{k_BT}=\mathscr{N}-\Big(Z(2)-\tfrac{1}{2}Z(1)^2\Big)\Big(\tfrac{\mathscr{N}}{Z(1)}\Big)^2. \tag{11.5}$$

Equation (11.5) then is the extended form of the equation of state (7.125) ($PV=Nk_BT$). For the pressure we obtain the first terms in an expansion according to powers of the density

$$n=\tfrac{\mathscr{N}}{V}, \tag{11.6}$$

i.e.

$$P=nk_BT(1+b(T)n+\cdots) \tag{11.7}$$

with

$$b(T)=-\tfrac{V}{Z(1)^2}\Big(Z(2)-\tfrac{1}{2}Z(1)^2\Big)=-\tfrac{VZ(2)}{Z(1)^2}+\tfrac{V}{2}. \tag{11.8}$$

The expansion (11.7) is called **virial expansion** and $b(T)$ (11.8) the **first virial coefficient**.

To calculate $b(T)$ we only need $Z(2)$, since $Z(1)=V/\lambda^3$ (6.28) is already known. Since an explicit calculation of $Z(2)$ within the framework of many-body theory is too complex here, first of all we will discuss the result in lowest (non-vanishing) order for Fermi/Bose particles at 'low' temperatures:

$$\begin{aligned}Z(2)\ &\approx \tfrac{1}{2}\textstyle\sum_{\mathbf{q},\mathbf{p}}\exp\left(-\tfrac{p^2+q^2}{2mk_BT}\right)\mp\tfrac{1}{2}\textstyle\sum_{\mathbf{p}}\exp\left(-\tfrac{p^2}{mk_BT}\right)\\ &=\tfrac{1}{2}Z(1)^2\mp\tfrac{1}{2}\textstyle\sum_{\mathbf{p}}\exp\left(-\tfrac{2p^2}{2mk_BT}\right)\end{aligned} \tag{11.9}$$

$$=\frac{1}{2}Z(1)^2\mp B(T),$$

where $\sum_p$ corresponds to the sum over all discrete momentum states in the volume *V*. The first term is proportional to the square of the partition function for free particles of mass *m* ($= 1/2Z(1)^2$), while the second term gives a correction for Fermi (upper-sign) and Bose statistics (lower + sign) of two particles, since for Fermi particles $\mathbf{p} = \mathbf{q}$ does not occur in *Z*(2) (with the same other quantum numbers); however, for Bose particles $\mathbf{p} = \mathbf{q}$ must occur, but without the factor 1/2, which clearly explains the second term in (11.9). The corrections in *Z*(2) therefore only contain effects of the Fermi/Bose statistics at 'low' temperatures!

With (11.8) we get for the first Virial coefficients ($Z(1) = V/\lambda^3$)

$$b(T) = -\frac{V}{Z(1)^2}\left(\frac{Z(1)^2}{2} \mp B(T) - \frac{Z(1)^2}{2}\right) = \pm\frac{VB(T)}{Z(1)^2}$$

$$= \pm\tfrac{V}{2Z(1)^2}\textstyle\sum_{\mathbf{p}} \exp\left(-\tfrac{p^2}{mk_BT}\right) = \pm\tfrac{\lambda^6}{2V}\textstyle\sum_{\mathbf{p}} \exp\left(-\tfrac{p^2}{mk_BT}\right). \qquad (11.10)$$

According to (11.7) the pressure *P* increases with increasing density *n* for fermions, while for bosons it decreases with *n*. In analogy to Sect. 6.4 we replace ($(2s+1) = 1$)

$$\begin{aligned} \textstyle\sum_{\mathbf{p}} \exp\left(-\tfrac{p^2}{mk_BT}\right) \quad &\rightarrow \tfrac{4\pi V}{h^3}\textstyle\int_0^\infty dp\ p^2\ \ \exp\left(-\tfrac{p^2}{mk_BT}\right) \\ = \tfrac{\pi V}{h^3}\sqrt{\pi}(mk_BT)^{3/2} &= \tfrac{V}{h^3}(\pi mk_BT)^{3/2}. \end{aligned} \qquad (11.11)$$

Inserting the result from (6.31) for λ, i.e. $\lambda = h/\sqrt{2\pi mk_BT}$, this gives

$$b(T) = \pm\tfrac{\lambda^6}{2V}\,\tfrac{V\sqrt{\pi mk_BT}^3}{h^3} = \pm\tfrac{\lambda^3}{2}2^{-3/2} = \pm 2^{-5/2}\lambda^3 \approx \pm\ 0.177\ \lambda^3. \qquad (11.12)$$

Since λ^2 decreases as $\sim 1/T$, *b*(*T*) decreases for high temperatures $\sim T^{-3/2}$ as expected. As already emphasized, however, with the approach (11.9) only Fermi/Bose corrections of the ideal classical gas are described at 'low' temperatures (and weak interactions). An explicit two-particle interaction is not yet included in (11.9)!

If, on the other hand, one considers real gases at not too 'low' temperatures with realistic interactions, we can calculate *b*(*T*) in semiclassical approximation (in Boltzmann statistics) by the phase-space integral

$$Z(2) = \frac{1}{2}\int \frac{d^3p_1}{(2\pi)^3}\int \frac{d^3p_2}{(2\pi)^3}\int d^3x_1 \int d^3x_2 \ \ \exp\left(-\beta\left(\frac{p_1^2+p_2^2}{2m} + v(\mathbf{x}_1-\mathbf{x}_2)\right)\right)$$

$$= \tfrac{1}{2\lambda^6}\int d^3x_1 d^3x_2 \ \ \exp\left(-\beta v(\mathbf{x}_1-\mathbf{x}_2)\right), \qquad (11.13)$$

where $v(\mathbf{x}_1 - \mathbf{x}_2)$ is the two-particle interaction in spatial coordinates. The normalization of (11.13) becomes transparent for $v(\mathbf{x}_1 - \mathbf{x}_2)) = 0$, since then $Z(2) = V^2/(2\lambda^6) = 1/2Z(1)^2$, i.e. the virial coefficient *b*(*T*) vanishes according to (11.8). The transformation to center-of-mass ($\mathbf{R} = (\mathbf{x}_1 + \mathbf{x}_2)/2$) and relative coordinate ($\mathbf{r} = (\mathbf{x}_1 - \mathbf{x}_2)$) gives

$$\begin{aligned} Z(2) &= \tfrac{1}{2\lambda^6}\int d^3R \int d^3r \ \ \exp\left(-\beta v(|\mathbf{r}|)\right) \\ &= \tfrac{V}{2\lambda^6} \ 4\pi\int_0^\infty dr \ r^2 \ \ \exp\left(-\beta v(r)\right) \end{aligned} \qquad (11.14)$$

for a rotation invariant two-particle interaction *v*(*r*). With $V^2/\lambda^6 = Z(1)^2$ we obtain from (11.8) ($b(T) = -VZ(2)/Z(1)^2 + V/2$)

$$\begin{aligned} b_{cl.}(T) &= -\tfrac{1}{2} \ 4\pi\int_0^\infty dr \ r^2 \ \ \exp\left(-\beta v(r)\right) + \tfrac{V}{2} \\ &= -2\pi\int_0^\infty dr \ r^2 \ \left(\exp\left(-\beta v(r)\right) - 1\right). \end{aligned} \qquad (11.15)$$

The evaluation of (11.15) is usually done numerically. For a rough estimate of the temperature dependency we consider a 'hard core' potential, i.e. assuming

$$\begin{aligned} &\exp\left(-\beta v(r)\right) - 1 \approx -1 \quad \text{if } \ r \le c; \\ &\exp\left(-\beta v(r)\right) - 1 \approx -\beta v(r) \quad \text{if } \ r > c, \end{aligned} \qquad (11.16)$$

where *c* denotes the 'hard core' radius and *v*(*r*) a (weakly) attractive interaction for $r > c$ (i.e. more precisely $|\beta v(r)| \ll 1$ for $r > c$). With the approximation (11.16) we get

$$b_{cl.}(T) = 2\pi\left(\tfrac{c^3}{3} + \beta\int_c^\infty dr \ r^2 v(r)\right). \qquad (11.17)$$

Considering the particles as hard spheres, then $c/2 = R$ is the radius of a particle while $c = 2R$ denotes the minimum distance between the hard spheres. One conveniently writes (11.17) as

$$b_{cl.} = b - \beta a = 4\left(\frac{4\pi}{3}\left(\frac{c}{2}\right)^3\right) - \frac{a}{k_BT} = 4V_k - \frac{a}{k_BT}. \tag{11.18}$$

In (11.18) $b = 4V_k$ then is four times the proper volume of a particle (in the case of hard spheres) and

$$a = -2\pi \int_c^\infty dr\ r^2 v(r), \tag{11.19}$$

a measure for the integrated interaction strength, which still depends on the explicit form of $v(r)$. For dominantly attractive interactions in the range $r > c$ the measure $a > 0$.

An application of this theory can be found in the experimental determination of the two-body potential under the assumption of a short-range repulsive and a long-range attractive interaction with a few free parameters. One often uses the **Lennard-Jones potential**

$$v(r) = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^5\right). \tag{11.20}$$

The constants ϵ and σ are obtained by fits to the virial coefficients; the interaction strength a is calculated as

$$a = -4\pi\epsilon\left(\frac{2\sigma^{12}}{9c^9} - \frac{\sigma^5}{c^2}\right) \tag{11.21}$$

and has the dimension [energy x volume].

11.2 The Van der Waals Equation

We will now derive an equation of state, that at least **qualitatively** can describe a **gas-liquid phase transition**. We divide the interaction again,

$$v(r) = v_c(r) + v_a(r), \tag{11.22}$$

where $v_c(r) = 0$ for $r > c$ and $v_c(r) = \infty$ for $r \leq c$ as in the case above for spherical particles; $v_a(r)$ then is a weaker attractive part, that can be taken into account in first order perturbation theory.

We write the free energy F as

$$F = F_0 + \langle V_a \rangle; \qquad \langle V_a \rangle = \tfrac{1}{2} \sum_{m \neq n} v_a(r_{nm}) \tag{11.23}$$

with $r_{nm} = |\mathbf{r}_n - \mathbf{r}_m|$. In (11.23) F_0 is the free energy of a system with purely repulsive interaction (v_c). For the ideal gas the partition function (for N particles) is

$$\boxed{Z_{ideal} = \tfrac{1}{N!} \left(\tfrac{V}{\lambda^3}\right)^N \approx \left(\tfrac{eV}{N\lambda^3}\right)^N \tag{11.24}}$$

with $N! \approx \sqrt{2\pi e}\ (N/e)^{(N+0.5)}(1 + (ne)^{-1} + (288n^2)^{-2} + \cdots) \sim (N/e)^N$ for large N. In case of an ideal, repulsive gas a part of the volume is restricted or forbidden by the interaction v_c. We therefore use:

$$\ln Z_0 \approx N \ln \left(\tfrac{e(V - V_0)}{N\lambda^3}\right). \tag{11.25}$$

In (11.25) V_0 is still a function of density, whose dependence we can determine by comparing to the virial expansion for small densities N/V. To this aim we form (with $F_0 = -k_B T \ln Z_0$)

$$P = -\tfrac{\partial F_0}{\partial V} \approx k_B T \tfrac{\partial}{\partial V} \ln Z_0 = N k_B T \tfrac{1}{V - V_0} \approx \tfrac{N}{V} k_B T (1 + \tfrac{V_0}{V}) \tag{11.26}$$

for $V \gg V_0$. This expression can be compared with the Virial expansion (11.7)

$$P = \tfrac{N}{V} k_B T \big(1 + b(T) \tfrac{N}{V} + \cdots\big) \tag{11.27}$$

for $b(T) = b$ in the case of the ‘hard core’ interaction (see (11.18)). The comparison for small particle densities N/V gives

$$\boxed{V_0 = Nb, \tag{11.28}}$$

i.e. the excluded volume per particle $V_0/N = b$ is equal to four times the particle volume V_K. In the following the relation (11.28) is also assumed at higher densities.

To calculate $\langle V_a \rangle$,

$$\langle V_a \rangle = \tfrac{1}{2} \langle \textstyle\sum_{m \neq n} v_a(|\mathbf{r}_m - \mathbf{r}_n)| \rangle = \tfrac{1}{2} \int d^3 r\ v_a(r)\ \langle \textstyle\sum_{m \neq n} \delta(r - |\mathbf{r}_m - \mathbf{r}_n|) \rangle \tag{11.29}$$

$$= \frac{N}{2} \int d^3 r\ v_a(r) S_c(r)$$

we introduce the correlation function $S_c(r)$ by

$$S_c(r) = \frac{1}{N}\langle \textstyle\sum_{m\neq n} \delta(r - |\mathbf{r}_m - \mathbf{r}_n|)\rangle. \tag{11.30}$$

The correlation function is normalized to the particle number (because of the double sum over $n \neq m$), i.e.

$$\int_0^\infty dr\ \ S_c(r) = N, \tag{11.31}$$

and is proportional to the probability to find two particles at a distance *r*. In the most simple approximation (for small densities) it is sufficient to consider two isolated particles. This approximation yields

$$S_C = 0 \quad \text{if } r < c; \qquad\qquad S_C = \frac{N}{V} = n \quad \text{if } r \geq c \tag{11.32}$$

for $V \gg V_0$. This results in

$$\begin{aligned} \langle V_a \rangle &= \frac{N}{2}\int d^3r\ \ v_a(r)\ \ S_c(r) = \frac{N}{2}\int_{r\rangle c} d^3r\ \ v_a(r)\frac{N}{V} \\ &= \frac{N^2}{2V} 4\pi \int_c^\infty dr\ \ r^2\ \ v_a(r) = -\frac{N^2}{V} a \end{aligned} \tag{11.33}$$

with *a* from (11.19) in the Viral expansion. Then the **free energy** reads (with the consideration of the interaction $v_a(r)$)

$$F = Nk_BT \ln\left(\frac{\lambda^3 N}{e(V-bN)}\right) - \frac{N^2 a}{V} = -k_BT \ln Z. \tag{11.34}$$

The energy *U* results from differentiating $-\ln Z$ with respect to β:

$$\begin{aligned} U &= -\frac{\partial}{\partial\beta}\ln Z = \frac{\partial}{\partial\beta}(\beta F) = F + \beta\frac{\partial F}{\partial\beta} \\ &= -\frac{N^2 a}{V} + N\frac{\partial}{\partial\beta}\ln\left(\frac{\lambda^3 N}{e(V-bN)}\right) = \frac{3}{2}Nk_BT - \frac{N^2 a}{V} \end{aligned} \tag{11.35}$$

with $\partial\lambda/\partial\beta = \lambda/(2\beta)$ or

$$\frac{U}{N} = \frac{3}{2}k_BT - \frac{N}{V}a.$$

The **Van der Waals equation** finally emerges from the differentiation of $-F$ with respect to V:

$$P = -\frac{\partial F}{\partial V} = \frac{Nk_BT}{V-Nb} - \frac{N^2a}{V^2} \approx \frac{N}{V}k_BT(1+\frac{N}{V}b) - \frac{N^2a}{V^2} \tag{11.36}$$

or

$$P \approx nk_BT + k_BTn^2b - n^2a = nk_BT + n^2(k_BTb - a)$$

with $n = N/V$. The approximation shows that with increasing temperature the finite proper volume leads to an effectively stronger repulsive interaction.

