Statistical Mechanics

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Books:

C. Kittel, H. Kroemer, Thermal Physic, Freeman and Company F. Reif, Fundamentals of Statistical and Thermal Physics, Mc Graw Hill L. Landau, E. Lifshitz, Statistical Physics (Volume 5) K. Huang, Statistical mechanics, John Wiley and Sons

0 Introduction

The subject of thermodynamics and statistical mechanics is the description of the macroscopic properties of systems with a large number of degrees of freedom on the basis of the microscopic laws of physics.
A complete description of very large systems is not possible. The number of degrees of freedom is too large. A complete measurement is not possible and in most cases it would bring the system into a completely different state. Instead one uses an incomplete description by only a small number of macroscopic quantities, as for example energy, volume, and particle number.
Originally such systems were described phanomenologically within the framework of thermodynamics. Starting point was the irreversibility of processes (second law of thermodynamics), which allowed to introduce the state variable entropy besides temperature. This allowed to derive thermodynamic relations without recourse to microscopic considerations.
A modern approach which we will follow here has a statistical microscopic basis, which is built upon the laws of mechanics, quantum mechanics, and electrodynamics.
Within this theory one considers ensembles instead of single systems. Questions, which arise, are: How are these ensembles to be described? Are the averages of the ensembles representative? It will turn out, that due to the law of large numbers the relative fluctuations will become very small. Another question is: How does the transition to equilibrium take place?
Statistical mechanics is applied in the physics of condensed matter in its broadest sense. This holds for the solid state, but also for other phases as well as in nuclear physics and elementary particle physics at high energies and in astrophysics.

A Basic Concepts in Statistics

1 Description of quantummechanical ensembles

1.a Statistical operator or density matrix

If we have only incomplete information of a quantum system, then we describe it by a *statistical ensemble*. The system be with probability p_i in the state $|i\rangle$. The probabilities have to obey

$$p_i \geq 0 \quad \text{and} \quad \sum_i p_i = 1. \tag{1.1}$$

The states $|i\rangle$ need not be orthogonal to each other and nedd not be complete, but they are supposed to be normalized. Then the expectation value of an operator A is given by

$$\langle A \rangle = \sum_i p_i \langle i|A|i\rangle. \tag{1.2}$$

We now insert a complete set of orthogonal and normalized states $|\nu\rangle$,

$$\sum_\nu |\nu\rangle\langle\nu| = \mathbb{1}. \tag{1.3}$$

Then we obtain for the expectation value of A

$$\langle A \rangle = \sum_{i,\nu} p_i \langle i|A|\nu\rangle\langle\nu|i\rangle = \sum_{i,\nu} \langle\nu|i\rangle p_i \langle i|A|\nu\rangle = \sum_\nu \langle\nu|\rho A|\nu\rangle = \mathrm{tr}(\rho A), \tag{1.4}$$

where

$$\rho = \sum_i |i\rangle p_i \langle i| \tag{1.5}$$

is the statistical operator or density matrix, which describes the statistical ensemble. In general it is not possible to determine the states $|i\rangle$ and their probabilities from ρ.
We consider some properties of ρ: α) ρ is hermitean,

$$\rho^\dagger = \rho, \tag{1.6}$$

since the probabilities p_i are real. β) The trace of ρ equals unity,

$$\mathrm{tr}(\rho) = \sum_{i,\nu} \langle\nu|i\rangle p_i \langle i|\nu\rangle = \sum_i p_i \underbrace{\sum_\nu \langle i|\nu\rangle\langle\nu|i\rangle}_{\langle i|i\rangle=1} = \sum_i p_i = 1, \tag{1.7}$$

since the sum of the probabilities adds up to one. γ) ρ is positive semi-definite, that is for each state $|a\rangle$ one has

$$\langle a|\rho|a\rangle = \sum_i \langle a|i\rangle p_i \langle i|a\rangle = \sum_i p_i |\langle a|i\rangle|^2 \geq 0, \tag{1.8}$$

since $p_i \geq 0$.

Since ρ is hermitean it can be diagonalized, that is there exists an orthonormal basis $\{|n\rangle\}$, for which

$$\rho = \sum_n |n\rangle \rho_n \langle n| \tag{1.9}$$

holds. From β) one concludes $\sum_n \rho_n = 1$ and from γ) that $0 \leq \rho_n \leq 1$ holds.
If the system consists of a pure state only, then one has

$$\rho_n = \begin{cases} 1 & \text{for one } n, \\ 0 & \text{for all other } n\text{s.} \end{cases} \tag{1.10}$$

Example The ensemble consists of neutrons, the spins of which are oriented in $+z$-direction with probability p_1 and in $+x$-direction with probability p_2, $p_1 + p_2 = 1$. With

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{1.11}$$

one obtains from $\sigma_z|+z\rangle = +|+z\rangle$ and $\sigma_x|+x\rangle = +|+x\rangle$

$$|+z\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \langle +z| = |+z\rangle^\dagger = \begin{pmatrix} 1 & 0 \end{pmatrix}, \quad |+x\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \quad \langle +x| = |+x\rangle^\dagger = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \end{pmatrix} \tag{1.12}$$

and therefore

$$\rho = p_1 \begin{pmatrix} 1 \\ 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \end{pmatrix} + p_2 \frac{1}{2} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \begin{pmatrix} 1 & 1 \end{pmatrix} = \begin{pmatrix} p_1 + \frac{p_2}{2} & \frac{p_2}{2} \\ \frac{p_2}{2} & \frac{p_2}{2} \end{pmatrix}. \tag{1.13}$$

We observe

$$\mathrm{tr}\rho = p_1 + p_2 = 1 \tag{1.14}$$

and find the eigenvalues

$$\rho_{1,2} = \frac{1}{2} \pm \sqrt{\frac{1}{4} - \frac{1}{2} p_1 p_2}. \tag{1.15}$$

1.b Reduced density matrix

One often deals with the situation, that a system consists of two subsystems, which can be described by complete orthonormal bases $|\nu_1\rangle$, $|\nu_2\rangle$. It may be that both are subsystems of the system we are investigating or subsystem 2 was or still is in contact with subsystem 1. The vectors $|\nu_1, \nu_2\rangle$ (direct product) in Hilbert space constitute a complete orthonormal basis of the total system. Be ρ the density matrix of the total system and A_1 an operator acting only in the first subsystem. Then one has

$$\langle A_1 \rangle = \sum_{\nu_1, \nu_2} \langle \nu_1, \nu_2 | \rho A_1 | \nu_1, \nu_2 \rangle = \sum_{\nu_1, \nu_2, \mu_1, \mu_2} \langle \nu_1, \nu_2 | \rho | \mu_1, \mu_2 \rangle \langle \mu_1, \mu_2 | A_1 | \nu_1, \nu_2 \rangle. \tag{1.16}$$

The operator A_1 acts only in subsystem 1, it leaves subsystem 2 unchanged, thhus acts like the unit-operator $\mathbb{1}_2$,

$$\langle \mu_1, \mu_2 | A_1 | \nu_1, \nu_2 \rangle = \langle \mu_1, \mu_2 | A_1 \mathbb{1}_2 | \nu_1, \nu_2 \rangle = \langle \mu_1 | A_1 | \nu_1 \rangle \langle \mu_2 | \mathbb{1}_2 | \nu_2 \rangle = \langle \mu_1 | A_1 | \nu_1 \rangle \delta_{\mu_2, \nu_2}. \tag{1.17}$$

Thus we may write

$$\langle A_1 \rangle = \sum_{\nu_1, \nu_2, \mu_1} \langle \mu_1 | A_1 | \nu_1 \rangle \langle \nu_1, \nu_2 | \rho | \mu_1, \nu_2 \rangle = \sum_{\nu_1, \mu_1} \langle \nu_1 | \rho_1 | \mu_1 \rangle \langle \mu_1 | A_1 | \nu_1 \rangle = \mathrm{tr}_1(\rho_1 A_1) \tag{1.18}$$

with the reduced density matrix ρ_1, defined by

$$\langle \nu_1 | \rho_1 | \mu_1 \rangle = \sum_{\nu_2} \langle \nu_1, \nu_2 | \rho | \mu_1, \nu_2 \rangle. \tag{1.19}$$

Thus one takes the trace on subsystem 2 and writes

$$\rho_1 = \mathrm{tr}_2\rho = \sum_{\nu_1,\mu_1} |\nu_1\rangle \sum_{\nu_2} \langle \nu_1, \nu_2|\rho|\mu_1, \nu_2\rangle\langle\mu_1|. \tag{1.20}$$

Even if ρ corresponds to a pure state, then in general ρ_1 will be a mixture. **Example.** Two electrons have total spin 0,

$$|\chi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle), \tag{1.21}$$

$$\rho = |\chi\rangle\langle\chi| = \frac{1}{2}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)(\langle\uparrow\downarrow| - \langle\downarrow\uparrow|), \tag{1.22}$$

$$\rho_1 = \frac{1}{2}|\uparrow\rangle\langle\uparrow| + \frac{1}{2}|\downarrow\rangle\langle\downarrow|. \tag{1.23}$$

Both eigenvalues of ρ_1 are 1/2; thus we deal with a mixture.

1.c von Neumann equation

In general ρ is a function of time t. We derive the equation of motion. Starting from the time-dependent Schrödinger equation

$$\mathrm{i}\hbar\frac{\mathrm{d}|i\rangle}{\mathrm{d}t} = H|i\rangle \leftrightarrow \mathrm{i}\hbar\frac{\partial\psi_i(x,t)}{\partial t} = H\psi_i(x,t) \tag{1.24}$$

and its hermitean adjoint

$$-\mathrm{i}\hbar\frac{\mathrm{d}\langle i|}{\mathrm{d}t} = \langle i|H. \tag{1.25}$$

we obtain

$$\mathrm{i}\hbar\frac{\mathrm{d}\rho}{\mathrm{d}t} = \mathrm{i}\hbar\sum_i p_i\frac{\mathrm{d}|i\rangle\langle i|}{\mathrm{d}t} = \sum_i p_i(H|i\rangle\langle i| - |i\rangle\langle i|H) = [H,\rho]. \tag{1.26}$$

This is the von-Neumann equation.
Stationary ensembles A stationary ensemble is an ensemble which does not change as a function of time. Thus it obeys the condition

$$\dot{\rho} = 0, \text{ id est } [H,\rho] = 0. \tag{1.27}$$

In the enrgy representation, that is in a basis of states, which are eigenstates of the Hamiltonian, $H|n\rangle = E_n|n\rangle$, one obtains from

$$\langle m|H\rho - \rho H|n\rangle = 0 \tag{1.28}$$

the condition

$$(E_m - E_n)\rho_{m,n} = 0, \tag{1.29}$$

that is $\rho_{m,n}$ vanishes , if $E_m \neq E_n$. If there is no degeneracy then one may write

$$\rho = \sum_n \rho(E_n)|n\rangle\langle n|. \tag{1.30}$$

2 Ensembles of Classical Mechanics

2.a Distribution function

In classical mechanics a system is defined by the momentum and position coordinates of its N particles,

$$(\mathbf{p},\mathbf{x}) = (\mathbf{p}_1,\mathbf{p}_2,...\mathbf{p}_N,\mathbf{x}_1,\mathbf{x}_2,...\mathbf{x}_N). \tag{2.1}$$

These coordinates span the $6N$-dimensional configuration space (phase space Γ-space).

$$\rho(\mathbf{p}_1,...\mathbf{p}_N,\mathbf{x}_1,...\mathbf{x}_N)\mathrm{d}^{3N}p\,\mathrm{d}^{3N}x \tag{2.2}$$

be the probability for the system to be in the volume-element $\mathrm{d}^{3N}p\,\mathrm{d}^{3N}x$ at $(\mathbf{p}_1,...\mathbf{x}_N)$. The expectation value of a function $A(\mathbf{p}_1,...\mathbf{x}_N)$ is then given by

$$\langle A(\mathbf{p},\mathbf{x})\rangle = \int \mathrm{d}^{3N}p\,\mathrm{d}^{3N}x\,\rho(\mathbf{p},\mathbf{x})A(\mathbf{p},\mathbf{x}). \tag{2.3}$$