For the discussion of the equation of state (11.36) it is useful to consider the behavior of isotherms (T =const.). Extrema follow from (N, T fixed)

$$P'_V(T) := \left(\frac{\partial P}{\partial V}\right)_T = -\frac{Nk_BT}{(V-bN)^2} + \frac{2aN^2}{V^3} = 0. \tag{11.37}$$

The explicit solution of the Eq. (11.37) shows two zeros for temperatures below a critical temperature T_c. At the **critical temperature**

$$k_BT_c = \frac{8a}{27b} \tag{11.38}$$

both extremes coincide. The corresponding **critical volume** results in

$$V_c = 3bN \text{ or } \frac{V_c}{N} = 3b =: n_c^{-1}. \tag{11.39}$$

For the **critical pressure** we get (11.38), (11.39) and (11.36)

$$P_c = \frac{N8a/(27b)}{2bN} - \frac{aN^2}{9b^2N^2} = \left(\frac{4}{27} - \frac{1}{9}\right)\frac{a}{b^2} = \frac{a}{27b^2}. \tag{11.40}$$

All critical variables are connected by the universal relation

$$\frac{Nk_BT_c}{P_cV_c} = \frac{8}{3}, \tag{11.41}$$

as verified by insertion.

11.3 Condensation

In Fig. 11.1 we show a typical $P - V$ diagram for a Van der Waals system at various temperatures below and above T_c; the red line displays the isotherm for the critical temperature T_c. Above the critical isothermal line the system is always in the gas phase while below the red line a mixture of gas and liquid may occur in some region of V.

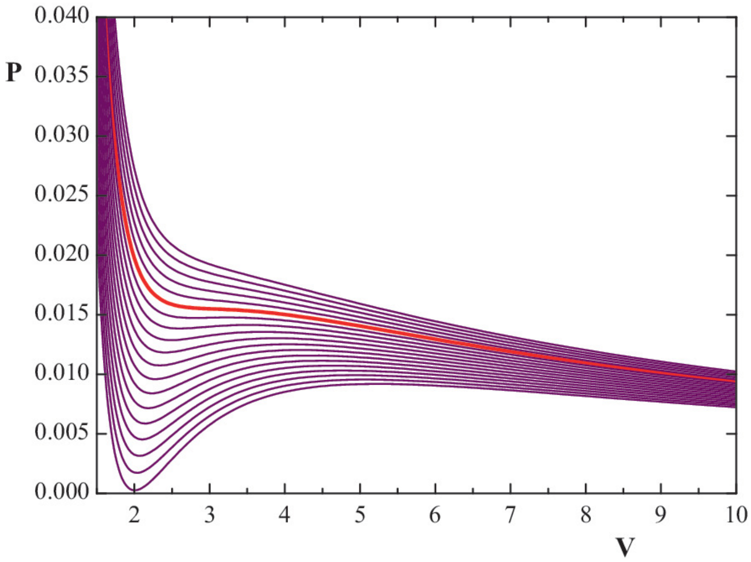

Fig. 11.1 A typical $P - V$ diagram for a Van der Waals system at various temperatures below and above T_c; the red line displays the pressure for the critical temperature T_c

In order to examine more closely the behaviour of the isotherms for $T < T_c$ we display in Fig. 11.2 a typical (isothermal) P-V diagram for a Van der Waals system at $T < T_c$, which has a minimum in the point B and a maximum in C.

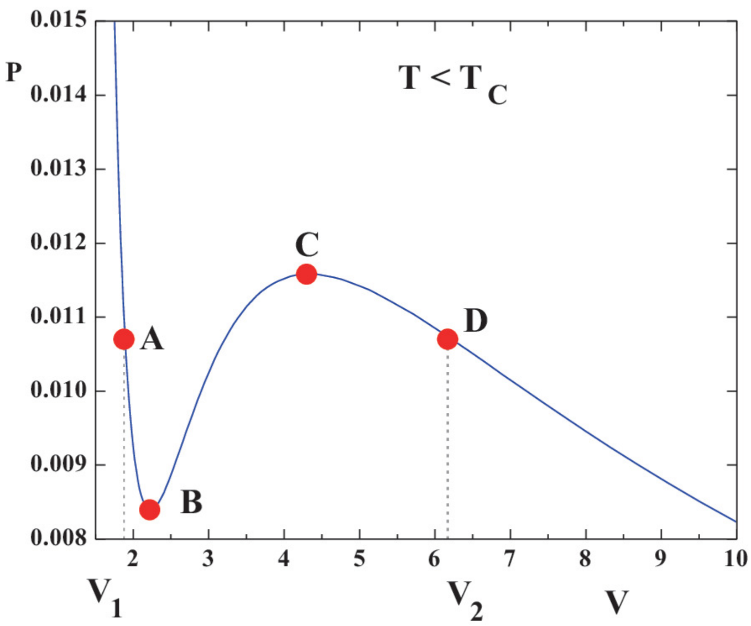

Fig. 11.2 Illustration of a typical (isothermal) P-V diagram for a Van der Waals system at $T < T_c$ with two extrema

The branch $B - C$ is unphysical, since here

$$\left(\frac{\partial P}{\partial V}\right)_T > 0, \tag{11.42}$$

which corresponds to an unstable state. The correct curve, however, is given by a constant (in pressure), i.e. $\partial P/\partial V = 0$, and describes a phase transition from the liquid to the gas phase. The—still to be determined—constant corresponds to the vapor pressure $P(T)$, in which both phases can coexist. Along the straight line $A - D$ then phase equilibrium must hold

$$\mu_1 = \mu_2. \tag{11.43}$$

Because of

$$\mu N = G = F + PV \tag{11.44}$$

then $F_1 + PV_1 = F_2 + PV_2$ or

$$\boxed{\begin{aligned} P(V_2 - V_1) &= -(F_2 - F_1) = -\int_{F_1}^{F_2} dF \\ &= -\int_{V_1}^{V_2} \left(\frac{\partial F}{\partial V}\right)_T dV = \int_{V_1}^{V_2} P(V)_T \, dV, \end{aligned} \qquad (11.45)}$$

with (11.36) for $P(V)_T$. When integrating over the line $(A - D)$ the (green) areas in Fig. 11.3 must be of the same size (**Maxwell construction**), i.e. the constant pressure P (in phase equilibrium) must fulfill

$$P = \frac{1}{V_2 - V_1} \int_{V_1}^{V_2} P(V)_T \; dV. \tag{11.46}$$

The Van der Waals equation—as well as the discussion above—implies that the interaction strength a must be $a > 0$, i.e. that the interaction for $r > c$ predominantly must be attractive. This requirement is fulfilled for most atomic and molecular gases, such that in ‘all’ these systems there is a phase transition ‘gas $\leftrightarrow$ liquid’ at sufficiently low temperatures.

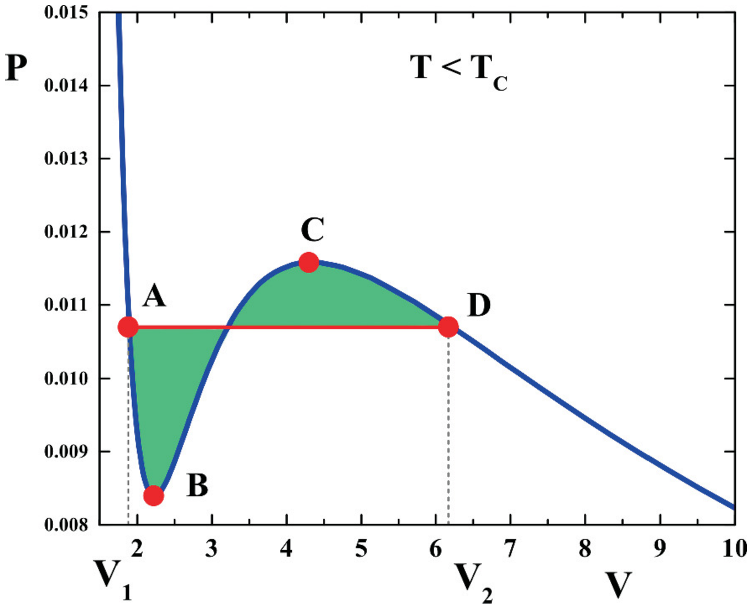

Fig. 11.3 Illustration of the Maxwell construction; Eq. (11.45) implies that the (green) areas below the straight red line $A - D$ and above the straight line $A - D$ must be identical, i.e. the (constant) pressure P must satisfy (11.46) at constant temperature T

11.4 Nuclear Matter

A simple example of an interacting Fermi gas is the following model (with effective two and three-particle interactions) describing the properties of ‘nuclear matter’ in a simple way. Here ‘nuclear matter’ is understood e.g. as the interior of a ^{208}Pb nucleus with constant nucleon density (protons and neutrons) of $\rho_0 \approx 0.16$ fm^{-3} and binding energy per particle $E_B/N \approx -16$ MeV. The nucleon density $\rho = N/V$ then for a Fermi gas at the temperature $T = 0$ is given by

$$\rho = \frac{g}{(2\pi)^3} \int_{k_F} d^3k = \frac{g4\pi}{(2\pi)^3} \int_0^{k_F} k^2 \; dk = \frac{g}{6\pi^2} k_F^3 \tag{11.47}$$

with degree of degeneracy $g = 4$ for 2 spin projections and 2 isospin components (protons and neutrons) and the Fermi momentum

$$P_F = \hbar k_F = \hbar \left(\frac{6\pi^2}{g} \rho \right)^{1/3}. \tag{11.48}$$

Setting $\rho = \rho_0$ then (11.48) gives $k_F \approx 1.33\ \mathrm{fm}^{-1}$ or $P_F \approx 263$ MeV/c. The Fermi energy becomes $\epsilon_F = P_F^2/(2m) \approx 36$ MeV (with $mc^2 \approx 938$ MeV), such that atomic nuclei at room temperature are always in the groundstate. The average kinetic energy per particle amounts to

$$\frac{\langle T_{kin} \rangle}{N} == \frac{1}{\rho} \frac{g 4\pi}{(2\pi)^3} \int_0^{k_F} k^2 \ \frac{\hbar^2}{2m} k^2 \ dk = \frac{3}{5} \epsilon_F. \tag{11.49}$$

The kinetic energy per particle given by (11.47) and (11.48) can also be written as a function of density,

$$\frac{\langle T_{kin} \rangle}{N} = \frac{3}{5} \ \frac{\hbar^2 c^2}{2mc^2} \left(\frac{6\pi^2}{g} \rho \right)^{2/3} = \frac{3\hbar^2 c^2}{10mc^2} \left(\frac{6\pi^2}{g} \right)^{2/3} \rho^{2/3} = C_T \rho^{2/3}. \tag{11.50}$$

The **kinetic energy density** $\langle T_{kin} \rangle / V$ is given by multiplying (11.50) by $N/V = \rho$,

$$\frac{\langle T_{kin} \rangle}{V} = C_T \rho^{5/3}. \tag{11.51}$$

However, this is a pure non-interacting Fermi gas, which is unbound due to the Pauli pressure, and one has to introduce an effective interaction to obtain a bound state of nuclear matter. A simple variant is to assume short-range 2 and 3-particle interactions $\sim \delta^3(\mathbf{r} - \mathbf{r}')$, such that the total energy density can be written as

$$\frac{\langle H \rangle}{V}(\rho) = C_T \rho^{5/3} - \frac{V_2}{2} \rho^2 + \frac{V_3}{3} \rho^3 \tag{11.52}$$

with the parameters V_2 for an attractive potential energy density (2-particle interaction) and V_3 for a repulsive potential energy density (3-particle interaction). This energy functional gives for the **mean field of nucleons**

$$U_H(\rho) = \frac{\partial}{\partial \rho} \frac{\langle V_{pot} \rangle}{V}(\rho) = -V_2 \rho + V_3 \rho^2 \tag{11.53}$$

as the derivative of the potential energy density with respect to ρ. The energy per particle is (after division by ρ)

$$\boxed{\frac{\langle H\rangle}{N}(\rho) = C_T\rho^{2/3} - \frac{V_2}{2}\rho + \frac{V_3}{3}\rho^2 = \frac{E_B}{N}. \qquad (11.54)}$$

The parameters V_2 and V_3 are determined from the requirement that (11.54) has a minimum for $\rho = \rho_0$,

$$\frac{d}{d\rho}\frac{\langle H\rangle}{N}\Big|_{\rho_0} = \frac{2C_T}{3}\rho_0^{-1/3} - \frac{V_2}{2} + \frac{2V_3}{3}\rho_0 = 0 \tag{11.55}$$

and the binding energy per particle (−16 MeV) amounts,

$$\frac{\langle H\rangle}{N}\Big|_{\rho_0} = C_T\rho_0^{2/3} - \frac{V_2}{2}\rho_0 + \frac{V_3}{3}\rho_0^2 = -16\ MeV. \tag{11.56}$$

From the Eqs. (11.55) and (11.56) we can now determine the parameters numerically to $V_2 \approx 765$ MeV fm^3 and $V_3 \approx 2782$ MeV fm^6, which gives the binding energy per particle (11.54) and thus the equation of state (EoS) of symmetric nuclear matter. As Fig. 11.4 shows, this results in a minimum of the binding energy due to the compensation of kinetic energy and the attractive and repulsive parts of the interaction (11.52).

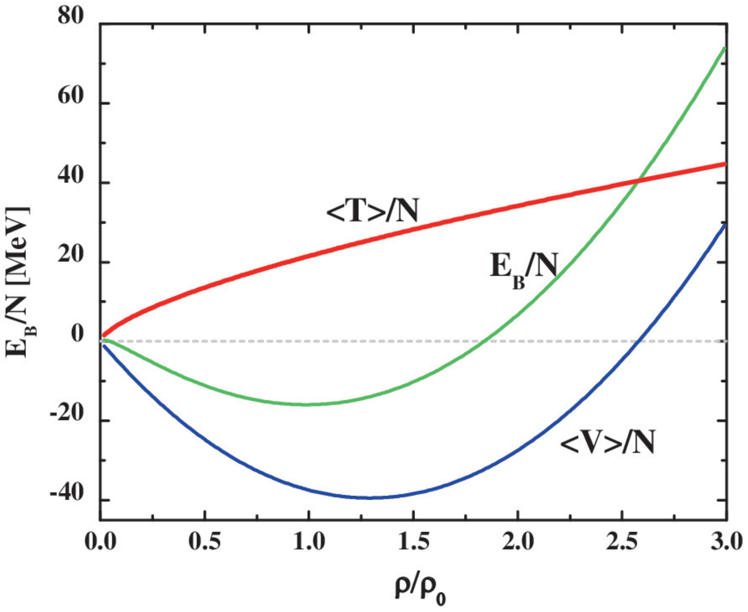

Fig. 11.4 Binding energy per nucleon E_B/N as a function of density ρ (in units of ρ_0). The kinetic energy per nucleon and the potential energy per nucleon are represented by the top (red) and bottom (blue) lines, respectively

Since at saturation ($\rho = \rho_0$) the (negative) potential energy per particle is larger than the kinetic energy per particle in magnitude,

$$\frac{\langle T_{kin}\rangle}{\langle |V|\rangle} < 1, \tag{11.57}$$

nuclear matter in its groundstate can be considered as a **liquid**.

A characteristic quantity for the EoS of nuclear matter is the **incompressibility** defined by

$$\boxed{K = 9\rho_0^2 \left(\frac{d^2}{d\rho^2}\frac{\langle H\rangle}{N}\right)|_{\rho_0} \approx 385\ MeV. \qquad (11.58)}$$

This value is a bit high compared to the current experimental knowledge, but a direct consequence of the simple functional (11.52).

The nuclear equation of state can be calculated (numerically) at finite temperature *T*, where the density is determined as a function of temperature *T* and the chemical potential μ as

$$\boxed{\rho(T,\mu) = \frac{2}{\pi^2}\frac{1}{\hbar^3 c^3}\int_0^\infty dp\ p^2 \frac{1}{(\exp((\epsilon(p)-\mu)/(k_B T))+1)} \qquad (11.59)}$$

with $\epsilon(p) = p^2/(2m)$. The kinetic energy density results in

$$\boxed{\frac{\langle T_{kin}\rangle}{V}(T,\mu) = \frac{2}{\pi^2}\frac{1}{\hbar^3 c^3}\int_0^\infty\ p^2 dp \frac{\epsilon(p)}{(\exp((\epsilon(p)-\mu)/(k_B T))+1)}. \qquad (11.60)}$$

Assuming that the potential energy density only depends on ρ and does not explicitly depend on *T* or μ, we obtain for the total energy density

$$\frac{\langle H\rangle}{V}(T,\mu) = \frac{\langle T_{kin}\rangle}{V}(T,\mu) - \frac{V_2}{2}\rho(T,\mu)^2 + \frac{V_3}{3}\rho(T,\mu)^3 \tag{11.61}$$

and the binding energy per particle

$$\boxed{\frac{E_B}{N}(T,\mu) = \frac{\langle H\rangle}{N}(T,\mu) = \frac{\langle T_{kin}\rangle}{V\rho(T,\mu)}(T,\mu) - \frac{V_2}{2}\rho(T,\mu) + \frac{V_3}{3}\rho(T,\mu)^2. \qquad (11.62)}$$

As Fig. 11.5 shows, the minimum in the binding energy per particle becomes flatter with increasing temperature *T* up to a critical temperature $T_c \approx 20$ MeV, above which E_B/N becomes ≥ 0. A bound state of nuclear matter then is no longer thermodynamically preferred compared to a free nucleon gas (with $\rho = 0$). The phase transition at T_c is of 1st order, since between the minima at $\rho = 0$ and finite ρ a positive maximum exists in E_B/N. Since for the critical temperature and density the potential energy density and the kinetic energy density have the same magnitude one can talk about a **liquid-gas phase transition**.

Note: The simple model presented here only delivers qualitatively the properties of symmetric nuclear matter, such that the explicit characteristic quantities quoted should not be identified with 'realistic' values.

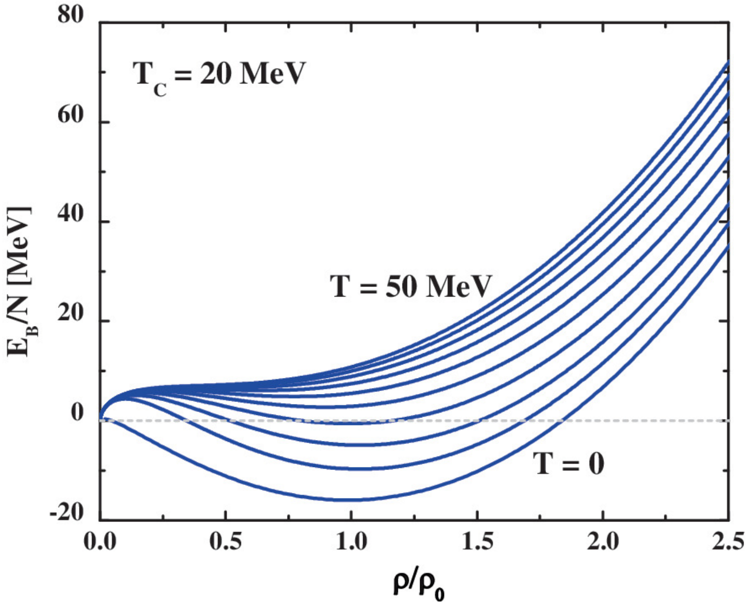

Fig. 11.5 Binding energy per nucleon (green line) as a function of the density ρ (in units of ρ_0) for various temperatures T (in MeV). At a temperature of $T \approx 20$ MeV a phase transition of 1st order can be seen, i.e. for $E_B/N \approx 0$

In summarizing this chapter we have set up the framework for the description of real interacting systems in terms of the Virial expansion and discussed classical Van der Waals systems as well as 'nuclear matter' as an example for an interacting Fermi system. Both systems are found to show a liquid-gas phase transition of 1st order.

W. Cassing, *Theoretical Physics Compact IV*
https://doi.org/10.1007/978-3-031-95518-1_12

12. Magnetic and Electrical Properties of Matter

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In this chapter we will discuss the response of matter to external perturbations by electromagnetic fields and point out the properties of matter in the limit of weak and strong fields.

If one inserts matter into a magnetic (electric) field, it creates a macroscopic magnetization (polarization). The two following effects play an opposite role:

1. Already existing dipole moments (permanent dipole moments) are aligned by the external field. This leads to the temperature dependent **paramagnetism** or the corresponding electrical analogue, the **orientation polarization** (see electrodynamics).

2. External fields can induce dipole moments: An electric field can move the centers of mass of positive and negative charges in atoms and molecules against each other and thus create (or change) electric dipoles. Magnetic fields change the electron states, especially the orbital angular momenta; associated with this is a change in the magnetic moments of the atoms: **diamagnetism**.

In practice, both phenomena occur simultaneously; the statement, that a substance is paramagnetic implies that that paramagnetism dominates the diamagnetism.

The field acting at an atomic moment stems from the **external field** and that—by the **atomic moments** of the environment—**generated field**. We will in the following neglect the second part; this is legitimate e.g. for the treatment of the paramagnetism of gases in contrast to **ferromagnetism**, where the second part is essential.

In the following we will examine a few simple cases for fields that are constant in space and time.

12.1 Definitions

We define the magnitude of **magnetization** *M* by (the field strength $\mathbf{B}$ is considered here as a classical quantity)

$$M =|\overrightarrow{M}|= -\left\langle \frac{\partial H}{\partial B} \right\rangle, \tag{12.1}$$

where *B* is the magnitude of the magnetic field and *H* is the Hamiltonian of the system in the presence of the external field. Such a definition is plausible since $-\overrightarrow{\boldsymbol{\mu}} \cdot \mathbf{B}$ is the energy of a magnetic moment $\overrightarrow{\boldsymbol{\mu}}$ in the field $\mathbf{B}$.

Accordingly, we have

$$P =: -\left\langle \frac{\partial H}{\partial E} \right\rangle \tag{12.2}$$

for the amount of **polarization**; *E* is the magnitude of the electric field $\mathbf{E}$.

12.2 Theorem of Bohr–van Leeuwen

Within the framework of a strictly classical theory the magnetization is always zero.

The proof of this theorem is extremely simple: Since there is no spin in classical physics, the magnetic field in $H_{cl.}$ appears only in the form

$$\sum_i \frac{1}{2m_i}\left(\mathbf{p}_i - \frac{e}{c}\ \mathbf{A}(\mathbf{r}_i;t)\right)^2. \tag{12.3}$$

The partition function $Z_{g,cl.}$—formed with $H_{cl.}$— is invariant with respect to the gauge transformation

$$\mathbf{p}_i \to \mathbf{p}_i - \frac{e}{c}\ \mathbf{A}(\mathbf{r}_i), \tag{12.4}$$

since the classical distribution function $\rho_{cl.}$ for the canonical ensemble only depends on the magnetic field via $H_{cl.}$.

Magnetism thus is a typical quantum mechanical phenomenon.

12.3 Quantummechanical Treatment of Paramagnetism

In order to be able to examine paramagnetism in its purest form, we consider a system of *N* localized magnetic moments in an external field

$$\mathbf{B} = (0, 0, B). \tag{12.5}$$

The magnetic moments arise from the spin of the particles under consideration, e.g. of atoms or atomic nuclei with total angular momentum $J \neq 0$.

The Hamiltonian of such a system then has the simple form (interactions between the individual spins are neglected):

$$\boxed{H = -\mu_B g\ \mathbf{J} \cdot \mathbf{B} = -\mu_B g\ B\ J_z \tag{12.6}}$$

with

$$\boxed{\mu_B = \frac{e\hbar}{2mc} = \frac{e\hbar c}{2mc^2}, \tag{12.7}}$$

where *m* is the electron or nucleon mass, *g* is the gyromagnetic factor $(= 2$ for electron spins) and

$$\mathbf{J} = \sum_{i=1}^{N} \mathbf{j}_i \tag{12.8}$$

the total angular momentum of the system (in units of $\hbar$). The possible energies of the system are

$$E_{mJ} = -\mu_B g\ B\ m_J \tag{12.9}$$

with

$$m_J = -J, -J+1, \ldots\ldots, +J. \tag{12.10}$$

For given temperature T the statistical operator (canonical ensemble) is

$$\boxed{\rho = \rho_c = \frac{\exp(-\beta H)}{Tr(\exp(-\beta H))}} \tag{12.11}$$

and we obtain, since $\langle H \rangle$ is additive from the contributions of the individual moments:

$$\boxed{\langle H \rangle = -K\ N \sum_m m\ \frac{\exp(\beta K m)}{\sum_n \exp(\beta K n)}} \tag{12.12}$$

with the abbreviation

$$K := \mu_B g\ B, \tag{12.13}$$

and

$$m = -j, -j+1, \ldots\ldots, +j \tag{12.14}$$

if *j* is the spin of the individual particles. From (12.12) follows

$$\boxed{M = \mu_B g\ N \sum_m m\ \frac{\exp(\beta K m)}{\sum_n \exp(\beta K n)},} \tag{12.15}$$

i.e. the average of the operator

(12.16)

$$M_z = \mu_B g \ J_z$$

as expected.

The summation in (12.15) can be carried out directly. With the abbreviation

$$\eta := \beta K = \frac{\mu_B g \ B}{k_B T} \tag{12.17}$$

we first get (geometric series!)

$$\sum_{m=-j}^{j} (\exp \, \eta)^m = \sum_m \exp \, (\eta m) = \frac{[\exp(-\eta j) - \exp\{\eta(j+1)\}]}{1-\exp(\eta)} \tag{12.18}$$

or in symmetrical form

$$\sum_{m=-j}^{j} \exp \, (\eta)^m = \frac{[\exp(-\eta j) - \exp\{\eta(j+1)\}]}{1-\exp(\eta)} \, \frac{\exp(-\eta/2)}{\exp(-\eta/2)} = \frac{\sinh[(j+1/2)\eta]}{\sinh(1/2\eta)}. \tag{12.19}$$

Writing the partition sum (for *N* particles) as

$$Z_c = \left(\sum_m \exp \, (\eta m)\right)^N, \tag{12.20}$$

then

$$\ln \ \ Z_c = N\{\ln \, [\sinh \, ((j+1/2)\eta)] - \ln \, [\sinh \, (1/2\eta)]\}. \tag{12.21}$$

From this we get

$$\boxed{M = k_B T \ \frac{\partial \ln \ Z_c}{\partial B} = -\frac{\partial \langle H \rangle}{\partial B}} \tag{12.22}$$

finally by differentiation of (12.21) (with $\partial\eta/\partial B = \beta\mu_B g$)

$$\boxed{\begin{aligned} M \ &= N \ \mu_B g \ \left\{\left(j+\tfrac{1}{2}\right) \coth \, \left(\left[j+\tfrac{1}{2}\right]\eta\right) - \tfrac{1}{2} \coth \, \left(\tfrac{1}{2} \ \eta\right)\right\} \\ &= N \ \mu_B g \ j \ B_j(\eta), \end{aligned}} \tag{12.23}$$

if we introduce the **Brillouin-function** by

$$B_j(\eta) =: \tfrac{1}{j}\left\{\left(j+\tfrac{1}{2}\right)\ \coth\ \left(\left[j+\tfrac{1}{2}\right]\eta\right) - \tfrac{1}{2}\ \coth\ \left(\tfrac{1}{2}\ \eta\right)\right\}. \tag{12.24}$$

To understand the shape of $B_j(\eta)$, we discuss the limiting cases $\eta \gg 1$ and $\eta \ll 1$.