The distribution function ρ has the properties

$$\rho(\mathbf{p},\mathbf{x}) \geq 0, \qquad \int \mathrm{d}^{3N}p\,\mathrm{d}^{3N}x\,\rho(\mathbf{p},\mathbf{x}) = 1. \tag{2.4}$$

2.b Liouville equation and Liouville theorem

The distribution function is a function of time, $\rho(\mathbf{p},\mathbf{x},t)$. A single system is described by a point in the Γ space, whose coordinates vary as a function of time. Since the number of systems is conserved, an equation of continuity holds in phase space. Equations of continuity have the form $\frac{\partial\rho}{\partial t} + \mathrm{div}\,(\rho\mathbf{v}) = 0$. In phase space both the time derivatives of $\mathbf{x}$ and of $\mathbf{p}$ are "velocities $\mathbf{v}$". Thus the equation of continuity reads

$$\frac{\partial\rho}{\partial t} + \sum_{i,\alpha}\frac{\partial}{\partial x_{i\alpha}}(\rho\dot{x}_{i\alpha}) + \sum_{i,\alpha}\frac{\partial}{\partial p_{i\alpha}}(\rho\dot{p}_{i\alpha}) = 0. \tag{2.5}$$

The particles are numbered by the index i and the cartesian components by α. We consider now the substantial (=total) derivative of ρ, that is, we follow how ρ changes, as we move with the corresponding point in phase space,

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \frac{\mathrm{d}\rho(\mathbf{p}(t),\mathbf{x}(t),t)}{\mathrm{d}t} = \frac{\partial\rho}{\partial t} + \sum_{i,\alpha}\dot{x}_{i\alpha}\frac{\partial\rho}{\partial x_{i\alpha}} + \sum_{i,\alpha}\dot{p}_{i\alpha}\frac{\partial\rho}{\partial p_{i\alpha}}. \tag{2.6}$$

If we express the partial derivative $\frac{\partial\rho}{\partial t}$ by the equation of continuity, then we are left with

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} + \sum_{i,\alpha}\left(\frac{\partial\dot{x}_{i\alpha}}{\partial x_{i\alpha}} + \frac{\partial\dot{p}_{i\alpha}}{\partial p_{i\alpha}}\right)\rho = 0. \tag{2.7}$$

Now we have

$$\dot{x}_{i\alpha} = \frac{\partial H}{\partial p_{i\alpha}}, \quad \dot{p}_{i\alpha} = -\frac{\partial H}{\partial x_{i\alpha}}. \tag{2.8}$$

From this we obtain

$$\frac{\partial\dot{x}_{i\alpha}}{\partial x_{i\alpha}} + \frac{\partial\dot{p}_{i\alpha}}{\partial p_{i\alpha}} = \frac{\partial^2 H}{\partial x_{i\alpha}\partial p_{i\alpha}} - \frac{\partial^2 H}{\partial p_{i\alpha}\partial x_{i\alpha}} = 0 \tag{2.9}$$

and thus Liouville's theorem

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = 0. \tag{2.10}$$

Consequence A system $\mathbf{p}_0$, $\mathbf{x}_0$ at time t_0 changes into the system $\mathbf{p}$, $\mathbf{x}$ at time t. Since the density in phase-space is conserved, the volume element will stay constant,

$$\frac{\partial(\mathbf{p},\mathbf{x})}{\partial(\mathbf{p}_0,\mathbf{x}_0)} = 1. \tag{2.11}$$

We finally determine the partial derivative of ρ,

$$\frac{\partial \rho}{\partial t} = \frac{\mathrm{d}\rho}{\mathrm{d}t} - \sum_{i\alpha} \dot{x}_{i\alpha} \frac{\partial \rho}{\partial x_{i\alpha}} - \sum_{i\alpha} \dot{p}_{i\alpha} \frac{\partial \rho}{\partial p_{i\alpha}} = -\sum_{i\alpha} \frac{\partial H}{\partial p_{i\alpha}} \frac{\partial \rho}{\partial x_{i\alpha}} + \sum_{i\alpha} \frac{\partial H}{\partial x_{i\alpha}} \frac{\partial \rho}{\partial p_{i\alpha}} = -\{\rho, H\}, \tag{2.12}$$

where $\{\rho, H\}$ is the Poisson-bracket between ρ and H.
Stationary Ensembles For them $\dot{\rho} = 0$ holds again. If ρ depends only on conserved quantities, then it is stationary, $\rho = \rho(H, \mathbf{P}, \mathbf{L}, N)$. Since normally the system is not in rotational invariant vessels, $\mathbf{P}$ and $\mathbf{L}$ are normally no conserved quantities, $\rho = \rho(H, N)$.

3 Probabilities, Correlations and Variances

3.a Probability and variance

Apart from the expectation value of an observable A one is also interested in its variance

$$(\Delta A)^2 = \langle (A - \langle A \rangle)^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2. \tag{3.1}$$

The quantity ΔA indicates, how strongly the measured a of A may deviate from the average $\langle A \rangle$ for a system, $a = \langle A \rangle \pm \Delta A$. This variance ΔA is also called standard deviation. If ΔA is negligible small, then $\langle A \rangle$ is the expected outcome of the measurement.
We now define the probability distribution for A,

$$w_A(a) = \langle \delta(a - A) \rangle = \mathrm{tr}(\rho \delta(a - A)). \tag{3.2}$$

The operator-valued function of an operator is understood in the following way: A be expressed in terms of its eigenstates $|i\rangle$

$$A = \sum_i |i\rangle a_i \langle i|. \tag{3.3}$$

Then the function $f(A)$ is defined as

$$f(A) = \sum_i |i\rangle f(a_i) \langle i|. \tag{3.4}$$

One may convince oneself that the definition is in agreement with the four basic arithmetical operations and the Taylor- and Laurent-expansion. This definition is a generalization, if such an expansion is not possible.

$$\delta(a - A) = \sum_i |i\rangle \delta(a - a_i) \langle i|. \tag{3.5}$$

The probability distribution is then given by

$$w_A(a) = \langle \delta(a - A) \rangle = \mathrm{tr}(\rho \sum_i |i\rangle \delta(a - a_i) \langle i|) = \sum_i \langle i|\rho|i\rangle \delta(a - a_i). \tag{3.6}$$

From this one obtains

$$\begin{aligned} \langle f(A) \rangle &= \sum_i f(a_i) \langle |i\rangle\langle i| \rangle = \sum_i f(a_i) \mathrm{tr}(\rho |i\rangle\langle i|) = \sum_i f(a_i) \langle i|\rho|i\rangle \\ &= \int \mathrm{d}a f(a) \sum_i \delta(a - a_i) \langle i|\rho|i\rangle = \int \mathrm{d}a f(a) w_A(a). \end{aligned} \tag{3.7}$$

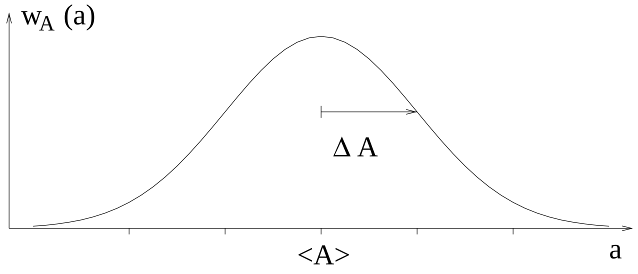
This yields immediately

$$\int \mathrm{d}a\, w_A(a) = 1, \tag{3.8}$$

$$\int \mathrm{d}a\, a w_A(a) = \langle A \rangle, \tag{3.9}$$

$$\int \mathrm{d}a\, (a - \langle A \rangle)^2 w_A(a) = (\Delta A)^2. \tag{3.10}$$

Half the width of the distribution equals approximately ΔA.
Example: Gauss distribution



If the spectrum of A is discrete, then it is useful to replace the distribution $\delta(a-A)$ by the Kronecker-Delta

$$\delta_{a,A} = \sum_i \delta_{a,a_i} |i\rangle\langle i| \tag{3.11}$$

and the integral by the sum

$$\begin{aligned} w_A(a) &= \operatorname{tr}(\rho\delta_{a,A}) = \sum_i \delta_{a,a_i} \langle i|\rho|i\rangle, && (3.12) \\ \langle f(A)\rangle &= \sum_a w_A(a) f(a). && (3.13) \end{aligned}$$

For classical statistical mechanics one has correspondingly

$$w_A(a) = \langle \delta(a-A)\rangle = \int \mathrm{d}^{3N}p\, \mathrm{d}^{3N}x\, \rho(\mathbf{p},\mathbf{x})\delta(a - A(\mathbf{p},\mathbf{x})). \tag{3.14}$$

This corresponds to the integration on the shell given by $a = A(\mathbf{p},\mathbf{x})$.

3.b Correlations

Apart from the fluctuations of one quantity A one is often interested in correlations of several observables A and B. If A and B commutate, then the correltion is defined by

$$K_{A,B} = \langle (A - \langle A\rangle)(B - \langle B\rangle)\rangle = \langle AB\rangle - \langle A\rangle\langle B\rangle. \tag{3.15}$$

If $K_{A,B} \neq 0$, then one says, that A and B are correlated.
One can define a probability distribution

$$w_{A,B}(a,b) = \langle \delta(a-A)\delta(b-B)\rangle = \operatorname{tr}(\rho\delta(a-A)\delta(b-B)) = \sum_i \langle i|\rho|i\rangle \delta(a-a_i)\delta(b-b_i) \tag{3.16}$$

for eigenstates $|i\rangle$ of A and B. Then one obtains

$$\langle f(A,B)\rangle = \int \mathrm{d}a\, \mathrm{d}b\, w_{A,B}(a,b) f(a,b), \tag{3.17}$$

e.g.

$$\langle AB\rangle = \int \mathrm{d}a\, \mathrm{d}b\, w_{A,B}(a,b) ab. \tag{3.18}$$

One finds

$$\int \mathrm{d}b\, w_{A,B}(a,b) = w_A(a). \tag{3.19}$$

If $w_{A,B}(a,b) = w_A(a) w_B(b)$, then A and B are called statistically independent. Then one has

$$\langle AB\rangle = \int \mathrm{d}a\, \mathrm{d}b\, ab w_{A,B}(a,b) = \int \mathrm{d}a\, w_A(a) \int \mathrm{d}b\, w_B(b) = \langle A\rangle\langle B\rangle, \tag{3.20}$$

thus $K_{A,B} = 0$. However, from $K_{A,B} = 0$ one cannot conclude statistical independence. For classical systems one introduces analogously the probability distribution

$$w_{A,B}(a,b) = \int \mathrm{d}^{3N}p\, \mathrm{d}^{3N}x\, \rho(\mathbf{p},\mathbf{x})\delta(a - A(\mathbf{p},\mathbf{x}))\delta(b - B(\mathbf{p},\mathbf{x})). \tag{3.21}$$

3.c Fluctuations in the thermodynamic limit

One often deals in statisitical mechanics with densities and volume-integrals of densities

$$A = \int \mathrm{d}^3 r \hat{a}(r), \tag{3.22}$$

as e.g. the particle density, energy density, magnetization etc. The variance of these quantities is

$$\begin{aligned}(\Delta A)^2 &= \int \mathrm{d}^3 r \mathrm{d}^3 r' (\langle \hat{a}(r)\hat{a}(r')\rangle - \langle \hat{a}(r)\rangle\langle \hat{a}(r')\rangle) \\ &= \int \mathrm{d}^3 r \mathrm{d}^3 r' \langle (\hat{a}(r) - \langle \hat{a}(r)\rangle)(\hat{a}(r') - \langle \hat{a}(r')\rangle)\rangle \\ &= \int \mathrm{d}^3 r \mathrm{d}^3 r' K_{\hat{a}(r),\hat{a}(r')} = \int \mathrm{d}^3 r \mathrm{d}^3 r' K_{\hat{a}\hat{a}}(r,r'). \end{aligned} \tag{3.23}$$

The correlations of macroscopic quantities have often a finite range. Measurements at loci far apart are statistically independent. The range of the correlations is often of the same order as the range of the microscopic interaction. (Exceptions: Continuous phase transitions, long-range order at broken symmetries). Then $(\Delta A)^2$ is of the order of the volume if we use that K often depends only on the distance, $K_{\hat{a},\hat{a}}(r,r') = K_{\hat{a},\hat{a}}(r-r',0)$.

$$(\Delta A)^2 = \int \mathrm{d}^3 r \mathrm{d}^3 r' K_{\hat{a},\hat{a}}(r-r',0) = V \int \mathrm{d}^3 r K_{\hat{a},\hat{a}}(r,0). \tag{3.24}$$

Since $\langle A\rangle$ is a volume integral and thus proportional to the volume V one has

$$\frac{\Delta A}{\langle A\rangle} \propto \frac{\sqrt{V}}{V} = \frac{1}{\sqrt{V}}. \tag{3.25}$$

For large systems the fluctuations become negligibly small and $\langle A\rangle$ agrees practically always the measured one.

3.d Example: Magnetic Moments

We consider N magnetic moments μ_i, which are statistically independent. The probability that the moment assumes $\mu_i = +\mu$ be p_1, and that it assumes $\mu_i = -\mu$ be p_2, $p_1 + p_2 = 1$. Then one obtains the total magnetic moment

$$\langle M\rangle = \sum_{i=1} \langle \mu_i\rangle = \sum_i (p_1 - p_2)\mu = N(p_1 - p_2)\mu. \tag{3.26}$$

and the variance

$$(\Delta M)^2 = \langle (M - \langle M\rangle)(M - \langle M\rangle)\rangle = \sum_{i=1}^{N}\sum_{j=1}^{N} \langle (\mu_i - \langle \mu_i\rangle)(\mu_j - \langle \mu_j\rangle)\rangle. \tag{3.27}$$

Considering that the moments are statistically independent directed all contributions with $i \neq j$ vanish in the sum and one is left with

$$(\Delta M)^2 = \sum_{i=1}^{N} \langle (\mu_i - \langle \mu_i\rangle)^2\rangle = \sum_{i=1}^{N} (\langle \mu_i^2\rangle - \langle \mu_i\rangle^2) = \sum_i (\mu^2 - \mu^2(p_1 - p_2)^2) = 4N\mu^2 p_1 p_2, \tag{3.28}$$

since $(p_1 - p_2)^2 = (p_1 + p_2)^2 - 4p_1p_2 = 1 - 4p_1p_2$. Then one obtains

$$\frac{\Delta M}{\langle M\rangle} = \frac{2\sqrt{p_1 p_2}}{\sqrt{N}(p_1 - p_2)}. \tag{3.29}$$

Probability distribution We now consider the probability distribution. $w_{N_\uparrow}(n)$ be the probability that precisely n of the total N moments are directed upward,

$$w(n) = p_1^n p_2^{N-n} W. \tag{3.30}$$

Here W is the number of sets of n moments out of N moments,

$$W = \binom{N}{n} = \frac{N!}{n!(N-n)!} \tag{3.31}$$

For large N one can apply the Stirling formula (A.5) for n factorial $n! \approx (n/e)^n\sqrt{2\pi n}$. Then one obtains

$$w(n) = \sqrt{\frac{N}{2\pi n(N-n)}} \left(\frac{p_1 N}{n}\right)^n \left(\frac{p_2 N}{N-n}\right)^{N-n}. \tag{3.32}$$

We are interested in $w(n)$ close to its maximum. Thus expand n around its average $p_1 N$ and put $n = p_1 N + \nu$, $N - n = p_2 N - \nu$

$$w(n) = \sqrt{\frac{N}{2\pi n(N-n)}} \underbrace{\left(1 + \frac{\nu}{p_1 N}\right)^{-p_1 N - \nu} \left(1 - \frac{\nu}{p_2 N}\right)^{-p_2 N + \nu}}_{g}. \tag{3.33}$$

and expand $\ln g$ in ν. We obtain

$$\begin{aligned}
\ln g &= (-p_1 N - \nu)\ln(1 + \frac{\nu}{p_1 N}) + (-p_2 N + \nu)\ln(1 - \frac{\nu}{p_2 N}) \\
&= (-p_1 N - \nu)\left(\frac{\nu}{p_1 N} - \frac{\nu^2}{2p_1^2 N^2} + \frac{\nu^3}{3p_1^3 N^3} - \ldots\right) \\
&+ (-p_2 N + \nu)\left(-\frac{\nu}{p_2 N} - \frac{\nu^2}{2p_2^2 N^2} - \frac{\nu^3}{3p_2^3 N^3} - \ldots\right) \qquad (3.34) \\
&= 0\cdot\nu - \frac{1}{2}\left(\frac{1}{p_1 N} + \frac{1}{p_2 N}\right)\nu^2 + \frac{1}{6}\left(\frac{1}{p_1^2 N^2} - \frac{1}{p_2^2 N^2}\right)\nu^3 + \ldots + \frac{\ldots\nu^k}{N^{k-1}} + \ldots \qquad (3.35)
\end{aligned}$$

If $\nu = O(N^{1/2})$ then the contribution ν^2/N is of order $O(N^0)$. The next one is $\nu^3/N^2 = O(N^{-1/2})$ and the higher ones $\nu^k/N^{k-1} = O(N^{1-k/2})$ with $k \geq 4$. These become negligibly small for large N and one obtains the Gaussian distribution in this limit

$$w(n) = \frac{1}{\sqrt{2\pi p_1 p_2 N}} \exp\left(-\frac{\nu^2}{2p_1 p_2 N}\right) = \frac{1}{\sqrt{2\pi p_1 p_2 N}} \exp\left(-\frac{(n - Np_1)^2}{2p_1 p_2 N}\right). \tag{3.36}$$

B Equilibrium Ensembles

4 Microcanonical ensemble (classical)

4.a Description of the ensemble

We consider a classical system with given particle number N in a volume V. The energy of the system be between $E-\Delta$ and E. Further infomation on the system be missing. Due to this missing information we replace the system by an ensemble of constant distribution function ρ_0 within this energy interval (equal partion).
Behind this is the idea, ensemble average equals time average. That is, in the course of a sufficiently long time interval all regions of the energy shell will be transversed by the system so that the average of an observable in time equals the ensemble average. Of course, this had to be proven.
Thus we set

$$\rho(H) = \begin{cases} \rho_0 & E-\Delta < H \le E, \\ 0 & \text{otherwise.} \end{cases} \tag{4.1}$$

This microcanonical ensemble is a stationary ensemble.
The volume of the phase space for the states with energy $H \le E$ amounts to

$$\Phi(E) = \int \mathrm{d}^{3N}x\mathrm{d}^{3N}p\Theta(E-H) \tag{4.2}$$

with the well-known Heaviside step-function

$$\Theta(x) = \begin{cases} 0 & x<0 \\ 1 & x \ge 0 \end{cases}. \tag{4.3}$$

We have chosen here $\Theta(0)=1$ somehow arbitrarily, since we wish to include the states with $H=E$. Then we obtain for the constant ρ_0

$$\int \mathrm{d}^{3N}x\mathrm{d}^{3N}p\rho(H) = \rho_0(\Phi(E)-\Phi(E-\Delta)) = 1, \tag{4.4}$$

thus

$$\rho_0 = \frac{1}{\Phi(E)-\Phi(E-\Delta)}. \tag{4.5}$$

If we require precisely $H=E$, then we perform the limit $\Delta \to 0$ and obtain $\rho(H) = c\delta(E-H)$ with

$$\int \mathrm{d}^{3N}x\mathrm{d}^{3N}pc\delta(E-H) = c\int \mathrm{d}^{3N}x\mathrm{d}^{3N}p\frac{\partial\Theta(E-H)}{\partial E} = c\frac{\partial\Phi(E)}{\partial E} = 1, \tag{4.6}$$

thus

$$\rho = \left(\frac{\partial\Phi(E,V)}{\partial E}\right)^{-1}\delta(E-H). \tag{4.7}$$

4.b Monatomic ideal gas

We consider now a monatomic ideal gas. The Hamiltonian consists only of the kinetic energy

$$H = \frac{1}{2m}\sum_{i=1}^{N} p_i^2. \tag{4.8}$$

We obtain for the volume of the phase-space

$$\begin{aligned}
\Phi(E) &= \int \mathrm{d}^{3N}x\mathrm{d}^{3N}p\Theta(E-H) = V^N \int \mathrm{d}^{3N}p\Theta(2mE - \sum_i p_i^2) && (4.9)\\
&= V^N \times \text{volume of the } 3N\text{-dimensional sphere of radius } \sqrt{2mE} && (4.10)\\
&= V^N\Omega_{3N}\int_0^{\sqrt{2mE}} p^{3N-1}\mathrm{d}p = V^N\frac{\Omega_{3N}}{3N}(2mE)^{3N/2}, && (4.11)
\end{aligned}$$

where Ω_{3N} is the full solid angle in $3N$ dimensions, which is equivalent to the surface of the $3N$-dimensional unit sphere, that is of the $3N$-dimensional sphere of radius 1.
This solid angle can be determined by evaluating the following integral in two different ways

$$\begin{aligned}
\int \mathrm{d}^d\alpha \mathrm{e}^{-\alpha_1^2-\ldots-\alpha_d^2} &= \left(\int_{-\infty}^{+\infty}\mathrm{d}\alpha_1\mathrm{e}^{-\alpha_1^2}\right)^d = \pi^{d/2} && (4.12)\\
&= \Omega_d\int_0^\infty \mathrm{e}^{-\alpha^2}\alpha^{d-1}\mathrm{d}\alpha = \frac{\Omega_d}{2}\int_0^\infty \mathrm{e}^{-\alpha^2}\left(\alpha^2\right)^{d/2-1}\mathrm{d}\alpha^2 = \frac{\Omega_d}{2}\left(\frac{d}{2}-1\right)! && (4.13)
\end{aligned}$$

I often write $a!$ ("a factorial") even for non-integer a with the understanding that $a! = \Gamma(a+1)$. Then one obtains

$$\Omega_d = \frac{2\pi^{d/2}}{(\frac{d}{2}-1)!}. \tag{4.14}$$

For $d=1$ one obtains with $(-\frac{1}{2})! = \Gamma(\frac{1}{2}) = \pi^{1/2}$ the result $\Omega_1 = 2$. This is the number of endpoints of the line from -1 to $+1$. For $d=2$ one has $0! = \Gamma(1) = 1$ and therefore $\Omega_2 = 2\pi$, the perimeter of the unit circle and for $d=3$ one obtains $(\frac{1}{2})! = \frac{1}{2}(-\frac{1}{2})! = \pi^{1/2}/2$ and thus the three-dimensional solid angle $\Omega_3 = 4\pi$.
The volume of the phase-space thus obtained

$$\Phi(E) = \frac{V^N(2mE)^{3N/2}\pi^{3N/2}}{(\frac{3N}{2})!} \tag{4.15}$$

increases as function of the energy E extremely rapidly. Thus we have chosen in (4.1) the bounds E and $E-\Delta$ and not $E+\Delta$ and E, since the result depends stronger on the upper then the lower bound. For the same reason one often chooses $\Delta = \infty$ and obtains in this way a result which no longer contains Δ. One says: Nearly the whole volume of the phase-space is in the energy shell.
One may, however, also choose the enrgy shell $H = E$ (4.7), that is $\Delta = 0$. Then we obtain for the normalization constant c

$$\frac{1}{c} = \frac{\partial\Phi(E,V)}{\partial E} = \frac{V^N(2mE)^{3N/2-1}\pi^{3N/2}2m}{(\frac{3N}{2}-1)!.}. \tag{4.16}$$

Upon demand we will choose one or the other possibility.