1. $\eta \gg 1$: **Strong fields/low temperatures**; in this case

$$\coth\ (x) \to 1\ \ \text{for}\ \ \mathrm{x} \to \infty \tag{12.25}$$

such that

$$B_j(\eta) \to \tfrac{1}{j}\left\{\left(j+\tfrac{1}{2}\right) - \tfrac{1}{2}\right\} = 1 \tag{12.26}$$

for $\eta \to \infty$. Accordingly,

$$M = N\ \mu_B g\ j. \tag{12.27}$$

All elementary moments are aligned in the direction of the field; M takes the maximum value.

2. $\eta \ll 1$: **Weak fields/high temperatures**. We use in this case

$$\coth\ (x) \approx \tfrac{1}{x} + \tfrac{1}{3}\ x\ \ \text{for}\ \ \mathrm{x} \ll 1, \tag{12.28}$$

such that

$$B_j(\eta) \approx \tfrac{(j+1)}{3}\ \ \eta, \tag{12.29}$$

or

$$M = \chi\ B \tag{12.30}$$

with the **magnetic susceptibility**

$$\chi = N\frac{g^2\mu_B^2 j(j+1)}{3k_BT} = \frac{\xi}{T}. \tag{12.31}$$

Equation (12.31) is called **Curie's law**.

12.4 Classical Theory of Paramagnetism and Orientation Polarization

Permanent magnetic moments classically can have any orientation with respect to an external magnetic field. The average value of the magnetic moment of a substance can thus be determined by averaging over all possible directions,

$$M_{cl.} = N\mu_0 \frac{\int_{-1}^{1} d(\cos\vartheta)\cos\vartheta \ \exp(\beta\mu_0 B\cos\vartheta)}{\int_{-1}^{1} d(\cos\vartheta)\exp(\beta\mu_0 B\cos\vartheta)}. \tag{12.32}$$

Here ϑ is the angle between $\mathbf{B}$ and $\overrightarrow{\mu}$; $-\overrightarrow{\boldsymbol{\mu}} \cdot \mathbf{B} = -\mu_0 B$ cos ϑ is the energy of the moment $\overrightarrow{\mu}$ in the magnetic field $\mathbf{B}$; every moment delivers the same contribution on average, hence the factor *N*. The integrals in (12.32) are straight forward, the result is:

$$M_{cl.} = N\mu_0 \left\{ \text{coth } (\beta\mu_0 B) - \frac{1}{\beta\mu_0 B} \right\}. \tag{12.33}$$

We get the same result if in (12.23) we examine the limiting case $j \to \infty$ with the identification

$$\mu_0 \equiv \mu_B g \ j. \tag{12.34}$$

This is plausible because with increasing *j* the number of magnetic states increases, each of which corresponds to a specific classical orientation.

According to (12.32) one can also calculate the polarization of a dielectric. For the average value of the electric dipole moment $\mathbf{P}$ in the field $\mathbf{E}_l$ we get

$$\boxed{P_{cl.} = N\ P_0\left\{\coth\left(\beta P_0 E\right) - \tfrac{1}{\beta P_0 E}\right\}. \qquad (12.35)}$$

Here P_0 is the magnitude of the elementary dipole moment.

12.5 Magnetic Cooling

The entropy of the spin system under consideration can be computed from (12.21) via (5.30). The result is shown qualitatively in Fig. 12.1.

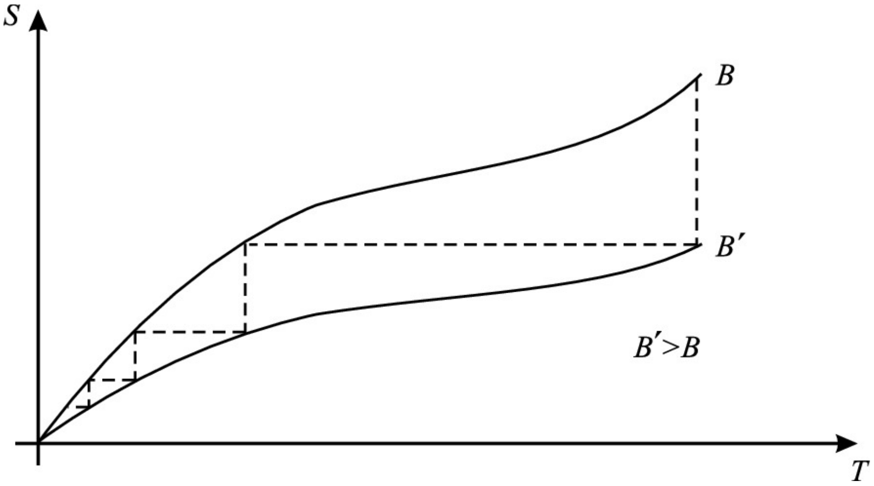

Fig. 12.1 Example for magnetic cooling by adiabatic switching off and isothermal switching on of a magnetic field *B*

The essential points are clear even without a calculation: according to the 3rd law of thermodynamics $S \to 0$ holds for $T \to 0$ regardless of the other parameters on which *S* depends, e.g. the magnetic field $\mathbf{B}$; according to our statistical introduction of entropy it is clear that—for other identical parameters—*S* decreases with increasing field strength *B*.

The principle of magnetic cooling is shown in Fig. 12.1: First we switch on a magnetic field isothermal; by adiabatic switching off $(S =$ const.) we then achieve a temperature reduction, which is larger for a stronger magnetic field. As in Sect. 7.9 we find that the absolute zero temperature cannot be achieved within a finite number of such steps.

12.6 Negative Temperatures

One would expect that the entropy of a system increases with increasing energy monotonically since the number of possible realizations of a macro-state usually grows with the energy. From

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} \tag{12.36}$$

then it follows that T is positive.

Now there are systems (like those discussed in Sect. 11.3, spin systems), whose energy not only has a lower, but also an upper limit. For particles with spin 1/2 e.g. $1/2\ NK$ is the upper limit, $-1/2\ NK$ the lower limit. Both states have the same number of possible realizations (i.e. exactly 1—all spins are parallel or antiparallel to the magnetic field); thus both states have the same entropy since the same information is available. Accordingly we get qualitatively the curve shown in Fig. 12.2.

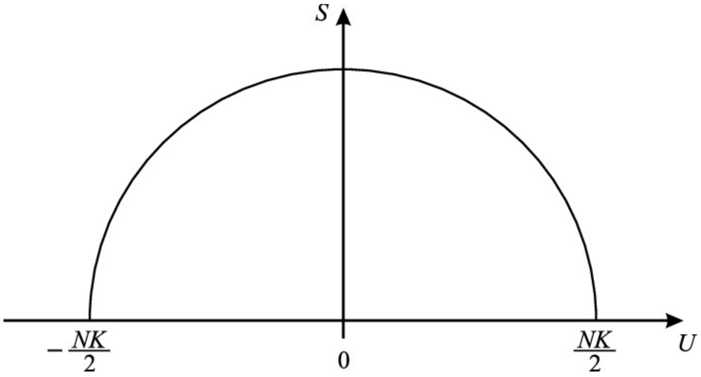

Fig. 12.2 Entropy S as a function of the internal energy U for an external spin system in a magnetic field

For $U < 0$ the derivative of S and therefore of T is positive, however, for $U > 0$ negative. To parameterize the line above it makes sense not to introduce T, but $\tau = -1/T$; then also τ grows with U.

States of negative temperature can be realized experimentally by nuclear moments in crystals, provided that the spin-lattice interaction is weak compared to the spin-spin interaction (which was not previously recorded), which is responsible for achieving thermal equilibrium in the spin system. The nuclear spins are first magnetized in a strong magnetic field and then their direction reversed so quickly that the spins cannot follow. Then from the original distribution $\rho_n \sim \exp\{-E_n/(k_B T)\}$ a new distribution emerges with a **population inversion** $\rho_n' \sim \exp\{E_n/(k_B T)\} = \exp\{-E_n/(-k_B T)\}$. States with population inversion play an important role in **maser** and **laser-physics**.

In summarizing this chapter we have investigated the paramagnetism of matter in an external magnetic field and presented the classical theory of paramagnetism and orientation polarization. Moreover, we have shown the principle of magnetic cooling and the impossibility to reach the absolute zero temperature within a finite number of cooling steps.

Part IV
Non-equilibrium Dynamics

W. Cassing, *Theoretical Physics Compact IV*
https://doi.org/10.1007/978-3-031-95518-1_13

13. Kinetic Theories

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While so far we have considered physical systems of fermions, bosons or classical particles in thermodynamic equilibrium, or their response with respect to external perturbations (Chap. 8), it remains unclear how these systems reach the final equilibrium state in time and what are the characteristic timescales to achieve equilibrium. The answer to these questions requires the formulation of a consistent non-equilibrium dynamics that describes the explicit time evolution of the physical system. On the one hand, one can use the time-dependent Schrödinger equation and derive a system of kinetic equations using Green's functions, on the other hand, the time evolution of the *N*-particle density matrix can also be considered directly in suitable approximations. In the following we will present the density-matrix formalism for weakly interacting *N*-particle fermion systems, that will provide the basis for the derivation of kinetic theories.

13.1 The Density Matrix Formalism

The starting point of a corresponding theory is the von Neumann equation (3.4) for the density operator ρ_N, which describes a *N*-particle fermion system in a pure or mixed state,

$$i\hbar \frac{\partial}{\partial t}\ \rho_N(1,\ldots,N;1'\ldots N';t) = [H_N,\rho_N], \tag{13.1}$$

where H_N represents the *N*-particle Hamiltonian. In (13.1) we have used $i\equiv\xi_i$ for the set of variables of particles *i* for abbreviation (e.g.: $i\equiv\mathbf{r}_i,\sigma_i,\tau_i\equiv$ position coordinate, spin, isospin etc.). If the system of fermions only interacts via a two-particle interaction *v*(*ij*) between particles *i* and *j*, which approximately applies to many physical cases, then the Hamiltonian operator is explicitly written as

$$\boxed{H_N=\sum_{i=1}^{N} h^0(i)+\sum_{i<j}^{N-1} v(ij),} \tag{13.2}$$

where

$$\boxed{h^0(i)=t(i)+U^0(i)} \tag{13.3}$$

represents the single-particle part of H_N, consisting of the operator of the kinetic energy of the particle *i* and possibly an **external** mean field $U^0(i)$. However, Eq. (13.1) in the form above is practically unsolvable for a many-particle system, such that one has to rely on approximate solutions.

For this purpose we introduce **reduced density matrices** $\rho_n(1\ldots n, 1'\ldots n';t)$, which are defined via the formation of traces over the particles $n+1,\ldots,N$ from the N particle density ρ_N:

$$\begin{aligned}&\rho_n(1\ldots n, 1'\ldots n';t)\\&=\tfrac{1}{(N-n)!}Tr_{(n+1,\ldots,N)}\rho_N(1\ldots n, n+1\ldots N, 1'\ldots n', n+1\ldots N;t).\end{aligned}\tag{13.4}$$

While the relative normalization between ρ_n and ρ_{n+1} is fixed, we can freely choose the absolute normalization of ρ_N. It is advisable not to choose the normalization to 1—as in the previous chapters—but to N!, such that the trace over the single-particle density matrix

$$Tr_{(1=1')}\rho(11';t) = \textstyle\sum_i \langle a_i^\dagger a_i\rangle = N,\tag{13.5}$$

where $a_i^\dagger$ and a_i are the fermion creation and annihilation operators with the known anti-commutation relations (see quantum mechanics). For the two-particle density matrix the following normalization follows:

$$\begin{aligned}Tr_{(1,2)}\rho_2 &= \textstyle\sum_{i,j}\langle a_i^\dagger a_j^\dagger a_j a_i\rangle = -\sum_{i,j}\langle a_i^\dagger a_j^\dagger a_i a_j\rangle\\&= \textstyle\sum_{i,j}\{\langle a_i^\dagger a_i a_j^\dagger a_j\rangle - \langle a_i^\dagger a_j\rangle\delta_{ij}\}\end{aligned}\tag{13.6}$$

$$= (N-1)\textstyle\sum_j\langle a_j^\dagger a_j\rangle = N(N-1).$$

The traces of the density matrices ρ_n are obtained in analogy (for $n \le N$),

$$Tr_{(1,\ldots,n)}\rho_n = \tfrac{N!}{(N-n)!},\tag{13.7}$$

since for $n = N$ the density matrix ρ_N is normalized to N! according to (13.7).

If one applies the partial trace formation (i.e. $Tr_{(n+1,\ldots,N)}$) to the von Neumann equation (13.1), one obtains a coupled system of first order differential equations in time, denoted by the **BBGKY** hierarchy (according to the authors **B**ogolyubov, **B**orn, **G**reen, **K**irkwood and **Y**von),

$$\begin{aligned}i\hbar\tfrac{\partial}{\partial t}\ \rho_n = {}&\left[\textstyle\sum_{i=1}^N h^0(i), \rho_n\right] + \left[\sum_{1=i<j}^{n-1} v(ij), \rho_n\right]\\&+\textstyle\sum_{i=1}^N Tr_{(n+1)}[v(i,n+1), \rho_{n+1}]\end{aligned}\tag{13.8}$$

for $1 \le n \le N$ with $\rho_{N+1} = 0$. The explicit equations for $n = 1$ and 2, which we only need in the following, are:

$$i\hbar\tfrac{\partial}{\partial t}\ \rho_1 = [h^0(1), \rho_1] + Tr_{(2)}[v(12), \rho_2],\tag{13.9}$$

$$i\hbar\frac{\partial}{\partial t}\ \rho_2 = \left[\sum_{i=1}^{2} h^0(i), \rho_2\right] + [v(12), \rho_2] + Tr_{(3)}[v(13) + v(23), \rho_3], \tag{13.10}$$

which are not yet closed since the time evolution of ρ_2 is still determined by the 3-particle density matrix ρ_3. In order to obtain a closed system of equations, an approximation for ρ_3 must be carried out.