5 Maxwell distribution and the equation of state of the ideal classical monatomic gas

5.a Maxwell-distribution

We ask now the question: What is the probability $w_{\mathbf{p}_1}(\mathbf{p}_1)\mathrm{d}^3 p_1$, to find the atom # 1 in the momentum interval $p_{1x}..p_{1x}+\mathrm{d}p_{1x}$, $p_{1y}..p_{1y}+\mathrm{d}p_{1y}$, $p_{1z}..p_{1z}+\mathrm{d}p_{1z}$? For this purpose we calculate

$$w(\mathbf{p}_1) = \int \rho(p,x)\mathrm{d}^3 p_2 ... \mathrm{d}^3 p_N \mathrm{d}^3 x_1 ... \mathrm{d}^3 x_N \tag{5.1}$$

with

$$\rho(p,x) = \frac{1}{\frac{\partial\Phi}{\partial E}}\delta(E-H). \tag{5.2}$$

Now we introduce the Hamiltonian function H' and the energy E' for the other $N-1$ atoms

$$H' = \frac{1}{2m}(p_2^2 + ...p_N^2), \quad E' = E - \frac{1}{2m}p_1^2, \quad E-H = E'-H' \tag{5.3}$$

and obtain

$$\begin{aligned} w(\mathbf{p}_1) &= \frac{1}{\frac{\partial\Phi_N(E)}{\partial E}}\int \delta(E'-H')\mathrm{d}^3 p_2 ... \mathrm{d}^3 p_N \mathrm{d}^3 x_1 ... \mathrm{d}^3 x_N = \frac{V\frac{\partial\Phi_{N-1}(E')}{\partial E'}}{\frac{\partial\Phi_N(E)}{\partial E}} \\ &= \frac{(\frac{3}{2}N-1)!}{\pi^{3/2}(\frac{3}{2}N-\frac{5}{2})!(2mE)^{3/2}}\left(\frac{E'}{E}\right)^{\frac{3N}{2}-\frac{5}{2}}. \end{aligned} \tag{5.4}$$

For $a \ll \frac{3N}{2}$, $b \ll \frac{3N}{2}$, $1 \ll \frac{3N}{2}$ one has

$$\frac{(\frac{3N}{2}-a)!}{(\frac{3N}{2}-b)!} \approx \frac{(\frac{3N}{2})!}{(\frac{3N}{2})^a}\frac{(\frac{3N}{2})^b}{(\frac{3N}{2})!} = \left(\frac{3N}{2}\right)^{b-a}, \tag{5.5}$$

since in $(\frac{3N}{2}-a)!$ a factors are missing to $(\frac{3N}{2})!$ approximately of size $\frac{3N}{2}$, which is immediately obvious for integer a, but holds true also for non-integer a. This can be derived from the Stirling formula (A.5). Thus one obtains

$$w(\mathbf{p}_1) = \left(\frac{3N}{4\pi mE}\right)^{3/2}\left(1-\frac{p_1^2}{2mE}\right)^{\frac{3N}{2}-\frac{5}{2}}. \tag{5.6}$$

In the average one atom carries the energy $\frac{E}{N}$. Thus one has $p_1^2 = O(\frac{2mE}{N})$. In the limit of large N we may thus use $(1-\frac{a}{N})^{bN} = \exp(-ab)$ and obtain

$$\left(1-\frac{p_1^2}{2mE}\right)^{\frac{3N}{2}-\frac{5}{2}} = \exp(-\frac{3N}{2}\frac{p_1^2}{2mE}), \tag{5.7}$$

where $(...)^{-5/2}$ converges for large N to 1. With the abreviation

$$\beta = \frac{3N}{2E} \tag{5.8}$$

one obtains the Maxwell distribution

$$w(\mathbf{p}_1) = \left(\frac{\beta}{2\pi m}\right)^{3/2}\exp\left(-\beta\frac{p_1^2}{2m}\right). \tag{5.9}$$

From this distribution we may calculate the expectation value of p_{1x}^2

$$\begin{aligned}
\langle p_{1x}^2\rangle &= \int \mathrm{d}^3 p_1 p_{1x}^2 w(\mathbf{p}_1) && (5.10)\\
&= \left(\frac{\beta}{2\pi m}\right)^{1/2} \int \mathrm{d}p_{1x} p_{1x}^2 \exp(-\beta \frac{p_{1x}^2}{2m}) \left(\left(\frac{\beta}{2\pi m}\right)^{1/2} \int \mathrm{d}p_{1y} \exp(-\beta \frac{p_{1y}^2}{2m}) \right)^2 && (5.11)\\
&= \frac{m}{\beta} 1^2 = \frac{2mE}{3N}. && (5.12)
\end{aligned}$$

5.b Equation of state

In order to determine the pressure P we assume that the gas is enclosed in a box of length l and exerts a force K on the boundary area F at the end of the box. Then the pressure is given by

$$P = \frac{\langle K\rangle}{F}. \tag{5.13}$$

The momentum transfer during time t is given by the force as $\int K \mathrm{d}t = t\langle K\rangle$. If we consider one atom then its momentum transfer per collision is $2p_{1x}$ and the time t, after which the atom hits again the wall is $t = 2lm/p_{1x}$. Then one obtains for the pressure

$$P = N\langle\frac{2p_{1x}}{tF}\rangle = N\langle\frac{2p_{1x}p_{1x}}{2lmF}\rangle = \frac{N}{Vm}\langle p_{1x}^2\rangle = \frac{N}{V}\frac{1}{\beta}, \tag{5.14}$$

that is one obtains the equation of state

$$PV = N\frac{1}{\beta}. \tag{5.15}$$

Comparison with the well-known equation of state

$$PV = Nk_{\mathrm{B}}T \tag{5.16}$$

shows that the quantity β is related to the temperature T by

$$\frac{1}{\beta} = k_{\mathrm{B}}T, \tag{5.17}$$

where $k_{\mathrm{B}} = 1.380 \cdot 10^{-16}\mathrm{erg\ K}^{-1}$ is the Boltzmann constant. The equation of state is often given for one mole of a gas. One mole contains $N_{\mathrm{mol}} = 6.025 \cdot 10^{23}$ atoms (Loschmidt number). This yields the equation of state

$$PV = RT \tag{5.18}$$

with the gas constant $R = N_{\mathrm{mol}}k_{\mathrm{B}} = 8.316 \cdot 10^7\mathrm{erg\ K}^{-1}$. Finally we express the energy as a function of temperature using (5.8)

$$E = \frac{3N}{2\beta} = \frac{3}{2}Nk_{\mathrm{B}}T. \tag{5.19}$$

The Boltzmann constant is a conversion factor between temperature and energy.

6 Microcanonical ensemble (quantummechanical)

6.a Ensemble

As in the classical case the system have fixed volume V and fixed particle number N. The energy be within $E-\Delta$ and E. The ensemble consists of all states in this energy interval with equal probability

$$\rho = \rho_0 \sum_{n|_{E-\Delta<E_n\le E}} |n\rangle\langle n| = \rho_0(\Theta(E-H) - \Theta(E-\Delta-H)), \tag{6.1}$$

where the states $|n\rangle$ are eigenstates of the Hamiltonian $H|n\rangle = E_n|n\rangle$. The number of states with energies E_n up to E be

$$W_N(E) = \mathrm{tr}(\Theta(E-H)) = \sum_n \Theta(E-E_n). \tag{6.2}$$

One obtains from the normalization condition $\mathrm{tr}(\rho) = 1$

$$\rho_0 \underbrace{(W_N(E) - W_N(E-\Delta))}_{W} = 1 \tag{6.3}$$

the constant ρ_0

$$\rho_0 = \frac{1}{W}. \tag{6.4}$$

One introduces the entropy for the microcanonical ensemble by

$$W = \mathrm{e}^{S/k_\mathrm{B}}, \quad S = k_\mathrm{B} \ln W. \tag{6.5}$$

This is the relation between entropy and the number of possible states according to Boltzmann, or expressed by ρ_0

$$S = -k_\mathrm{B} \ln \rho_0. \tag{6.6}$$

6.b Example: Free atom in a cuboid

We consider one free particle ($N=1$) in a cuboid with lengths of edges L_1,L_2, and L_3, $0 \le x \le L_1$, $0 \le y \le L_2$, $0 \le z \le L_3$. We consider two boundary conditions:
Boundary condition 1 (RB1) The wave-function vanishes at the boundary (e.g. in an infinitely deep potential. Then the solutions can be written in the form

$$\psi(x,y,z) = \sqrt{\frac{8}{V}} \sin(k_1 x)\sin(k_2 y)\sin(k_3 z), \quad k_\alpha = \frac{\pi n_\alpha}{L_\alpha}, \quad n_\alpha = 1,2,3,... \tag{6.7}$$

Boundary condition 2 (RB2) We assume periodic boundary conditions

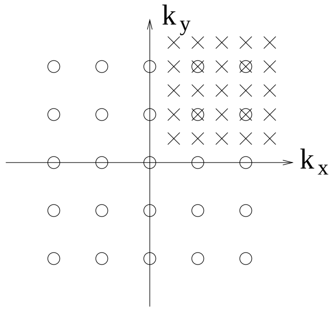
$$\psi(x,y,z) = \psi(x+L_1,y,z) = \psi(x,y+L_2,z) = \psi(x,y,z+L_3). \tag{6.8}$$

Then the solution can be written in the form

$$\psi(x,y,z) = \frac{1}{\sqrt{V}} \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}, \quad k_\alpha = \frac{2\pi n_\alpha}{L_\alpha}, \quad n_\alpha = 0,\pm1,\pm2,\pm3,... \tag{6.9}$$

Now we consider the density of states in k-space (momentum space)

Density of states in k-space. Crosses indicate the permitted k-vectors for boundary condition RB1, circles those for RB2.



We obtain for the two boundary conditions

$$
\begin{aligned}
& \text{(RB1)} && \text{(RB2)} && (6.10)\\
\mathrm{d}W &= \frac{L_1L_2L_3}{\pi^3}\mathrm{d}^3k && \mathrm{d}W = \frac{L_1L_2L_3}{(2\pi)^3}\mathrm{d}^3k && (6.11)\\
&= \frac{V}{\pi^3}\mathrm{d}^3k && = \frac{V}{(2\pi)^3}\mathrm{d}^3k && (6.12)\\
k_1 > 0, k_2 &> 0, k_3 > 0. && && (6.13)\\
\Delta n_\alpha &= \frac{L_\alpha}{\pi}\Delta k_\alpha && \Delta n_\alpha = \frac{L_\alpha}{2\pi}\Delta k_\alpha && (6.14)
\end{aligned}
$$

Then one obtains for the number $W(E)$ of states up to energy E

$$
\left.\begin{array}{ll}\text{(RB1)} & W = \frac{V}{\pi^3}\int \mathrm{d}^3k \\ \text{(RB2)} & W = \frac{V}{(2\pi)^3}\int \mathrm{d}^3k\end{array}\right\} = \frac{V}{(2\pi)^3}\frac{4\pi}{3}\left(\frac{2mE}{\hbar^2}\right)^{3/2} \qquad (6.15)
$$

For the boundary condition 1 the integral extends over one eighth of a sphere, for the boundary condition 2 over the whole sphere of radius $(2mE/\hbar^2)^{1/2}$. Boundary condition 1 yields standing waves. Contributions with components k_α include those with $-k_\alpha$, so that only $k_\alpha > 0$ has to be considered. Then the states lie doubly dense in all directions in **k**-space in comparison to periodic boundary conditions. In total one obtains the same number $W(E)$ of states. In most cases one works with periodic boundary conditions.

7 Comparison between quantum mechanical and classical behavior

7.a Normalization of Phase-space

For one free particle in a cuboid of volume V we obtained (for $W \gg 1$)

$$W_1^{\rm qu}(E) = \frac{4\pi}{3}\frac{V(2mE)^{3/2}}{h^3}, \quad \Phi_1^{\rm cl}(E) = \frac{4\pi}{3}V(2mE)^{3/2}, \tag{7.1}$$

that is the connection

$$W_1^{\rm qu}(E) = \frac{1}{h^3}\Phi_1^{\rm cl}(E). \tag{7.2}$$

In general there is not such a simple relation between $W_N^{\rm qu}$ and $\Phi_N^{\rm cl}$. There is however the question which relation holds between $W_N^{\rm qu}$ and $\Phi_N^{\rm cl}$, if one is in the limit in which a quantum mechanical system can be described within classical approximation. Is in such a case generally the phase space $\mathrm{d}^3p\,\mathrm{d}^3x$ to be divided by h^3, such that it becomes a dimensionless number?
We consider how dense a complete system of wave-functions is packed in phase space and perform the reflection for one space coordinate x and one momentum coordinate p. The generalzation to $3N$ pairs is obvious. For this purpose we divide x into intervals of length x_0; the nth interval be

$$nx_0 \le x \le (n+1)x_0, \quad n = 0, \pm 1, \pm 2, \pm 3, ... \tag{7.3}$$

A complete orthonormal basis of wave functions in this interval is given by

$$\psi_{n,m}(x) = \frac{1}{\sqrt{x_0}}\begin{cases} \mathrm{e}^{\mathrm{i}kx} & \text{in the interval} \\ 0 & \text{elsewhere} \end{cases} \tag{7.4}$$

with $kx_0 = 2\pi m$, m integer, that is

$$p = \hbar k = \frac{2\pi\hbar m}{x_0} = p_0 m, \quad p_0 = \frac{h}{x_0}. \tag{7.5}$$

One function requires the space $x_0 p_0 = h$ in (p, x) space. Thus one finds within the phase space Φ approximately Φ/h states. For $3N$ pairs (p, x) one expects $W_N^{\rm cl}(E) = \Phi_N(E)/h^{3N}$, where $W_N^{\rm cl}(E)$ is the number of quantum mechanical states in a quasiclassical approximation.

7.b Undistinguishability of particles

One and the same kind of quantum mechanical particles are undistinguishable. In phase space we distinguish

$$p_1 = p,\ p_2 = p' \text{ and } p_1 = p',\ p_2 = p. \tag{7.6}$$

The states in phase space which transform into each other under permutations are generally quantum mechanical undistinguishable. Thus one has to divide Φ_N by $N!$ in the semi-classical limit

$$W_N^{\rm cl}(E) = \frac{1}{h^{3N}N!}\Phi_N(E). \tag{7.7}$$

7.c Application to the ideal gas

We apply this result to the ideal gas

$$W_N^{\rm cl}(E) = \frac{1}{h^{3N}N!}\Phi_N(E) = \frac{V^N(2mE)^{3N/2}\pi^{3N/2}}{h^{3N}N!(\frac{3N}{2})!} = \frac{1}{\sqrt{6}\pi N}\left(\frac{V(2mE)^{3/2}\pi^{3/2}\mathrm{e}^{5/2}}{h^3N(\frac{3N}{2})^{3/2}}\right)^N \tag{7.8}$$

and introduce the volume v per atom, the energy ϵ per atom and the thermal de Broglie wave-length λ,

$$v = \frac{V}{N}, \quad \epsilon = \frac{E}{N}, \quad \lambda^2 = \frac{h^2}{\frac{4\pi}{3} m\epsilon} = \frac{h^2}{2\pi m k_{\mathrm{B}} T}. \tag{7.9}$$

The thermal de Broglie wave-length is the quantum mechanical wave-length of a particle of energy $\frac{2\pi}{3}\epsilon = \pi k_{\mathrm{B}} T$. Then W reads

$$W_N^{\mathrm{cl}}(E, V) = \frac{1}{\sqrt{6\pi N}} \left(\frac{v}{\lambda^3} \mathrm{e}^{5/2}\right)^N. \tag{7.10}$$

This is a good approximation for a quantum mechanical gas as long as $v\lambda^{-3}\mathrm{e}^{5/2} \gg 1$ holds, that is for a dilute hot gas. The entropy of this gas reads

$$S_N^{\mathrm{cl}}(E, V) = k_{\mathrm{B}} \ln W_N^{\mathrm{cl}}(E, V) = N k_{\mathrm{B}} \ln\left(\frac{v\mathrm{e}^{5/2}}{\lambda^3}\right) - k_{\mathrm{B}} \ln(\sqrt{6}\pi N), \tag{7.11}$$

where for large systems the last term is negligible in comparison to the predecessing one.

8 Systems in heat (thermal) contact

We consider two systems with particle numbers N_1, N_2 in volumes V_1, V_2 described by Hamiltonians H_1 and H_2, which interact via an interaction H_{12}. The total system is described by

$$H = H_1 + H_2 + H_{1,2}. \tag{8.1}$$

The interaction allows an exchange of energy between the two single systems. We assume however, that the contribution $H_{1,2}$ to the energy of the total system be negligible. The maximum energy of the total system be E and we ask for the number of eigenvalues $E_n \leq E$, and in classical systems for the normalized phase-space of the total system,

$$\text{quantum mechanical} \qquad W(E) = \mathrm{tr}\Theta(E-H) \tag{8.2}$$

$$\text{classical} \qquad W(E) = \frac{1}{N_1!N_2!h^{3N_1+3N_2}} \int \mathrm{d}^{3N_1+3N_2}p\, \mathrm{d}^{3N_1+3N_2}x\, \Theta(E-H). \tag{8.3}$$

We assume in the quasiclassical case, that we can distinguish between the N_1 particles in the volume V_1 and the N_2 particles inside volume V_2. Neglection of $H_{1,2}$ yields

$$\Theta(E-H) = \Theta(E-H_1-H_2) = \int \mathrm{d}E_1 \int \mathrm{d}E_2 \Theta(E-E_1-E_2)\delta(E_1-H_1)\delta(E_2-H_2). \tag{8.4}$$

We obtain in the quantum mechanical case

$$\mathrm{tr}\delta(E_1-H_1)\delta(E_2-H_2) = \mathrm{tr}_1\delta(E_1-H_1)\mathrm{tr}_2\delta(E_2-H_2) = \frac{\partial W_1(E_1)}{\partial E_1}\frac{\partial W_2(E_2)}{\partial E_2}. \tag{8.5}$$

Here tr_1 and tr_2 are the traces in the Hilbert spaces of the subsystems 1 and 2. The derivatives

$$\frac{\partial W_i(E_i)}{\partial E_i} = \omega_i(E_i) \tag{8.6}$$

are the densities of the (N_i-particle) states per energy. This yields

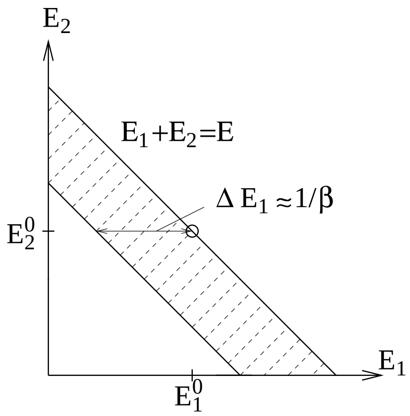
$$W(E) = \int \mathrm{d}E_1 \mathrm{d}E_2 \Theta(E-E_1-E_2)\omega_1(E_1)\omega_2(E_2). \tag{8.7}$$

The same expression is obtained in the classical case with

$$\omega_i(E_i) = \frac{1}{N_i!h^{3N_i}} \frac{\partial \Phi_{N_i}(E_i, V_i)}{\partial E_i}. \tag{8.8}$$

Thus the product $\omega_1(E_1)\omega_2(E_2)$ has to be integrated over all energies $E_1 + E_2 \leq E$. Since $W_i(E_i)$ increases rapidly as a function of energy, the same is true for $\omega_i(E_i)$. Thus one expects the maximum of the integrand $\omega_1\omega_2$ at a point, where the sum of both energies has reached its maximum, $E_1^0 + E_2^0 = E$.

The region of integration E_1, E_2. Integration is performed over $E_1 + E_2 \leq E$. The main contribution comes from the hatched region.



Then the maximum obeys

$$\frac{\partial}{\partial E_1^0}\left(\omega_1(E_1^0)\omega_2(E-E_1^0)\right)=0, \tag{8.9}$$

that is after division by $\omega_1\omega_2$

$$\frac{\partial \ln \omega_1(E_1^0)}{\partial E_1^0}=\frac{\partial \ln \omega_2(E_2^0)}{\partial E_2^0}=:\beta. \tag{8.10}$$

This is the equilibrium condition for two systems in thermal equilibrium.
Two such systems have the same temperature. We conclude, that β is a function of temperature independent of the system under consideration. For the ideal gas we have already found that $\beta = 1/(k_B T)$. If we choose as system 2 an ideal gas then we conclude that for an arbitrary system 1 we have $\beta = 1/(k_B T)$.
In order to estimate the integral for $W(E)$ we integrate $\partial \ln \omega_1/\partial E_1 = \beta$ and obtain

$$\omega_1(E_1)=\omega_1(E_1^0)\mathrm{e}^{\beta(E_1-E_1^0)} \tag{8.11}$$

for energies close to E_1^0. A second integration yields

$$W_1(E_1)=\frac{1}{\beta}\omega_1(E_1), \tag{8.12}$$

where no constant of integration has to be added, since $W_1(E_1) \ll W_1(E_1^0)$ for $\beta(E_1^0 - E_1) \gg 1$. Then we obtain for $W(E)$

$$W(E)\approx \omega_1(E_1^0)\omega_2(E_2^0)\frac{1}{\beta}\Delta E_1 = W_1(E_1^0)W_2(E_2^0)\beta\Delta E_1, \tag{8.13}$$

where $\Delta E_1/\beta$ is the area of the (E_1, E_2)-plane in which $\omega_1\omega_2$ is of the order of magnitude of the maximum of this function.
Large numbers and extremely large numbers The number of particles N and the entropy in units of the microscopic k_B are for macroscopic systems of the order of the Loschmidt number, thus large numbers of the order of 10^{23} or similarly. The number of quantum states of a macroscopic system is however a number of the order of 10 or e to the power of 10^{23}, thus a number which cannot be expressed by 23 or so digits but by 10^{23} digits. We call such numbers extremely large. The quantities W and ω which we have considered here have this property. Also the partition functions which we will consider later have this property. Similarly as here it will happen, that we have to multiply two quantities of this type and to integrate the product over a variable (here the energy). Then it is sufficient to look for its maximum and to take the corresponding value of the product. More precisely we had to multiply by the width over which the function decays (the ΔE_1 in (8.13)). Normally this factor is small in comparison to the product at its maximum. Since finally nearly always we have to take the logarithm of the integral we can neglect this width. Also this is the reason why we can neglect the last term in (7.11). Sometimes we will need the width in order to determine the fluctuations of the quantity over which we integrated. This can be determined in many cases from the second derivative of the logarithm.