13.2 Separation of Correlation Functions

Since for independent particles (without residual interactions) the *N* particle states can be written as antisymmetric products of single-particle wave functions (Slater determinants), where ρ_N becomes a bilinear form of Slater determinants $\rho_N = \sum_{i,j} p_{ij}|\Psi_i\rangle\langle\Psi_j|$, one first represents the reduced density matrices ρ_n as antisymmetric products of single-particle density matrices and introduces corrections for interacting particles in the form of correlation functions or matrices. This procedure is known in the literature as **cluster expansion**. In the present context only the explicit cluster expansion up to the 3rd order is of interest, which is introduced as follows,

$$\rho_1(11') = \rho(11'), \tag{13.11}$$

$$\rho_2(12, 1'2') = \rho(11')\rho(22') - \rho(12')\rho(21') + c_2(12, 1'2') \tag{13.12}$$

$$= \rho_{20}(12, 1'2') + c_2(12, 1'2') = \mathscr{A}_{12}\rho(11')\rho(22') + c_2(12, 1'2'),$$

with the 2-particle antisymmetrization operator $\mathscr{A}_{ij} = 1 - P_{ij}$, where P_{ij} denotes the operator for the exchange of particles *i* and *j*. The expansion of ρ_3 includes the antisymmetrized triple products of ρ and the antisymmetrized products of ρc_2,

$$\rho_3(123, 1'2'3') = \rho(11')\rho(22')\rho(33') - \rho(12')\rho(21')\rho(33') \tag{13.13}$$

$$-\rho(13')\rho(22')\rho(31') - \rho(11')\rho(32')\rho(23') + \rho(13')\rho(21')\rho(32')$$

$$+\rho(12')\rho(31')\rho(23') + \rho(11')c_2(23, 2'3') - \rho(12')c_2(23, 1'3')$$

$$-\rho(13')c_2(23, 2'1') + \rho(22')c_2(13, 1'3') - \rho(21')c_2(13, 2'3')$$

$$-\rho(23')c_2(13, 1'2') + \rho(33')c_2(12, 1'2') - \rho(31')c_2(12, 3'2')$$

$$-\rho(32')c_2(12, 1'3') + c_3(123, 1'2'3'),$$

where c_3 captures residual 3-body correlations.

If one neglects the 2-particle correlation function c_2 in (13.12), one obtains the well-known limit of independent particles; this also implies that all effects of the residual interaction are described by c_2 in (13.12).

The 2-particle correlation function c_2 has the same symmetries under particle exchange as the hermitian 2-particle density matrix ρ_2, i.e.

$$c_2(12,1'2') = -c_2(12,2'1') = -c_2(21,1'2') = c_2^*(1'2',12) \ etc. \tag{13.14}$$

The crucial step in the cluster expansions required here is now the neglect of the 3-particle correlation function c_3 in (13.13) since for moderate residual interactions the 3-particle density matrix ρ_3 is represented quite well by the remaining terms in (13.13). With the approximation $c_3 = 0$ the system of equations (13.9) and (13.10) is closed and by inserting (13.12) and (13.13) into (13.9) and (13.10) we obtain the first equations of the **correlation dynamics** for the time evolution of $\rho(11';t)$

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\ \rho(11';t) &= [h^0(1) - h^0(1')]\rho(11';t) \\ &+Tr_{(2=2')}[v(12)\mathscr{A}_{12} - v(1'2')\mathscr{A}_{1'2'}]\rho(11';t)\rho(22';t) \\ &+Tr_{(2=2')}[v(12) - v(1'2')]c_2(12,1'2';t) \end{aligned} \tag{13.15}$$

and for the time evolution of c_2 (after some lengthy calculation),

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\ c_2(12,1'2';t) &= [h^0(1) + h^0(2) - h^0(1') - h^0(2')]c_2(12,1'2';t) \\ &+ \ Tr_{(3=3')}[v(13)\mathscr{A}_{13} + v(23)\mathscr{A}_{23} - v(1'3')\mathscr{A}_{1'3'} - v(2'3')\mathscr{A}_{2'3'}] \\ &\quad \rho(33';t)c_2(12,1'2';t) \\ &+[v(12) - v(1'2')]\rho_{20}(12,1'2') \\ &-Tr_{(3=3')}\{v(13)\rho(23';t)\rho_{20}(13,1'2';t) - v(1'3')\rho(32';t)\rho_{20}(12,1'3';t) \\ &+v(23)\rho(13';t)\rho_{20}(32,1'2';t) - v(2'3')\rho(31';t)\rho_{20}(12,3'2';t)\} \\ &+[v(12) - v(1'2')]c_2(12,1'2';t) \\ &-Tr_{(3=3')}\{v(13)\rho(23';t)c_2(13,1'2';t) - v(1'3')\rho(32';t)c_2(12,1'3';t) \\ &+v(23)\rho(13';t)c_2(32,1'2';t) - v(2'3')\rho(31';t)c_2(12,3'2';t)\} \\ &+Tr_{(3=3')}\{[v(13)\mathscr{A}_{13}\mathscr{A}_{1'2'} - v(1'3')\mathscr{A}_{1'3'}\mathscr{A}_{12}]\ \rho(11';t)c_2(32,3'2';t) \\ &+[v(23)\mathscr{A}_{23}\mathscr{A}_{1'2'} - v(2'3')\mathscr{A}_{2'3'}\mathscr{A}_{12}]\ \rho(22';t)c_2(13,1'3';t)\}. \end{aligned} \tag{13.16}$$

Equations (13.15) and (13.16) so far have only been solved numerically for special problems, such that an explicit discussion goes beyond the scope of this presentation. To compactify and clarify the physical terms, it is useful to introduce the **single-particle Hamiltonian operator**

$$h(i) = h^0(i) + U^s(i) = h^0(i) + Tr_{(n=n')} v(in) \mathscr{A}_{in} \rho(nn';t), \tag{13.17}$$

$$h(i') = h^0(i') + U^s(i') = h^0(i') + Tr_{(n=n')} v(i'n') \mathscr{A}_{i'n'} \rho(nn';t)$$

which not only describes the interaction with the external field U^0 but also with the average self-interaction $U^s(i)$ of the particles among each other. Furthermore, the **Pauli-blocking operator**

$$\begin{aligned} Q^{=}_{ij} &= 1 - Tr_{(n=n')} (P_{in} + P_{jn}) \rho(nn';t); \\ Q^{=}_{i'j'} &= 1 - Tr_{(n=n')} (P_{i'n'} + P_{j'n'}) \rho(nn';t), \end{aligned} \tag{13.18}$$

and the effective interaction in the medium $V^{=}(ij)$ is defined by

$$V^{=}(ij) = Q^{=}_{ij} v(ij); V^{=}(i'j') = Q^{=}(i'j') v(i'j'), \tag{13.19}$$

where the exchange operators in $Q^{=}$ (13.18) act on all terms to the right.

The equations for ρ and c_2 can then be written in more compact form,

$$\begin{aligned} & i\hbar \frac{\partial}{\partial t} \rho(11';t) - [h(1) - h(1')] \rho(11';t) \\ & = Tr_{(2=2')} [v(12) - v(1'2')] c_2(12, 1'2';t), \end{aligned} \tag{13.20}$$

and

$$\begin{aligned} & i\hbar \frac{\partial}{\partial t} c_2(12, 1'2';t) - \left[\sum_{i=1}^{2} h(i) - \sum_{i'=1'}^{2'} h(i') \right] c_2(12, 1'2';t) = \\ & [V^{=}(12) - V^{=}(1'2')] \rho_{20}(12, 1'2';t) \\ & + [V^{=}(12) - V^{=}(1'2')] c_2(12, 1'2';t) \\ & + Tr_{(3=3')} \{ [v(13) \mathscr{A}_{13} \mathscr{A}_{1'2'} - v(1'3') \mathscr{A}_{1'3'} \mathscr{A}_{12}] \ \rho(11';t) c_2(23, 2'3';t) \\ & + [v(23) \mathscr{A}_{23} \mathscr{A}_{1'2'} - v(2'3') \mathscr{A}_{2'3'} \mathscr{A}_{12}] \ \rho(22';t) c_2(13, 1'3';t) \}. \end{aligned} \tag{13.21}$$

Equation (13.20) describes the propagation of a particle in the mean-field $U^0(i) + U^s(i)$ taking into account the two-particle dynamics, which is specified in more detail in (13.21). While in (13.21) the terms with $h(i)$ now describe the propagation of 2 particles in the mean field, the terms with $V^{=}$ can be traced back to 2-particle interactions in the medium (**short-range** correlations). The residual terms describe **long-range** correlations, which are important for the damping of collective modes. Since a detailed discussion of the individual terms goes beyond the scope of this book we refer the interested reader to the respective literature.

Focussing on weakly interacting Fermi systems we will in the following consider (13.21) in lowest order in the interaction, i.e.

$$i\hbar\frac{\partial}{\partial t}\ c_2(12,1'2';t) - \left[\sum_{i=1}^{2} h(i) - \sum_{i'=1'}^{2'} h(i')\right] c_2(12,1'2';t) = \qquad (13.22)$$

$$[V^{=}(12) - V^{=}(1'2')]\rho_{20}(12,1'2';t)$$

13.3 Expansion in a Single-Particle Basis

The spatial representation of the coupled equations for ρ and c_2 (13.20) and (13.21) is not particularly suitable in its current form for numerical integration or for further analytical approximations. Therefore, we expand ρ and c_2 within an initially arbitrary single-particle basis $\varphi_\alpha \equiv |\alpha\rangle$,

$$\rho(11';t) = \sum_{\lambda\lambda'} \rho_{\lambda\lambda'}(t)\varphi_\lambda(\mathbf{r})\varphi^*_{\lambda'}(\mathbf{r}'), \qquad (13.23)$$

$$c_2(12,1'2';t) = \sum_{\lambda\gamma\lambda'\gamma'} C_{\lambda\gamma\lambda'\gamma'}(t)\varphi_\lambda(\mathbf{r}_1)\varphi_\gamma(\mathbf{r}_2)\varphi^*_{\lambda'}(\mathbf{r}'_1)\varphi^*_{\gamma'}(\mathbf{r}'_2), \qquad (13.24)$$

and insert these expansions into (13.20) and (13.22). By multiplying from the left with $\varphi^*_\alpha(\mathbf{r}_1)\varphi_{\alpha'}(\mathbf{r}_{1'})$ or $\varphi^*_\alpha(\mathbf{r}_1)\varphi^*_\beta(\mathbf{r}_2)\varphi_{\alpha'}(\mathbf{r}_{1'})\varphi_{\beta'}(\mathbf{r}_{2'})$ for (13.21) and integration over $d^3r_1 d^3r_{1'}$ or $d^3r_1 d^3r_2 d^3r_{1'} d^3r_{2'}$ we obtain the equations for the time evolution of the coefficients $\rho_{\alpha\alpha'}(t)$,

$$\begin{aligned} &i\hbar\frac{\partial}{\partial t}\ \rho_{\alpha\alpha'} - \sum_\lambda [h_{\alpha\lambda}\rho_{\lambda\alpha'} - \rho_{\alpha\lambda}h_{\lambda\alpha'}] \\ &\ = \sum_\beta \sum_{\lambda\gamma} \{\langle\alpha\beta|v|\lambda\gamma\rangle C_{\lambda\gamma\alpha'\beta} - C_{\alpha\beta\lambda\gamma}\langle\lambda\gamma|v|\alpha'\beta\rangle\} \end{aligned} \qquad (13.25)$$

or from (13.22) for $C_{\alpha\beta\alpha'\beta'}(t)$

$$i\hbar\frac{\partial}{\partial t}\ C_{\alpha\beta\alpha'\beta'} - \sum_\lambda \{h_{\alpha\lambda}C_{\lambda\beta\alpha'\beta'} + h_{\beta\lambda}C_{\alpha\lambda\alpha'\beta'} - C_{\alpha\beta\lambda\beta'}h_{\lambda\alpha'} - C_{\alpha\beta\alpha'\lambda}h_{\lambda\beta'}\} \qquad (13.26)$$

$$= \sum_{\lambda\lambda'\gamma\gamma'} \{Q^{=}_{\alpha\beta\lambda'\gamma'}\langle\lambda'\gamma'|v|\lambda\gamma\rangle(\rho_{20})_{\lambda\gamma\alpha'\beta'} - (\rho_{20})_{\alpha\beta\lambda'\gamma'}\langle\lambda'\gamma'|v|\lambda\gamma\rangle Q^{=}_{\lambda\gamma\alpha'\beta'}\}$$

with

$$Q^{=}_{\alpha\beta\lambda'\gamma'} = \delta_{\alpha\lambda'}\delta_{\beta\gamma'} - \delta_{\alpha\lambda'}\rho_{\beta\gamma'} - \rho_{\alpha\lambda'}\delta_{\beta\gamma'}, \qquad (13.27)$$

and the one-particle Hamiltonian (cf. (13.17))

$$h_{\alpha\lambda} = \langle\alpha|t|\lambda\rangle + \langle\alpha|U^0|\lambda\rangle + \sum_{\gamma\gamma'}\langle\alpha\gamma'|v|\lambda\gamma\rangle_{\mathscr{A}}\rho_{\gamma\gamma'}. \qquad (13.28)$$

Furthermore, we have used

$$(\rho_{20})_{\alpha\beta\alpha'\beta'} = \rho_{\alpha\alpha'}\rho_{\beta\beta'} - \rho_{\alpha\beta'}\rho_{\beta\alpha'} = \mathscr{A}_{\alpha\beta}\rho_{\alpha\alpha'}\rho_{\beta\beta'} \tag{13.29}$$

and

$$\langle\alpha\beta|v|\alpha'\beta'\rangle_{\mathscr{A}} = \langle\alpha\beta|v|\alpha'\beta'\rangle - \langle\alpha\beta|v|\beta'\alpha'\rangle \tag{13.30}$$

for the antisymmetric matrix element of the interaction *v*.

Equations (13.25) and (13.26) form the starting point for the formulation of **kinetic theories** to be considered in the following; they are completely antisymmetric in the matrix elements, closed in ρ and c_2 and allow for the quantum mechanical description of fermion systems of weak residual interaction also far from equilibrium. As will be shown in the next section, they satisfy the conservation laws of fermion number, momentum, angular momentum and total energy.

13.4 Conservation Laws

(i) Particle number conservation

The particle number of the system is given by the trace of ρ or in the discrete basis by

$$N(t) = \textstyle\sum_\alpha \rho_{\alpha\alpha}(t). \tag{13.31}$$

Differentiating with respect to time and inserting the equation of motion for $\rho_{\alpha\alpha}(t)$ gives

$$\tfrac{d}{dt}\ N(t) = \textstyle\sum_\alpha \dot{\rho}_{\alpha\alpha}(t) = -\tfrac{i}{\hbar}\textstyle\sum_{\alpha\lambda}[h_{\alpha\lambda}\rho_{\lambda\alpha} - \rho_{\alpha\lambda}h_{\lambda\alpha}] \tag{13.32}$$

$$-\tfrac{i}{\hbar}\textstyle\sum_{\alpha\beta\gamma\lambda}[\langle\alpha\beta|v|\gamma\lambda\rangle C_{\gamma\lambda\alpha\beta} - C_{\alpha\beta\gamma\lambda}\langle\gamma\lambda|v|\alpha\beta\rangle] = 0,$$

as can easily be seen by renaming the summation indices. This implies that the particle number is always a conserved quantity.

(ii) Conservation of momentum (angular momentum)

The expectation value of the total momentum of the system is given by

$$\langle\mathbf{P}\rangle = Tr(\mathbf{p}\ \rho) = \textstyle\sum_\alpha\langle\alpha|\mathbf{p}\ \rho|\alpha\rangle = \textstyle\sum_{\alpha\lambda}\langle\alpha|\mathbf{p}|\lambda\rangle\rho_{\lambda\alpha}, \tag{13.33}$$

since the momentum **p** is a single-particle operator. To prove the conservation of momentum, the time derivative of (13.33) is calculated and the equation of motion for $\rho_{\lambda\alpha}(t)$ is inserted again;

$$i\hbar\tfrac{d}{dt}\langle\mathbf{P}\rangle = \textstyle\sum_{\alpha\lambda}\langle\alpha|\mathbf{p}|\lambda\rangle i\hbar\dot{\rho}_{\lambda\alpha} \tag{13.34}$$

$$= \textstyle\sum_{\alpha\lambda\lambda'}\langle\alpha|\mathbf{p}|\lambda\rangle[h_{\lambda\lambda'}\rho_{\lambda'\alpha} - \rho_{\lambda\lambda'}h_{\lambda'\alpha}]$$

$$+\textstyle\sum_{\alpha\beta\gamma\lambda\lambda'}\langle\alpha|\mathbf{p}|\lambda\rangle[\langle\lambda\beta|v|\lambda'\gamma\rangle C_{\lambda'\gamma\alpha\beta} - C_{\lambda\beta\lambda'\gamma}\langle\lambda'\gamma|v|\alpha\beta\rangle] = 0,$$

as can be shown again by renaming the summation indices. In analogy to the momentum $\mathbf{P}$, one also proves the conservation of the total angular momentum $\mathbf{L}$, which results from the sum of the single-particle angular momenta $\mathbf{l}_i$, provided that $[v, \mathbf{l}_i] = 0$.

(iii) Conservation of energy
For every closed system (here $U^0 \equiv 0$) the total energy must be a conserved quantity. It is made up of the kinetic energy

$$E_{kin} = \sum_{\alpha\lambda} \langle\alpha|t|\lambda\rangle \rho_{\lambda\alpha}, \tag{13.35}$$

the energy of the **mean field**

$$E_{MF} = \tfrac{1}{2} \sum_{\alpha\alpha'\lambda\lambda'} \rho_{\alpha\alpha'} \langle\alpha'\lambda'|v|\alpha\lambda\rangle_{\mathscr{A}} \rho_{\lambda\lambda'}, \tag{13.36}$$

and the **correlation energy**

$$E_{cor} = \tfrac{1}{2} \sum_{\alpha\alpha'\lambda\lambda'} \langle\alpha\lambda|v|\alpha'\lambda'\rangle C_{\alpha'\lambda'\alpha\lambda}. \tag{13.37}$$

Since the total energy is a two-particle operator, to prove the conservation of energy one now needs the explicit equation of motion for the matrix elements of $C_{\alpha\beta\alpha'\beta'}$, i.e.

$$\tfrac{d}{dt}\ E = \tfrac{d}{dt}\{E_{kin} + E_{MF} + E_{cor}\} \tag{13.38}$$

$$= \sum_{\alpha\lambda} \langle\alpha|t|\lambda\rangle \dot{\rho}_{\lambda\alpha} + \tfrac{1}{2} \sum_{\alpha\alpha'\lambda\lambda'} \langle\alpha'\lambda'|v|\alpha\lambda\rangle_{\mathscr{A}} [\dot{\rho}_{\lambda\lambda'}\rho_{\alpha\alpha'} + \rho_{\lambda\lambda'}\dot{\rho}_{\alpha\alpha'}]$$

$$+\tfrac{1}{2} \sum_{\alpha\alpha'\lambda\lambda'} \langle\alpha'\lambda'|v|\alpha\lambda\rangle \dot{C}_{\alpha\lambda\alpha'\lambda'} = \cdots = 0,$$

as is found by inserting $\dot{\rho}$ from (13.25) and $\dot{C}$ from (13.26). This implies that the energy is also a conserved quantity for all times within the framework of the coupled Eqs. (13.25) and (13.26).

13.5 The Vlasov Equation

In order to clarify the physical content of Eqs. (13.25) and (13.26) more closely, we first consider Eq. (13.25) in the limit $C_{\alpha\beta\alpha'\beta'} \equiv 0$, i.e.

$$\tfrac{\partial}{\partial t}\ \rho_{\alpha\alpha'} + \tfrac{i}{\hbar}[\sum_{\lambda} h_{\alpha\lambda}\rho_{\lambda\alpha'} - \rho_{\alpha\lambda}h_{\lambda\alpha'}] = 0, \tag{13.39}$$

and transform to the spatial representation $\rho(\mathbf{x}, \mathbf{x}';t) = \langle\mathbf{x}'|\rho(t)|\mathbf{x}\rangle$. To simplify the notation, we omit the explicit indices for spin (isospin etc.) in the following (as in (13.39)), since they are initially irrelevant for the physical considerations.

Furthermore, we restrict ourselves to local potentials $U(\mathbf{x};t)$, which may consist of an external field $U^0(\mathbf{x};t)$ as well as the self-interaction of the fermions $U^s(\mathbf{x}, t)$ (see (13.17)),

$$U(\mathbf{x};t) = U^0(\mathbf{x};t) + \sum_{spin,\ isospin} \int d^3x_2\ v(\mathbf{x} - \mathbf{x}_2)\rho(\mathbf{x}_2, \mathbf{x}_2;t), \tag{13.40}$$

where the exchange term of the interaction (Fock term) has been neglected for the sake of simplicity.

In the spatial representation for local potentials $U(\mathbf{x};t)$ Eq. (13.39) reads as follows,

$$\boxed{\tfrac{\partial}{\partial t}\ \rho(\mathbf{x}, \mathbf{x}';t) + \tfrac{i}{\hbar}\{-\tfrac{\hbar^2}{2m}\nabla_x^2 + U(\mathbf{x};t) + \tfrac{\hbar^2}{2m}\nabla_{x'}^2 - U(\mathbf{x}';t)\}\rho(\mathbf{x}, \mathbf{x}';t) = 0,} \tag{13.41}$$

which, however, does not improve our understanding very much. It is useful to transform to the phase-space representation using a **Wigner transformation**

$$\rho(\mathbf{r},\mathbf{p};t) = \int d^3s \ \ \exp\left(-\tfrac{i}{\hbar}\mathbf{p}\cdot\mathbf{s}\right)\ \rho(\mathbf{r}+\mathbf{s}/2,\mathbf{r}-\mathbf{s}/2;t) \tag{13.42}$$

with

$$\mathbf{x} = \mathbf{r}+\mathbf{s}/2, \mathbf{x}' = \mathbf{r}-\mathbf{s}/2 \text{ or } \quad \mathbf{r} = (\mathbf{x}+\mathbf{x}')/2, \mathbf{s} = \mathbf{x}-\mathbf{x}'. \tag{13.43}$$

The quantum mechanical phase-space density $\rho(\mathbf{r},\mathbf{p};t)$ in the classical limiting case transforms into the probability of finding a particle at position $\mathbf{r}$ with momentum $\mathbf{p}$ at time t. Independently of the classical limit, the integration of (13.42) over the momentum yields

$$\rho(\mathbf{r};t) = \tfrac{1}{(2\pi\hbar)^3}\int d^3p\ \rho(\mathbf{r},\mathbf{p};t) \tag{13.44}$$

the spatial density $\rho(\mathbf{r};t)$, while integration over space yields the momentum space density $\rho(\mathbf{p};t)$,

$$\rho(\mathbf{p};t) = \int d^3r\ \rho(\mathbf{r},\mathbf{p};t); \tag{13.45}$$

the factor $1/(2\pi\hbar)^3 = h^{-3}$ in (13.44) is responsible for the quantization in phase space per intrinsic degree of freedom of the particles (spin, isospin, etc.).

Remark: The Wigner transform (13.42) is generally not a positive definite function of real numbers for quantum mechanical systems, but a hermitian operator with complex values in phase-space representation. For systems with a sufficiently large number of particles, however, the imaginary parts of $\rho(\mathbf{r},\mathbf{p};t)$ become arbitrarily small, such that one can accept the interpretation in the classical limiting case when considering suitable averages over phase-space volumes.

If we now carry out a Wigner transformation of (13.41), we obtain after a few lines (using $\nabla^2_{\mathbf{r}+\mathbf{s}/2} - \nabla^2_{\mathbf{r}-\mathbf{s}/2} = 2\nabla_{\mathbf{s}}\cdot\nabla_{\mathbf{r}}$) and partial integration:

$$\begin{aligned}&\tfrac{\partial}{\partial t}\ \rho(\mathbf{r},\mathbf{p};t) + \tfrac{\mathbf{p}}{m}\cdot\nabla_{\mathbf{r}}\rho(\mathbf{r},\mathbf{p};t) \\ &+\tfrac{i}{\hbar}\int d^3s\ \ \exp\left(-\tfrac{i}{\hbar}\mathbf{p}\cdot\mathbf{s}\right)[U(\mathbf{r}+\mathbf{s}/2;t) - U(\mathbf{r}-\mathbf{s}/2;t)] \\ &\rho(\mathbf{r}+\mathbf{s}/2,\mathbf{r}-\mathbf{s}/2;t) = 0.\end{aligned} \tag{13.46}$$

This equation—due to the unitarity of the Wigner transformation—is equivalent to (13.41). In (13.46) we can now insert the approximation

$$[U(\mathbf{r}+\mathbf{s}/2) - U(\mathbf{r}-\mathbf{s}/2)] \approx \mathbf{s}\cdot\nabla_{\mathbf{r}}U(\mathbf{r}) \tag{13.47}$$

for the case of weakly varying $U(\mathbf{r};t)$ in space—which is exact for the harmonic oscillator—and obtain with the identity

$$\mathbf{s} \ \exp\left(-\tfrac{i}{\hbar}\mathbf{p}\cdot\mathbf{s}\right) = i\hbar \ \nabla_p \exp\left(-\tfrac{i}{\hbar}\mathbf{p}\cdot\mathbf{s}\right) \tag{13.48}$$

the **Vlasov equation**:

$$\boxed{\tfrac{\partial}{\partial t} \ \rho(\mathbf{r},\mathbf{p};t) + \tfrac{\mathbf{p}}{m}\cdot\nabla_{\mathbf{r}}\rho(\mathbf{r},\mathbf{p};t) - \nabla_{\mathbf{r}}U(\mathbf{r};t)\cdot\nabla_{\mathbf{p}}\rho(\mathbf{r},\mathbf{p};t) = 0.} \tag{13.49}$$

It is equivalent to

$$\tfrac{d}{dt} \ \rho = 0 = \left\{\tfrac{\partial}{\partial t} + \dot{\mathbf{r}}\cdot\nabla_{\mathbf{r}} + \dot{\mathbf{p}}\cdot\nabla_{\mathbf{p}}\right\} \ \rho(\mathbf{r},\mathbf{p};t), \tag{13.50}$$

from which, by comparison with (13.49), the classical equations of motion for $\dot{\mathbf{r}}$ and $\dot{\mathbf{p}}$ follow,

$$\boxed{\dot{\mathbf{r}} = \tfrac{\mathbf{p}}{m} \ ;\dot{\mathbf{p}} = -\nabla_{\mathbf{r}}U(\mathbf{r};t).} \tag{13.51}$$

Consequently, in the limit $A \to \infty$ the distribution

$$\boxed{\rho_t(\mathbf{r},\mathbf{p};t) = \tfrac{1}{A}\sum_{i=1}^{N\cdot A}\delta^3(\mathbf{r}-\mathbf{r}_i(t)) \ \delta^3(\mathbf{p}-\mathbf{p}_i(t))} \tag{13.52}$$

is a solution of the Vlasov equation (13.49), if $\mathbf{r}_i(t)$, $\mathbf{p}_i(t)$ are solutions of the classical equations of motion (13.51).

The approach (13.52) with (13.51) is generally referred to as the **testparticle method** and allows for the dynamical simulations of many-particle systems in a time-dependent (self-consistent) mean field $U(\mathbf{r};t)$, which is built up by the two-particle interaction $v(\mathbf{r}-\mathbf{r}_2)$ in (13.40).

As one can easily show, the Vlasov equation again conserves the particle number, the total momentum and angular momentum as well as the total energy. However, relaxation phenomena are not correctly described within the framework of (13.49), since these are dominantly based on the 2-particle correlations neglected here.

13.6 The Uehling-Uhlenbeck Collision Term

While the derivation of the Vlasov equation in Sect. 13.5 was relatively easy to carry out, the collision term in (13.20) requires to compute

$$I(11';t) := -\tfrac{i}{\hbar}Tr_{(2=2')}[v(12), c_2(12,1'2';t)] \tag{13.53}$$

or in a single-particle basis

$$I_{\alpha\alpha'}(t) = -\tfrac{i}{\hbar}\sum_\beta\sum_{\lambda\gamma}\{\langle\alpha\beta|v|\lambda\gamma\rangle C_{\lambda\gamma\alpha'\beta}(t) - C_{\alpha\beta\lambda\gamma}(t)\langle\lambda\gamma|v|\alpha'\beta\rangle\}, \tag{13.54}$$

i.e. the explicit knowledge of the 2-particle correlation function in an arbitrary basis $|\alpha\rangle$.