9 Entropy as additive and extensive quantity

9.a Additivity

If a system consists of two systems with volumina V_1 and V_2 and particle numbers N_1 and N_2, then the volume V and the particle number N of the total system are

$$V = V_1 + V_2, \quad N = N_1 + N_2. \tag{9.1}$$

Therefore one calls volume and particle number additive quantities. Momentum, angular momentum, magnetic and electric moment have the same property. It holds for the energy of two non-interacting systems, too. If they interact, then the interaction energy has to be divided appropriately to the two subsystems.
Similarly the same property holds for two non-interacting (weakly interacting) systems, if the single systems are microcanonical systems. If the ensemble of system 1 contains W_1 states $|n\rangle$ and that of system 2 W_2 states $|m\rangle$, then the total system contains $W = W_1 W_2$ states $|n,m\rangle$. Thus the entropy is additive

$$S = k_\mathrm{B} \ln W = k_\mathrm{B} \ln W_1 + k_\mathrm{B} \ln W_2 = S_1 + S_2. \tag{9.2}$$

Note however, that the total ensemble is not microcanonical.
In the preceeding section we considered a macrocanonical system consisting of two subsystems in thermal contact. For this ensemble one obtains from $W = W_1 W_2 \beta \Delta E_1$

$$S = S_1 + S_2 + k_\mathrm{B} \ln(\beta \Delta E_1), \tag{9.3}$$

where S_1 and S_2 are the entropies of the subsystems at defined energies E_1^0 and E_2^0. Since now $S_1 + S_2$ is large for macroscopical systems (see ideal gas) in comparison to $k_\mathrm{B} \ln(\beta\Delta E_1)$, this last term can be neglected.

9.b Entropy as extensive quantity

If we halve the system into two subsystems $V_1 = V_2 = \frac{1}{2}V$, $N_1 = N_2 = \frac{1}{2}N$, then the maximum of $\omega_{N_1}(E_1)\omega_{N_2}(E - E_1 = E_2)$ will normally be found at $E_1^0 = E_2^0 = \frac{1}{2}E$. Then one obtains for the entropy

$$S(E,V,N) = 2S(\frac{E}{2}, \frac{V}{2} \frac{N}{2}). \tag{9.4}$$

The same consideration can be applied for ν equal systems in thermal equilibrium. Then similarly one has

$$S(E,V,N) = \nu S(\frac{E}{\nu}, \frac{V}{\nu}, \frac{N}{\nu}). \tag{9.5}$$

We now choose $\nu = N/N_0$ where N_0 is a fixed particle number large in comparison to one; then one obtains

$$S(E,V,N) = N\sigma(\frac{E}{N}, \frac{V}{N}), \quad \sigma(\frac{E}{N}, \frac{V}{N}) := \frac{1}{N_0} S(N_0 \frac{E}{N}, N_0 \frac{V}{N}, N_0). \tag{9.6}$$

Thus at fixed densities of energy and particles the entropy grows proportional to the number of particles. Such quantities are called extensive. In contrast one calls quantities which stay constant with increasing size of the system at constant quality of the system intensive. Such quantities are for example the densities of energy and particle number, but also temperature and pressure.
Remarks. For gases and fluids one has to allow for the exchange of particles besides energy exchange. This can be done similarly to the enrgy exchange (see section 12.) If the subsystems are small, then the terms $\beta\Delta E$ can become important, which then appear in the $(\nu - 1)$-th power. They can be taken into account without problems.
It is more difficult to estimate the contributions of the interactions $H_{1,2}$ at the boundary surfaces of the partial volumina. We do not consider this. If long-range interactions are present then the situation becomes particularly difficutl. There are proofs, that the entropy of a neutral system consisting of

positive nuclei and negative electrons (fermions!) with Coulomb-interaction is extensive. Compare Thirring, Vorlesungen über Mathematische Physik. Quantenmechanik großer Systeme und Lebowitz and Lieb, Adv. in Math. 9, 316 (1972). The entropy is not extensive in the case of gravitation (stars).

9.c Derivative of the entropy with respect to the energy

We derive a relation between β and the entropy for macroscopic systems. According to section 8 one has

$$\beta = \left.\frac{\partial \ln \omega(E)}{\partial E}\right|_{V,N}, \quad \omega(E) = \beta W(E). \tag{9.7}$$

From this one obtains with $W = \mathrm{e}^{S/k_\mathrm{B}}$

$$\left.\frac{\partial S(E,V,N)}{\partial E}\right|_{V,N} = k_\mathrm{B} \left.\frac{\partial \ln W}{\partial E}\right|_{V,N} = k_\mathrm{B} \left.\frac{\partial \ln \omega}{\partial E}\right|_{V,N} - k_\mathrm{B} \left.\frac{\partial \ln \beta}{\partial E}\right|_{V,N}. \tag{9.8}$$

The last term is of order $1/N$ and thus negligible for large systems. Then one obtains

$$\left.\frac{\partial S(E,V,N)}{\partial E}\right|_{V,N} = k_\mathrm{B}\beta = \frac{1}{T}. \tag{9.9}$$

For constant volume and particle number one obtains for the transition between equilibrium states $\mathrm{d}E = T\mathrm{d}S$, where the energy is transmitted by means of thermal contacts. Thus $T\mathrm{d}S$ is the amount of heat added to the system.

10 Canonical ensemble

10.a Canonical ensemble quantum mechanical

Again we consider two systems in thermal contact and ask for the statistical operator of system 1. One has

$$\rho = \rho_0 \Theta(E - H_1 - H_2) = \rho_0 \sum_{n,m} \Theta(E - E_n - E_m)|n,m\rangle\langle n,m|. \tag{10.1}$$

Here $|n\rangle$ are the energy eigenstates in the subsystem 1 and $|m\rangle$ are the states in the subsystem 2. We calculate the reduced densitiy matrix

$$\rho_1 = \mathrm{tr}_2\rho = \rho_0 \sum_n \left(\sum_m \Theta(E - E_n - E_m) \right) |n\rangle\langle n| = \rho_0 \sum_n W_2(E - E_n)|n\rangle\langle n|. \tag{10.2}$$

Now we have

$$\ln W_2(E - E_n) = \frac{1}{k_\mathrm{B}} S_2(E - E_n) = \frac{N_2}{k_\mathrm{B}} \sigma_2(\frac{E - E_n}{N_2}, \frac{V_2}{N_2}). \tag{10.3}$$

Here we use, that the entropy is extensive. (comp. section 9). We expand now in E_n

$$\ln W_2(E - E_n) = \frac{N_2}{k_\mathrm{B}} \sigma_2(\frac{E}{N_2}) - \frac{E_n}{k_\mathrm{B}} \frac{\partial \sigma_2}{\partial(E/N_2)} + \frac{E_n^2}{2k_\mathrm{B}N_2} \frac{\partial^2 \sigma_2}{\partial(E/N_2)^2} - ... \tag{10.4}$$

If we keep E/N, V_2/N_2 fixed and consider the limit of large N_2 then we are left with

$$\ln W_2(E - E_n) = \ln W_2(E) - \beta E_n, \tag{10.5}$$

where $\beta = 1/(k_\mathrm{B}T)$ is given by the temperature of the second system, since

$$\frac{\partial \sigma_2}{\partial(E/N_2)} = \frac{\partial S_2}{\partial E} = \frac{1}{T_2}. \tag{10.6}$$

Then one obtains

$$\rho_1 = \frac{1}{Z} \sum_n \mathrm{e}^{-\beta E_n} |n\rangle\langle n| = \frac{1}{Z} \mathrm{e}^{-\beta H_1}. \tag{10.7}$$

In a heat bath (system 2) which is large in comparison to system 1, the system 1 is an ensemble described by $\rho_1 \propto \mathrm{e}^{-\beta H_1}$. This ensemble is called canonical enmsemble. (Now we drop the index 1). The normalization factor

$$Z(\beta, V, N) = \mathrm{tr}\mathrm{e}^{-\beta H} = \sum_n \mathrm{e}^{-\beta E_n} = \int \mathrm{d}E \omega(E, V, N)\mathrm{e}^{-\beta E} \tag{10.8}$$

is called canonical partition function.

10.b Classical case

Corresponding considerations apply to the classical limit. There one obtains

$$\rho_1(p^{(1)}, x^{(1)}) = \int \mathrm{d}^{3N_2}p^{(2)}\mathrm{d}^{3N_2}x^{(2)}\rho_0\Theta(E - H_1 - H_2) = \rho_0 \Phi^{(2)}_{N_2}(E - H_1) = \rho_0 N_2! h^{3N_2} W^{(2)}(E - H_1) \tag{10.9}$$

and in the limit of a large system 2 (heat reservoir)

$$\rho_1(p^{(1)}, x^{(1)}) \propto \mathrm{e}^{-\beta H_1}. \tag{10.10}$$

If we define (we drop now the index 1) the partition function

$$Z = \frac{1}{h^{3N}N!} \int \mathrm{d}^{3N}p\mathrm{d}^{3N}x\mathrm{e}^{-\beta H}, \tag{10.11}$$

then one obtains

$$\rho(p,x) = \frac{1}{Z\,h^{3N}N!}\mathrm{e}^{-\beta H}. \tag{10.12}$$

For

$$H = \sum_i \frac{p_i^2}{2m} + H_{\mathrm{pot}}(x) \tag{10.13}$$

one can perform the p-integration which yields

$$Z = \frac{1}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{3N/2}\int \mathrm{d}^{3N}x \mathrm{e}^{-\beta H_{\mathrm{pot}}(x)} = \frac{1}{N!\lambda^{3N}}\int \mathrm{d}^{3N}x \mathrm{e}^{-\beta H_{\mathrm{pot}}(x)} \tag{10.14}$$

with the thermal de Broglie wave-length (section 7)

$$\lambda = \frac{h}{\sqrt{2\pi m k_{\mathrm{B}}T}}. \tag{10.15}$$

10.c Barometric pressure equation

We consider now a gas, whose atoms are in an external potential $V(\mathbf{x})$, which however, do not interact with each other.

$$H = \sum_i \left(\frac{p_i^2}{2m} + V(x_i)\right). \tag{10.16}$$

In an interaction-free system we have

$$\rho(\mathbf{p}_1,...\mathbf{p}_N,\mathbf{x}_1,...\mathbf{x}_N) = \prod_{i=1}^N \rho_1(\mathbf{p}_i,\mathbf{x}_i) \tag{10.17}$$

with

$$\rho_1(\mathbf{p},\mathbf{x}) = c\mathrm{e}^{-\beta p^2/(2m)-\beta V(x)}. \tag{10.18}$$

One obtains for the particle density $n(\mathbf{x})$ at point $\mathbf{x}$

$$n(\mathbf{x}) = \sum_i \langle \delta^3(\mathbf{x}-\mathbf{x}_i)\rangle = N\int \mathrm{d}^3p\rho_1(\mathbf{p},\mathbf{x}) = n_0\mathrm{e}^{-\beta V(x)} \tag{10.19}$$

with

$$n_0 = \frac{N}{\int \mathrm{d}^3x \mathrm{e}^{-\beta V(x)}} \tag{10.20}$$

The barometric pressure formula (10.19) can also be derived from mechanical equilibrium. Let us denote the pressure at $\mathbf{x}$ by $P(\mathbf{x})$. The force acting on a particle is $-\operatorname{grad} V(\mathbf{x})$. Thus the average force density is given by $\mathbf{k}(\mathbf{x}) = -n(\mathbf{x})\operatorname{grad} V(\mathbf{x})$. It must coincide with the gradient of the pressure

$$\operatorname{grad} P(\mathbf{x}) = -n(\mathbf{x})\operatorname{grad} V(\mathbf{x}). \tag{10.21}$$

On the other hand one has the equation of state $P(\mathbf{x}) = n(\mathbf{x})k_{\mathrm{B}}T$. Using this expression one obtains

$$\begin{aligned} k_{\mathrm{B}}T\operatorname{grad} n(\mathbf{x}) &= -n(\mathbf{x})\operatorname{grad} V(\mathbf{x}), && (10.22)\\ k_{\mathrm{B}}T\operatorname{grad} \ln n(\mathbf{x}) &= -\operatorname{grad} V(\mathbf{x}), && (10.23)\\ n(\mathbf{x}) &= n_0\mathrm{e}^{-\beta V(\mathbf{x})}. && (10.24) \end{aligned}$$