To calculate the 2-particle correlation function in leading order, we use a discrete basis in which the single-particle Hamiltonian $h_{\alpha\lambda}(t)$ and in particular $\rho_{\alpha\alpha'}(t)$ is diagonal, i.e.

$$h_{\alpha\lambda}(t) \approx \epsilon_\alpha(t)\delta_{\alpha\lambda};\rho_{\alpha\alpha'}(t) = n_\alpha(t)\delta_{\alpha\alpha'}. \tag{13.55}$$

In this basis the equation of motion for the expansion coefficients $C_{\alpha\beta\alpha'\beta'}(t)$ then reduces according to (13.26) to (omitting the explicit time dependence of all quantities):

$$\begin{aligned}\{i\hbar\tfrac{\partial}{\partial t} - [\epsilon_\alpha + \epsilon_\beta - \epsilon_{\alpha'} - \epsilon_{\beta'}]\}C_{\alpha\beta\alpha'\beta'}(t) \\ = \textstyle\sum_{\lambda\gamma}\{\langle\alpha\beta|Q^{=}v|\lambda\gamma\rangle(\rho_{20})_{\lambda\gamma\alpha'\beta'} - (\rho_{20})_{\alpha\beta\lambda\gamma}\langle\lambda\gamma|vQ^{=}|\alpha'\beta'\rangle\} \\ = \langle\alpha\beta|v|\alpha'\beta'\rangle_{\mathscr{A}}[n_{\alpha'}n_{\beta'}(1-n_\alpha-n_\beta) - n_\alpha n_\beta(1-n_{\alpha'}-n_{\beta'})] \\ =: \langle\alpha\beta|V_B(t)|\alpha'\beta'\rangle,\end{aligned} \tag{13.56}$$

where we have taken advantage of the fact, that in this basis $Q^{=}$ is also diagonal

$$Q^{=}_{\alpha\beta\lambda\gamma} = \delta_{\alpha\lambda}\delta_{\beta\gamma}[1-n_\alpha-n_\beta]. \tag{13.57}$$

Equation (13.56) is a differential equation of first order in time that can be integrated directly. With regards to approximations to be carried out later (within the framework of the energy conservation in 2-particle collisions), we assume in the following, that in particular the single-particle energies $\epsilon_\alpha(t) \approx \epsilon_\alpha$ are weakly varying functions of time.—This approximation is particularly well or exactly fulfilled for the electron states in solids as well as for the single-particle states in a sufficiently large normalization volume.—For a vanishing homogeneous solution of (13.56) $C_{\alpha\beta\alpha'\beta'}(t)$ then is given by

$$\begin{aligned}&C_{\alpha\beta\alpha'\beta'}(t) = \\ &-\tfrac{i}{\hbar}\textstyle\int_{-\infty}^{t} dt' \quad \exp\{-\tfrac{i}{\hbar}[\epsilon_\alpha+\epsilon_\beta-\epsilon_{\alpha'}-\epsilon_{\beta'}](t-t')\}\cdot\langle\alpha\beta|V_B(t')|\alpha'\beta'\rangle,\end{aligned} \tag{13.58}$$

as one can easily verify by insertion in (13.56).

For the diagonal element of the collision term (13.54) we obtain with (13.58)

$$\begin{aligned}I_{\alpha\alpha}(t) = -\tfrac{i}{\hbar}\textstyle\sum_\beta\sum_{\lambda\gamma}\{\langle\alpha\beta|v|\lambda\gamma\rangle C_{\lambda\gamma\alpha\beta}(t) - C_{\alpha\beta\lambda\gamma}(t)\langle\lambda\gamma|v|\alpha\beta\rangle\} \\ = -\tfrac{1}{\hbar^2}\textstyle\sum_\beta\sum_{\lambda\gamma}\int_{-\infty}^{t} dt'\{\exp\{-\tfrac{i}{\hbar}[\epsilon_\lambda+\epsilon_\gamma-\epsilon_\alpha-\epsilon_\beta](t-t')\} \\ \cdot\langle\alpha\beta|v|\lambda\gamma\rangle\langle\lambda\gamma|V_B(t')|\alpha\beta\rangle \\ - \exp\{-\tfrac{i}{\hbar}[\epsilon_\alpha+\epsilon_\beta-\epsilon_\lambda-\epsilon_\gamma](t-t')\}\langle\alpha\beta|V_B(t')|\lambda\gamma\rangle\langle\lambda\gamma|v|\alpha\beta\rangle\}\end{aligned} \tag{13.59}$$

$$= \frac{1}{\hbar^2} \sum_\beta \sum_{\lambda\gamma} \int_{-\infty}^{t} dt' \ 2 \ \cos\left\{\frac{1}{\hbar}[\epsilon_\alpha + \epsilon_\beta - \epsilon_\lambda - \epsilon_\gamma](t-t')\right\}$$

$$\cdot\langle\alpha\beta|v|\lambda\gamma\rangle\langle\lambda\gamma|v|\alpha\beta\rangle_{\mathscr{A}}[n_\lambda(t')n_\gamma(t')\bar{n}_\alpha(t')\bar{n}_\beta(t') - n_\alpha(t')n_\beta(t')\bar{n}_\lambda(t')\bar{n}_\gamma(t')]$$

with $\bar{n}_\alpha(t') = 1 - n_\alpha(t')$ and $V_B(t')$ from (13.56).

The further assumption is that the occupation numbers $n_\alpha(t') \approx n_\alpha(t)$ are approximately constant in time. In this case we can carry out the time integration in (13.59) for systems of low density or weak residual interaction and get:

$$\int_{-\infty}^{t} dt' \ \cos\left(\frac{1}{\hbar}[\epsilon_\alpha + \epsilon_\beta - \epsilon_\lambda - \epsilon_\gamma](t-t')\right) \approx \hbar\pi \ \delta(\epsilon_\alpha + \epsilon_\beta - \epsilon_\lambda - \epsilon_\gamma), \tag{13.60}$$

i.e. the energy conservation in the 2-body collisions.—Equation (13.60) implies that the time between two subsequent collisions τ_s is large compared to the actual collision time τ_c, such that the energy uncertainty associated to τ_s, i.e. $\Delta\epsilon \approx \hbar/\tau_s$ will be small.—For the diagonal elements of the collision term we then get

$$\boxed{\begin{aligned} I_{\alpha\alpha}(t) \approx \frac{2\pi}{\hbar} \sum_\beta \sum_{\lambda\gamma} \delta(\epsilon_\alpha + \epsilon_\beta - \epsilon_\lambda - \epsilon_\gamma)\langle\alpha\beta|v|\lambda\gamma\rangle\langle\lambda\gamma|v|\alpha\beta\rangle_{\mathscr{A}} \\ \cdot[n_\lambda n_\gamma \bar{n}_\alpha \bar{n}_\beta - n_\alpha n_\beta \bar{n}_\lambda \bar{n}_\gamma](t) \end{aligned}} \tag{13.61}$$

in the basis $|\alpha\rangle$, in which the matrix $\rho_{\alpha\alpha'}$ is diagonal.

We now evaluate (13.61) in the basis of plane waves $|\alpha\rangle \sim$exp $\{i\mathbf{p}_\alpha \cdot \mathbf{r}\}$, such that the matrix ρ becomes diagonal in momentum space:

$$\boxed{\rho(\mathbf{p},\mathbf{p}') = (2\pi)^3\delta^3(\mathbf{p}-\mathbf{p}')n(\mathbf{p}).} \tag{13.62}$$

In (13.62) then $n(\mathbf{p})$ has the physical interpretation of the occupation number of a plane wave with wave number $\mathbf{p}$ (or momentum $\hbar\mathbf{p}$).

Next, we assume for simplicity that the matrix elements of the interaction v in (13.61) are independent of spin σ (and isospin τ) and in spatial representation given by:

$$\begin{aligned} &\langle\mathbf{r}_1\mathbf{r}_2\sigma_1\sigma_2\tau_1\tau_2|v|\sigma_{1'}\sigma_{2'}\tau_{1'}\tau_{2'}\mathbf{r}_{1'}\mathbf{r}_{2'}\rangle \\ &= \delta_{\sigma_1\sigma_{1'}}\delta_{\sigma_2\sigma_{2'}}\delta_{\tau_1\tau_{1'}}\delta_{\tau_2\tau_{2'}} \\ &\cdot\delta^3(\mathbf{r}_1 - \mathbf{r}_{1'})\delta^3(\mathbf{r}_2 - \mathbf{r}_{2'})v(\mathbf{r}_1 - \mathbf{r}_2), \end{aligned} \tag{13.63}$$

or in momentum representation by

$$\begin{aligned} &\langle\mathbf{p}_1\mathbf{p}_2\sigma_1\sigma_2\tau_1\tau_2|v|\sigma_{1'}\sigma_{2'}\tau_{1'}\tau_{2'}\mathbf{p}_{1'}\mathbf{p}_{2'}\rangle \\ &= \delta_{\sigma_1\sigma_{1'}}\delta_{\sigma_2\sigma_{2'}}\delta_{\tau_1\tau_{1'}}\delta_{\tau_2\tau_{2'}} \\ &\cdot(2\pi)^3\delta^3(\mathbf{p}_1 + \mathbf{p}_2 - \mathbf{p}_{1'} - \mathbf{p}_{2'})v(\mathbf{p}_2 - \mathbf{p}_{2'}), \end{aligned} \tag{13.64}$$

which expresses the conservation of momentum in the 2-body collision.

With these approximations we can evaluate (13.61) and obtain with $\epsilon(\mathbf{p}) = \hbar^2/2m\ \mathbf{p}^2$

$$\begin{aligned} I(\mathbf{p}_1, \mathbf{p}_1; t) = {} & \tfrac{2\pi}{\hbar}(2s+1)(2\tau+1)\tfrac{1}{(2\pi)^9}\int d^3p_2 d^3p_3 d^3p_4 \\ & \delta\Big(\tfrac{\hbar^2}{2m}[p_1^2+p_2^2-p_3^2-p_4^2]\Big)\delta^3(\mathbf{p}_1+\mathbf{p}_2-\mathbf{p}_3-\mathbf{p}_4)(2\pi)^6 \\ & \delta^3(\mathbf{p}_3+\mathbf{p}_4-\mathbf{p}_1-\mathbf{p}_2)v(\mathbf{p}_2-\mathbf{p}_4)v_{\mathscr{A}}(\mathbf{p}_4-\mathbf{p}_2) \\ & \{n(\mathbf{p}_3;t)n(\mathbf{p}_4;t)\bar{n}(\mathbf{p}_1;t)\bar{n}(\mathbf{p}_2;t) - n(\mathbf{p}_1;t)n(\mathbf{p}_2;t)\bar{n}(\mathbf{p}_3;t)\bar{n}(\mathbf{p}_4;t)\}. \end{aligned} \tag{13.65}$$

Equation (13.65) describes scattering processes $\mathbf{p}_1 + \mathbf{p}_2 \to \mathbf{p}_3 + \mathbf{p}_4$ ('loss' term) and $\mathbf{p}_3 + \mathbf{p}_4 \to \mathbf{p}_1 + \mathbf{p}_2$ ('gain' term) with the conservation of energy and momentum (see Fig. 13.1).

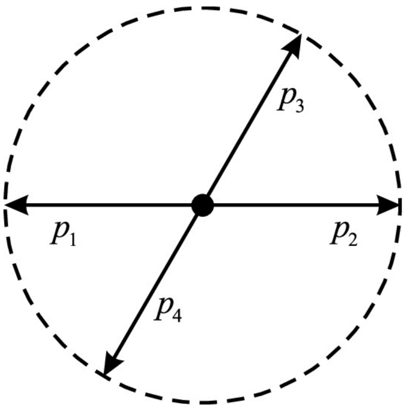

Fig. 13.1 Example of a collision process $\mathbf{p}_1 + \mathbf{p}_2 \to \mathbf{p}_3 + \mathbf{p}_4$ in the center-of-mass system obeying the conservation of energy and momentum

Furthermore, the momentum states $\mathbf{p}_3$, $\mathbf{p}_4$ (for the 'loss' terms) or $\mathbf{p}_1$, $\mathbf{p}_2$ (for the 'gain' terms) cannot be completely occupied due to the factors $\bar{n}(\mathbf{p}_i;t)$, which contain the Pauli principle for fermions.

The factors $(2s+1)$ for the summation over the spin of particle 2 and $(2\tau+1)$ for the summation over the isospin (or other internal degrees of freedom) of particle 2 are summarized in a factor g; in the case of electrons we have $(s = 1/2, \tau = 0)$ $g = 2$, while for nucleons we get $(s = 1/2, \tau = 1/2)$ $g = 4$ (in case of spin-isospin symmetry).

The connection with 2-particle scattering processes becomes immediately clear when we link the product $v \cdot v_{\mathscr{A}}$ with the differential cross section $d\sigma/d\Omega$ in **Born approximation** (cf. quantum theory),

$$\tfrac{d\sigma}{d\Omega}(\mathbf{p}_1+\mathbf{p}_2, \mathbf{p}_2-\mathbf{p}_4) = \tfrac{m^2}{(16\pi^2\hbar^4)}v(\mathbf{p}_2-\mathbf{p}_4)v_{\mathscr{A}}(\mathbf{p}_4-\mathbf{p}_2), \tag{13.66}$$

which leads to

$$I(\mathbf{p}_1,\mathbf{p}_1';t) = (2\pi)^3\delta^3(\mathbf{p}_1-\mathbf{p}_1')\frac{16\pi^2\hbar^3}{m^2}\frac{g}{(2\pi)^5}\int d^3p_2d^3p_3d^3p_4 \tag{13.67}$$

$$\delta\left(\frac{\hbar^2}{2m}[p_1^2+p_2^2-p_3^2-p_4^2]\right)\ \delta^3(\mathbf{p}_1+\mathbf{p}_2-\mathbf{p}_3-\mathbf{p}_4)\ \frac{d\sigma}{d\Omega}(\mathbf{p}_1+\mathbf{p}_2,\mathbf{p}_2-\mathbf{p}_4)$$

$$\{n(\mathbf{p}_3;t)n(\mathbf{p}_4;t)\bar{n}(\mathbf{p}_1;t)\bar{n}(\mathbf{p}_2;t)-n(\mathbf{p}_1;t)n(\mathbf{p}_2;t)\bar{n}(\mathbf{p}_3;t)\bar{n}(\mathbf{p}_4;t)\}$$

where we have introduced the auxiliary variable $\mathbf{p}_1'$ in one of the two δ-functions in the momentum. Equation (13.67) can be simplified further by integrating (after transformation to relative and center of mass momenta) over the δ-functions in (13.67). With the magnitude of the relative velocity

$$v_{12} = \frac{\hbar}{m}|\mathbf{p}_1-\mathbf{p}_2| \tag{13.68}$$

we finally obtain

$$I(\mathbf{p}_1,\mathbf{p}_1';t) = (2\pi)^3\delta^3(\mathbf{p}_1-\mathbf{p}_1')\frac{g}{(2\pi)^3}\int d^3p_2\int d\Omega\ \ v_{12}\frac{d\sigma}{d\Omega}(\mathbf{p}_1+\mathbf{p}_2,\mathbf{p}_2-\mathbf{p}_4) \tag{13.69}$$

$$\{n(\mathbf{p}_3;t)n(\mathbf{p}_4;t)\bar{n}(\mathbf{p}_1;t)\bar{n}(\mathbf{p}_2;t)-n(\mathbf{p}_1;t)n(\mathbf{p}_2;t)\bar{n}(\mathbf{p}_3;t)\bar{n}(\mathbf{p}_4;t)\},$$

where Ω denotes the scattering angle in the center of mass system: it should be noted that the momenta $\mathbf{p}_3$ and $\mathbf{p}_4$ are still linked to $\mathbf{p}_1$ and $\mathbf{p}_2$ via energy and momentum conservation!