11 Equipartition theorem and virial theorem

11.a Equipartition theorem

We derive the equipartition theorem for classical systems, where we start with the canonical ensemble ($\rho \propto \mathrm{e}^{-\beta H}$). For this purpose we consider

$$\int \mathrm{d}^{3N}p\mathrm{d}^{3N}x \frac{\partial}{\partial p_{i\alpha}}(A(\mathbf{p},\mathbf{x})\rho(\mathbf{p},\mathbf{x})) = \int \mathrm{d}^{3N}p\mathrm{d}^{3N}x \left(\frac{\partial A}{\partial p_{i\alpha}} - \beta A\frac{\partial H}{\partial p_{i\alpha}}\right)\rho = \langle\frac{\partial A}{\partial p_{i\alpha}}\rangle - \beta\langle A\frac{\partial H}{\partial p_{i\alpha}}\rangle = 0. \tag{11.1}$$

The integral vanishes, if $A\rho$ decays sufficiently rapidly as function of $p_{i\alpha}$, since then the integral over $p_{i\alpha}$ vanishes

$$\langle A\frac{\partial H}{\partial p_{i\alpha}}\rangle = k_{\mathrm{B}}T\langle\frac{\partial A}{\partial p_{i\alpha}}\rangle. \tag{11.2}$$

Similarly one shows

$$\langle A\frac{\partial H}{\partial x_{i\alpha}}\rangle = k_{\mathrm{B}}T\langle\frac{\partial A}{\partial x_{i\alpha}}\rangle. \tag{11.3}$$

This yields for example

$$\langle p_{i\alpha}\frac{\partial H}{\partial p_{i\alpha}}\rangle = k_{\mathrm{B}}T, \tag{11.4}$$

$$\langle x_{i\alpha}\frac{\partial H}{\partial x_{i\alpha}}\rangle = k_{\mathrm{B}}T. \tag{11.5}$$

The second relation holds only if the potential experienced by the mass point increases suffiently rapidly. For

$$H = \sum_i \frac{p_i^2}{2m_i} + H_{\mathrm{pot}}(\mathbf{x}) \tag{11.6}$$

one obtains

$$\langle\frac{p_{i\alpha}^2}{m_i}\rangle = k_{\mathrm{B}}T, \tag{11.7}$$

$$\langle x_{i\alpha}\frac{\partial H_{\mathrm{pot}}}{\partial x_{i\alpha}}\rangle = k_{\mathrm{B}}T. \tag{11.8}$$

One obtains for the harmonic oscillator $H_{\mathrm{pot}} = \frac{f}{2}x_\alpha^2$

$$\langle\frac{f}{2}x_\alpha^2\rangle = \frac{1}{2}k_{\mathrm{B}}T. \tag{11.9}$$

A harmonic solid, more precisely for a solid whose atoms are elongated in the average so weakly that it is sufficient to expand the potential up to second order in the elongation $\mathbf{x}$,

$$H_{\mathrm{pot}} = \frac{1}{2}\sum f_{i\alpha,j\beta}x_{i\alpha}x_{j\beta} \tag{11.10}$$

(and which on the other hand is so strongly excited that its quantum mechanical behavior can be neglected) obeys

$$\sum_{i\alpha}\langle x_{i\alpha}\frac{\partial H}{\partial x_{i\alpha}}\rangle = 2\langle H_{\mathrm{pot}}\rangle = 3Nk_{\mathrm{B}}T, \tag{11.11}$$

$$\sum_{i\alpha}\langle p_{i\alpha}\frac{\partial H}{\partial p_{i\alpha}}\rangle = 2\langle H_{\mathrm{kin}}\rangle = 3Nk_{\mathrm{B}}T. \tag{11.12}$$

From these relations one obtains the law of Dulong and Petit

$$\langle H\rangle = 3Nk_{\mathrm{B}}T. \tag{11.13}$$

For real solids there are deviations from this law; at low temperatures the degrees of freedom are frozen in (quantum effects), at high temperatures anharmonicities of the interaction become important.

11.b Virial theorem classical

The potential energy of a gas or a liquid which is confined in a vessel is composed of the interaction energies w between the atoms or molecules and the interaction W_a with the wall,

$$H_\mathrm{pot} = H_\mathrm{int} + H_\mathrm{w}, \quad H_\mathrm{w} = \sum_i W_\mathrm{a}(\mathbf{x}_i), \quad H_\mathrm{int} = \frac{1}{2}\sum_{ij} w(\mathbf{x}_i - \mathbf{x}_j). \tag{11.14}$$

We transform now the sum

$$\begin{aligned}
\sum_{i\alpha} x_{i\alpha}\frac{\partial H_\mathrm{int}}{\partial x_{i\alpha}} &= \frac{1}{2}\sum_{i\alpha,j,k} x_{i\alpha}\frac{\partial w(\mathbf{x}_j - \mathbf{x}_k)}{\partial x_{i\alpha}} \\
&= \frac{1}{2}\sum_{i\alpha,j,k\beta} x_{i\alpha}\frac{\partial w(\mathbf{x}_j - \mathbf{x}_k)}{\partial(x_{j\beta} - x_{k\beta})}\frac{\partial(x_{j\beta} - x_{k\beta})}{\partial x_{i\alpha}} \\
&= \frac{1}{2}\sum_{i\alpha,j,k\beta} x_{i\alpha}\frac{\partial w(\mathbf{x}_j - \mathbf{x}_k)}{\partial(x_{j\beta} - x_{k\beta})}(\delta_{ij} - \delta_{ik})\delta_{\alpha\beta} \\
&= \frac{1}{2}\sum_{j,k}(\mathbf{x}_j - \mathbf{x}_k)\frac{\partial w(\mathbf{x}_j - \mathbf{x}_k)}{\partial(\mathbf{x}_j - \mathbf{x}_k)}.
\end{aligned} \tag{11.15}$$

On the other hand we have

$$\sum_i \langle \mathbf{x}_i \frac{\partial W_\mathrm{a}}{\partial \mathbf{x}_i}\rangle = \int \mathbf{x}\cdot\mathbf{k}\mathrm{d}^3x = \int \mathbf{x}\cdot P\mathbf{d}f = P\int \operatorname{div}\mathbf{x}\mathrm{d}^3x = 3PV. \tag{11.16}$$

Here $\mathbf{k}$ is the force density (force per volume) acting on the wall. Obviously its range is given by the range of W_a. We have used Gauss' theorem and $\operatorname{div}\mathbf{x} = 3$. From (11.11), (11.15), and (11.16) one obtains the virial theorem

$$PV = Nk_\mathrm{B}T - \frac{1}{6}\sum_{ij}\langle \mathbf{x}_{ij}\frac{\partial w}{\partial \mathbf{x}_{ij}}\rangle. \tag{11.17}$$

11.c Virial theorem quantum mechanical

It is not possible to derive an equipartition theorem for quantum mechanical systems as for classical systems. Indeed a commutator of $x_{j\alpha}$ with $A\rho$ is basically the same as a derivative of $A\rho$ with respect to $p_{j\alpha}$. But since the commutator of H with $x_{j\alpha}$ in generally does not commute with H, it is not possible to express the commutator of $x_{j\alpha}$ with $\rho \propto \mathrm{e}^{-\beta H}$ in a simple way.
Instead we consider the commutator of H with $A\rho$, where A is an operator to be choosen. Then one obtains

$$\mathrm{tr}([H, A\rho]) = 0 = \mathrm{tr}([H, A]\rho), \tag{11.18}$$

since $[H,\rho] = 0$. Thus one has

$$\langle [H, A]\rangle = 0. \tag{11.19}$$

With $A = \sum_j \mathbf{x}_j\cdot\mathbf{p}_j$ and the Hamiltonian (11.6) one obtains

$$[H, A] = \sum_{ji\alpha}[\frac{p_{i\alpha}^2}{2m_i}, \mathbf{x}_j]\cdot\mathbf{p}_j + \sum_j \mathbf{x}_j\cdot[H_\mathrm{pot}(\mathbf{x}), \mathbf{p}_j] = \frac{\hbar}{\mathrm{i}}\sum_{j\alpha}\frac{p_{j\alpha}^2}{m_j} + \mathrm{i}\hbar\sum_i \mathbf{x}_i\cdot\frac{\partial H_\mathrm{pot}(\mathbf{x})}{\partial \mathbf{x}_i}. \tag{11.20}$$

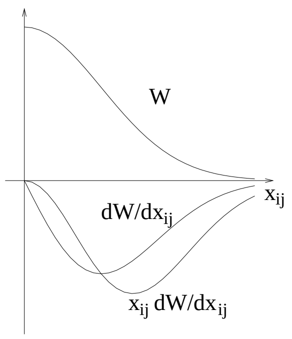
This yields

$$\sum_{i\alpha}\langle x_{i\alpha}\frac{\partial H_\mathrm{pot}}{\partial x_{i\alpha}}\rangle = 2\langle H_\mathrm{kin}\rangle. \tag{11.21}$$

Using (11.15), (11.21) one obtains

$$PV = \frac{2}{3}\langle H_\mathrm{kin}\rangle - \frac{1}{6}\sum_{ij}\langle \mathbf{x}_{ij}\frac{\partial w}{\partial \mathbf{x}_{ij}}\rangle. \tag{11.22}$$

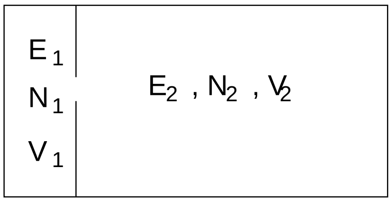
Example: W, $\partial W/\partial x$ and $x\partial W/\partial x$ for a repulsive potential.



12 Systems with exchange of particles: Grandcanonical Ensemble

We divide a microcanonical system into two subsystems with volumes V_1 and V_2. There can be an exchange of both energy and particles between these two subsystems; only an upper limit E for the total energy and a total number N of particles is fixed.

Two subsystems



$$E_1 + E_2 \leq E, \quad N_1 + N_2 = N. \tag{12.1}$$

We treat the subsystems similarly as in the case of heat exchange. The statistical operator of the total system is

$$\rho = \rho_0 \Theta(E - H_1 - H_2)\delta_{N,\hat{N}_1+\hat{N}_2} = \rho_0 \sum_{n,m} \Theta(E - E_n^{(1)} - E_m^{(2)})\delta_{N,N_n^{(1)}+N_m^{(2)}} |n,m\rangle\langle n,m|, \tag{12.2}$$

where $|n,m\rangle$ are the eigenstates of the Hamiltonians and the operators of the particle numbers

$$H_1|n,m\rangle = E_n^{(1)}|n,m\rangle, \quad H_2|n,m\rangle = E_m^{(2)}|n,m\rangle, \quad \hat{N}_1|n,m\rangle = N_n^{(1)}|n,m\rangle, \quad \hat{N}_2|n,m\rangle = N_m^{(2)}|n,m\rangle. \tag{12.3}$$

If we perform the trace over subsystem 2, then there remains the reduced density operator for system 1

$$\rho_1 = \mathrm{tr}_2 \rho = \rho_0 \sum_n W^{(2)}(E - E_n^{(1)}, N - N_n^{(1)}, V_2)|n\rangle\langle n|. \tag{12.4}$$

We now transform the logarithm of $W^{(2)}$ similarly as we did before, where we use that the entropy is extensive (9.6),

$$\ln W^{(2)}(E,N,V_2) = \frac{1}{k_\mathrm{B}} S^{(2)}(E,N,V_2) = \frac{1}{k_\mathrm{B}} V_2 \frac{N}{V_2} \sigma(\frac{E/V_2}{N/V_2}, \frac{1}{N/V_2}) = \frac{1}{k_\mathrm{B}} V_2 \tilde{\sigma}(\frac{E}{V_2}, \frac{N}{V_2}). \tag{12.5}$$