The transition from the momentum-space representation examined here to the phase-space representation (see Sect. 13.5) is now carried out by an inverse Wigner transformation,

$$I(\mathbf{r},\mathbf{p};t) = \frac{1}{(2\pi)^3}\int d^3q\ \ \exp\{i\mathbf{q}\cdot\mathbf{r}\}I(\mathbf{p}+\mathbf{q}/2,\mathbf{p}-\mathbf{q}/2;t) \tag{13.70}$$

$$= \int d^3q\ \ \exp\{i\mathbf{q}\cdot\mathbf{r}\}\delta(\mathbf{q})I_{coll}(\mathbf{p};t) = I_{coll}(\mathbf{p};t)$$

$$= \frac{g}{(2\pi)^3}\int d^3p_2\int d\Omega\ \ v_{12}\frac{d\sigma}{d\Omega}(\mathbf{p}_1+\mathbf{p}_2,\mathbf{p}_2-\mathbf{p}_4)$$

$$\{n(\mathbf{p}_3;t)n(\mathbf{p}_4;t)\bar{n}(\mathbf{p}_1;t)\bar{n}(\mathbf{p}_2;t)-n(\mathbf{p}_1;t)n(\mathbf{p}_2;t)\bar{n}(\mathbf{p}_3;t)\bar{n}(\mathbf{p}_4;t)\},$$

with which we have reached the result for further applications.

In the case of thermodynamic equilibrium (for $t\to\infty$), i.e. $I_{coll}(\mathbf{p};t)\to 0$ for all $\mathbf{p}$, the Fermi distribution $n(\epsilon)$ (9.1) satisfies the necessary condition

$$\{n(\mathbf{p}_3;t)n(\mathbf{p}_4;t)\bar{n}(\mathbf{p}_1;t)\bar{n}(\mathbf{p}_2;t)-n(\mathbf{p}_1;t)n(\mathbf{p}_2;t)\bar{n}(\mathbf{p}_3;t)\bar{n}(\mathbf{p}_4;t)\} = 0 \tag{13.71}$$

and is thus the solution of (13.70) for $I_{coll}=0$.

Proof With $\epsilon(\mathbf{p}) = \hbar^2/2m\ \mathbf{p}^2$ and the identity—valid for the Fermi distribution for all β and μ—

$$\bar{n}(\epsilon) = 1 - n(\epsilon) = \frac{\exp\{\beta(\epsilon-\mu)\}}{1+\exp\{\beta(\epsilon-\mu)\}} \tag{13.72}$$

Equation (13.71) leads to the condition

$$\exp\{\beta(\epsilon(\mathbf{p}_1) - \mu)\} \exp\{\beta(\epsilon(\mathbf{p}_2) - \mu)\} - \exp\{\beta(\epsilon(\mathbf{p}_3) - \mu)\} \exp\{\beta(\epsilon(\mathbf{p}_4) - \mu) = 0, \tag{13.73}$$

which is equivalent to

$$\exp\{\beta(\epsilon(\mathbf{p}_1) + \epsilon(\mathbf{p}_2))\} = \exp\{\beta(\epsilon(\mathbf{p}_3) + \epsilon(\mathbf{p}_4)\}. \tag{13.74}$$

This latter identity, however, is fulfilled according to (13.67) due to the energy conservation in a 2-particle collision. (i.e. $\delta(\epsilon(\mathbf{p}_1) + \epsilon(\mathbf{p}_2) - \epsilon(\mathbf{p}_3) - \epsilon(\mathbf{p}_4))$), which proves the statement above.

13.7 The Vlasov-Uehling-Uhlenbeck Equation

With the results of Sects. 13.5 and 13.6 we can now specify the semiclassical limit of Eq. (13.25) in phase-space representation, if we identify $n(\mathbf{p};t)$ with the local phase-space occupation probability $\rho(\mathbf{r},\mathbf{p};t)$ for sufficiently extended systems. The combination of the Vlasov equation (13.49) and the collision term I_{coll} (13.70) then yields the **V**lasov-**U**ehling-**U**hlenbeck (**VUU**) equation, which is also known in the literature as Vlasov-Nordheim or Boltzmann-Uehling-Uhlenbeck (BUU) equation,

$$\{\tfrac{\partial}{\partial t} + \tfrac{\mathbf{p}_1}{m} \cdot \nabla_{\mathbf{r}} - \nabla_{\mathbf{r}} U(\mathbf{r},t) \cdot \nabla_{\mathbf{p}_1}\}\rho(\mathbf{r},\mathbf{p}_1;t) = I_{coll}(\mathbf{r},\mathbf{p}_1;t) \tag{13.75}$$

$$= \tfrac{g}{(2\pi)^3} \int d^3p_2 \int d\Omega\ v_{12} \tfrac{d\sigma}{d\Omega}(\mathbf{p}_1 + \mathbf{p}_2, \mathbf{p}_2 - \mathbf{p}_4)$$

$$\begin{aligned}&\{\rho(\mathbf{r},\mathbf{p}_3;t)\rho(\mathbf{r},\mathbf{p}_4;t)\bar{\rho}(\mathbf{r},\mathbf{p}_1;t)\bar{\rho}(\mathbf{r},\mathbf{p}_2;t)\\ &\quad -\rho(\mathbf{r},\mathbf{p}_1;t)\rho(\mathbf{r},\mathbf{p}_2;t)\bar{\rho}(\mathbf{r},\mathbf{p}_3;t)\bar{\rho}(\mathbf{r},\mathbf{p}_4;t)\},\end{aligned}$$

which describes the time evolution of a system of fermions under the influence of a time-dependent self-consistent mean field $U(\mathbf{r};t)$ as well as energy and momentum conserving 2-particle collisions. It serves as the starting point for various test-particle simulations in solid-state, atomic and nuclear physics and has made a decisive contribution to our understanding of the dynamics of Fermi systems far from equilibrium.

Remark: In the case of classical particles, (13.75) is simplified in that the Pauli blocking factors $\bar{\rho}(\mathbf{r},\mathbf{p}_i;t) = 1$ are omitted as well as the antisymmetrization in the cross section (13.66). The further approximation $\nabla_{\mathbf{r}} U(\mathbf{r};t) = 0$ then yields the **Boltzmann equation**

$$\{\tfrac{\partial}{\partial t} + \tfrac{\mathbf{p}_1}{m} \cdot \nabla_{\mathbf{r}}\}\rho(\mathbf{r},\mathbf{p}_1;t) = \tfrac{g}{(2\pi)^3} \int d^3p_2 \int d\Omega\ v_{12} \tfrac{d\sigma}{d\Omega}(\mathbf{p}_1 + \mathbf{p}_2) \tag{13.76}$$

$$\cdot\{\rho(\mathbf{r},\mathbf{p}_3;t)\rho(\mathbf{r},\mathbf{p}_4;t) - \rho(\mathbf{r},\mathbf{p}_1;t)\rho(\mathbf{r},\mathbf{p}_2;t)\},$$

which is used to describe the dynamics of a classical gas of particles.

13.8 Collision Rate, Mean Free Path

In order to obtain an estimate for the time scales necessary to reach the equilibrium configuration or statistical equilibrium, we consider the special case of a particle with momentum **p**, which propagates in a sufficiently (or infinitely) large and homogeneous Fermi system, which is represented (for temperature $T = 0$) in momentum space by a Fermi sphere with radius p_F. Such a case can be realized experimentally by either shooting an electron on a metallic solid or a proton on a large atomic nucleus such as *Pb*. The corresponding configuration in momentum space is shown in Fig. 13.2.

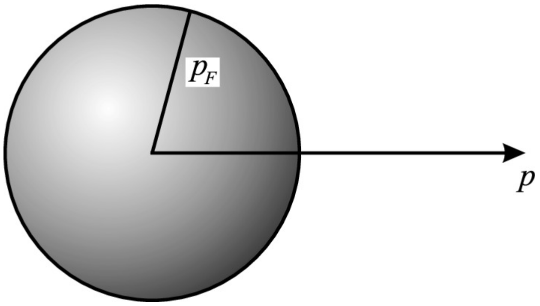

Fig. 13.2 Example of the momentum space configuration when scattering a proton with momentum *p* on an 'atomic nucleus' with Fermi momentum p_F

Due to the homogeneity of the system, the phase-space density does not depend on the position **r** and the change in the occupation number of the state with momentum **p** due to collision processes of **p** with $\mathbf{p}_2$ is described by the **loss term**

$$\frac{d}{dt}\ n(\mathbf{p};t) = -\frac{g}{(2\pi)^3}\int d^3p_2 \int d\Omega\ v_{12}\frac{d\sigma}{d\Omega}(\mathbf{p}+\mathbf{p}_2, \mathbf{p}_2-\mathbf{p}_4) \\ n(\mathbf{p};t)n(\mathbf{p}_2)\bar{n}(\mathbf{p}_3)\bar{n}(\mathbf{p}_4), \tag{13.77}$$

where the impact of the scattering processes on the system is neglected. Due to the linearity of (13.77) in $n(\mathbf{p};t)$ we can also write

$$\frac{d}{dt}\ n(\mathbf{p};t) = -\frac{1}{\tau_r(\mathbf{p})}n(\mathbf{p};t) \tag{13.78}$$

with the **collision rate**

$$\tau_r(\mathbf{p})^{-1} = \frac{g}{(2\pi)^3}\int d^3p_2 \int d\Omega\ v_{12}\frac{d\sigma}{d\Omega}(\mathbf{p}+\mathbf{p}_2, \mathbf{p}_2-\mathbf{p}_4)n(\mathbf{p}_2)\bar{n}(\mathbf{p}_3)\bar{n}(\mathbf{p}_4). \tag{13.79}$$

The quantity $\tau_r(\mathbf{p})$ is also called **relaxation time**, since the solution of the differential Eq. (13.78) with the boundary condition $n(\mathbf{p};t=0) = 1$ is given by

$$n(\mathbf{p};t) = \exp\left\{-\frac{t}{\tau_r(\mathbf{p})}\right\}. \tag{13.80}$$

The relaxation time therefore indicates the time within which a single-particle state, that is not occupied in thermodynamic equilibrium, decreases to the probability $1/e$ by scattering processes.

Looking at Fig. 13.2 we immediately find that, due to the energy conservation in 2-particle collisions at the temperature $T = 0$, the relaxation time $\tau_r(\mathbf{p}) = \infty$ for all $p < p_F$ due to Pauli blocking, i.e. despite possibly strong interactions the particles in the ground state cannot carry out collisions! Only for $p > p_F$ the allowed phase space opens up and the collision rate grows quadratically (without proof) with the energy above the Fermi energy, i.e.

$$\tau_r(\epsilon(\mathbf{p}))^{-1} \sim \frac{(\epsilon(\mathbf{p})-\epsilon_F)^2}{\epsilon_F^2} \tag{13.81}$$

with $\epsilon_F = \hbar^2/2m\ p_F^2$. For $p \gg p_F$ the Pauli blocking finally loses importance and we obtain the classical result for the collision rate with $v = p/m = \langle v_{12}\rangle$,

$$\boxed{\begin{aligned}\tau_r(\mathbf{p})^{-1} &\approx \frac{g}{(2\pi)^3} v\ \int d^3p_2 \int d\Omega\ \frac{d\sigma}{d\Omega}(\mathbf{p})n(\mathbf{p}_2) \\ &= \frac{g}{(2\pi)^3} v\ \int d^3p_2\ \sigma(\mathbf{p})n(\mathbf{p}_2) = v\ \sigma(\mathbf{p})\rho\end{aligned}} \tag{13.82}$$

with the density $\rho = g/(6\pi^2)p_F^3$. In the classical limit,—as expected—the collision rate is directly proportional to the relative velocity v, the total cross-section σ and the density ρ of the system.

Using the relation (valid for homogeneous systems),

$$\frac{d}{dt}\ n(\mathbf{p};t) = \mathbf{v}\ \cdot \frac{\partial}{\partial \mathbf{r}}\ n(\mathbf{p};\mathbf{r}), \tag{13.83}$$

we obtain alternatively

$$\frac{\partial}{\partial r}\ n(\mathbf{p};\mathbf{r}) = -\frac{1}{\lambda(\mathbf{p})}n(\mathbf{p};\mathbf{r}) \tag{13.84}$$

with the **mean free path**

$$\boxed{\lambda(\mathbf{p}) = \frac{1}{\sigma(\mathbf{p})\rho}} \tag{13.85}$$

for classical particles.

Without explicit proof, the comparable result for Bose systems should be mentioned: we set in (13.75) $\bar{\rho}(\mathbf{r},\mathbf{p};t) = 1 + \rho(\mathbf{r},\mathbf{p};t)$, where $\rho(\mathbf{r},\mathbf{p};t)$ in this case represents the phase-space density of the bosons. In analogy to Eq. (13.71), the equilibrium solution then is the Bose distribution (6.13).

In summarizing this chapter, with the VUU equation (13.75) or the Boltzmann equation (13.76) we have set the framework for the description of Fermi systems or classical particles far from equilibrium up to the thermodynamic equilibrium for $t \rightarrow \infty$. The solution of these equations can conveniently be achieved within the testparticle framework.

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