Then we may write

$$\ln W^{(2)}(E - E_n^{(1)}, N - N_n^{(1)}, V_2) = \frac{1}{k_\mathrm{B}} V_2 \tilde{\sigma}(\frac{E}{V_2} - \frac{E_n^{(1)}}{V_2}, \frac{N}{V_2} - \frac{N_n^{(1)}}{V_2}). \tag{12.6}$$

Now we keep E/V_2 and N/V_2 constant and let V_2 become very large. Then we obtain

$$\ln W^{(2)}(E - E_n^{(1)}, N - N_n^{(1)}, V_2) = \ln W^{(2)}(E,N,V_2) - E_n^{(1)} \underbrace{\frac{1}{k_\mathrm{B}} \frac{\partial S^{(2)}}{\partial E}}_{\beta} - N_n^{(1)} \underbrace{\frac{1}{k_\mathrm{B}} \frac{\partial S^{(2)}}{\partial N}}_{\alpha} + O(\frac{1}{V_2}), \tag{12.7}$$

from which we conclude in the limit $V_2 \to \infty$

$$\rho_1 = \frac{1}{Y} \sum_n \mathrm{e}^{-\beta E_n^{(1)} - \alpha N_n^{(1)}} |n\rangle\langle n|. \tag{12.8}$$

This ensemble is called grandcanonical ensemble. It contains states of arbitrary particle number $N_n^{(1)}$. Only the two quantities α and β of the reservoir system 2 have an effect on system 1.
For two systems with particle exchange one has similarly as for energy exchange

$$\frac{\partial \ln W^{(1)}}{\partial N^{(1)}} = \frac{\partial \ln W^{(2)}}{\partial N^{(2)}} = \alpha, \tag{12.9}$$

since $W^{(1)}(N^{(1)})W^{(2)}(N^{(2)} = N - N^{(1)})$ has to assume a maximum as function of $N^{(1)}$. Usually one writes $\alpha = -\beta\mu$ and calls μ the chemical potential. In equilibrium one has for heat and particle exchange

$$\beta_1 = \beta_2, \quad \mu_1 = \mu_2. \tag{12.10}$$

As we see for system 2, eq. (12.7) one has

$$\mathrm{d}\ln W = \frac{1}{k_\mathrm{B}}\mathrm{d}S = \beta\mathrm{d}E - \beta\mu\mathrm{d}N \tag{12.11}$$

and due to (9.9, 12.9) this holds similarly for system 1. Thus we obtain

$$\mathrm{d}E = T\mathrm{d}S + \mu\mathrm{d}N \tag{12.12}$$

for fixed volume V.
We may now write the density operator ρ of the grandcanonical ensemble

$$\rho = \frac{1}{Y}\sum_n \mathrm{e}^{-\beta(E_n - \mu N_n)}|n\rangle\langle n| = \frac{1}{Y}\mathrm{e}^{-\beta(H - \mu\hat{N})}. \tag{12.13}$$

The normalization factor Y is the grandcanonical partition function

$$Y(\mu,\beta,V) = \sum_n \mathrm{e}^{-\beta(E_n - \mu N_n)} = \mathrm{tr}\mathrm{e}^{-\beta(H-\mu\hat{N})} = \sum_N Z(N,\beta,V)\mathrm{e}^{\beta\mu N}. \tag{12.14}$$

We have now in the exponent

$$H - \mu\hat{N} = \sum_i \frac{p_i^2}{2m_i} + \sum_i (V_1(r_i) - \mu) + \frac{1}{2}\sum_{i,j} V_2(r_i - r_j). \tag{12.15}$$

As soon as the particle number is variable there is no more an arbitrary additive constant to the one-particle potential V_1. It is now determined by the chemical potential μ. Furthermore we observe in (12.13) that a larger μ favors a larger number of particles. Thus N increases with μ.

13 Pressure and enthalpy

Until now we considered systems in fixed volumina V. Instead we may close the system with a piston, which exerts a pressure P. The area of the piston be F. The pressure can be realized by a mass $m = PF/g$. Then the potential energy of the piston is

$$mgz = PFz = PV. \tag{13.1}$$

The total of the internal energy E of the system and the potential energy of the piston is called enthalpy

$$I = E + PV. \tag{13.2}$$

In a microcanonical ensemble one obtains (classically, similarly for the quantum mechanical case)

$$\tilde{W}_N(I,P) = \frac{1}{h^{3N}N!a}\int \mathrm{d}^{3N}x\mathrm{d}^{3N}p\mathrm{d}z\Theta(I - H(\mathbf{p},\mathbf{x}) - PV(z)), \tag{13.3}$$

where a is a microscopic length, so that $\tilde{W}$ becomes dimensionless. More precisely the kinetic energy of the piston had to be considered, too. Together with the corresponding momentum integration one has to write h instead of a. After the momentum integration one finds, that a is the thermal de-Broglie wavelength of the piston. In practice this factor in front is not important. Now we perform the $\mathbf{x}$ and the $\mathbf{p}$ integrations,

$$\tilde{W}_N(I,P) = \frac{1}{a}\int \mathrm{d}z W_N(I - PV(z), V(Z)). \tag{13.4}$$

We evaluate the integral by looking for the maximum of the integrand

$$\tilde{W}_N(I,P) \approx \max_V W_N(I - PV, V) = W_N(E,V) = \mathrm{e}^{S/k_\mathrm{B}}. \tag{13.5}$$

The equation which determines V reads

$$\frac{\partial W_N(I-PV,V)}{\partial V} = -P\frac{\partial W_N}{\partial E} + \frac{\partial W_N}{\partial V} = \left(-\frac{P}{k_\mathrm{B}}\frac{\partial S}{\partial E} + \frac{1}{k_\mathrm{B}}\frac{\partial S}{\partial V}\right)\mathrm{e}^{S/k_\mathrm{B}}, \tag{13.6}$$

thus we obtain

$$\left.\frac{\partial S}{\partial V}\right|_{N,E} = P\left.\frac{\partial S}{\partial E}\right|_{N,V} = \frac{P}{T}. \tag{13.7}$$

14 First law of thermodynamics: Energy conservation

14.a Energy Balance

The first law of thermodynamics deals with the conservation of energy. Its validity follows from the theorem of the conservation of energy in mechanics, electrodynamics and quantum mechanics, generally from the translational invariance of the laws of nature with respect to time; thus it need not to be proven here. Originally it was not clear that heat is a form of energy, too, so that one had different units for mechanical and thermal energy (calories). Here we are left with considering various forms of energy changes. We had derived (12.12), (13.7)

$$\left.\frac{\partial S(E,V,N)}{\partial E}\right|_{V,N} = \frac{1}{T}, \quad \left.\frac{\partial S}{\partial N}\right|_{E,V} = -\frac{\mu}{T}, \quad \left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{P}{T}. \tag{14.1}$$

Thus we have

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}E - \frac{\mu}{T}\mathrm{d}N + \frac{P}{T}\mathrm{d}V \tag{14.2}$$

or solved with respect to $\mathrm{d}E$

$$\mathrm{d}E = T\mathrm{d}S + \mu\mathrm{d}N - P\mathrm{d}V. \tag{14.3}$$

Two contributions have a simple meaning: a) If we keep volume and particle number fixed then energy can only be fed in or removed in the form of heat. Denoting the amount of added heat by δQ we find

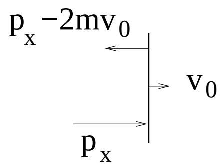
$$\delta Q = T\mathrm{d}S. \tag{14.4}$$

The amount of heat Q is not a state variable; therefore here we do not write $\mathrm{d}Q$, but δQ. If the system is thermally isolated so that it cannot absorb or loose heat and if we carry out mechanical work at the system by compression then the mechanical work delivered is

$$\delta A = -P\mathrm{d}V \tag{14.5}$$

for a slow movement of the piston. Since this is the energy added to the system it follows that the entropy is conserved under this process (adiabatic invariance, conservation of phase-space volume). However, the process has to be performed slowly, so that the system is always in equilibrium. Otherwise the expression for $\mathrm{d}E$ is no longer valid. For a rapid movement of the piston one has $\delta A \neq -P\mathrm{d}V$, since the gas molecules do not trnsfer the momentum $2p_x$ but $2(p_x - mv_x)$ to the piston.

Reflection of a gas molecule at the piston



Finally there is a third contribution

$$\delta_N E = \mu\mathrm{d}N \tag{14.6}$$

by adding $\mathrm{d}N$ particles without any change of entropy and volume. This process is not conspicuous. Instead we derive a relation for μ by adding to the system $\mathrm{d}N$ particles in a volume $\mathrm{d}V$ with energy $\mathrm{d}E$ of same quality, that is at the same temperature, pressure and chemical potential,

$$\mathrm{d}V = \frac{\mathrm{d}N}{N}V, \quad \mathrm{d}E = \frac{\mathrm{d}N}{N}E. \tag{14.7}$$

Since the entropy is extensive one obtains

$$\mathrm{d}S = \frac{\mathrm{d}N}{N}S \tag{14.8}$$

and therefore

$$\mathrm{d}E = \frac{\mathrm{d}N}{N}E = T\mathrm{d}S + \mu\mathrm{d}N - P\mathrm{d}V = \frac{\mathrm{d}N}{N}(TS + \mu N - PV), \tag{14.9}$$

that is we obtain the relation

$$E = TS + \mu N - PV \tag{14.10}$$

and thus for μ

$$\mu = \frac{E - TS + PV}{N}. \tag{14.11}$$

Taking the total derivative of (14.10)

$$\mathrm{d}E = T\mathrm{d}S + S\mathrm{d}T + \mu\mathrm{d}N + N\mathrm{d}\mu - P\mathrm{d}V - V\mathrm{d}P \tag{14.12}$$

we obtain with (14.3)

$$S\mathrm{d}T + N\mathrm{d}\mu - V\mathrm{d}P = 0. \tag{14.13}$$

This relation is called Gibbs-Duhem relation.

14.b Enthalpy

Similarly as for the energy we can derive the differential for the enthalpy. From

$$I = E + PV, \quad \mathrm{d}E = T\mathrm{d}S + \mu\mathrm{d}N - P\mathrm{d}V \tag{14.14}$$

one obtains

$$\mathrm{d}I = \mathrm{d}E + P\mathrm{d}V + V\mathrm{d}P = T\mathrm{d}S + \mu\mathrm{d}N + V\mathrm{d}P. \tag{14.15}$$

We obtained I by a Legendre transformation from E by replacing the natural variable V by P.

$$\begin{array}{ccc} E & \text{natural variable} & S, N, V \\ I & & S, N, P \end{array} \tag{14.16}$$

For the ideal classical gas we may express the entropy by I, N, P. We use

$$I = E + PV = E + Nk_{\mathrm{B}}T = \frac{5}{3}E, \quad E = \frac{3}{5}I, \quad PV = \frac{2}{3}E = \frac{2}{5}I, \quad V = \frac{2I}{5P}. \tag{14.17}$$

from which

$$\begin{aligned} S &= k_{\mathrm{B}}N \ln\left(\frac{VE^{3/2}}{N^{5/2}}\left(\frac{4\pi m}{3h^2}\right)^{3/2} \mathrm{e}^{5/2}\right) && (14.18) \\ &= k_{\mathrm{B}}N \ln\left(\frac{I^{5/2}}{PN^{5/2}}\left(\frac{4\pi m}{5h^2}\right)^{3/2} \frac{2}{5}\mathrm{e}^{5/2}\right) && (14.19) \end{aligned}$$

is obtained. If one solves these two relations with respect to E and I, resp., then one obtains these quantities as functions of their natural variables.

15 Partition functions and Potentials

15.a Canonical partition function and free energy

The canonical partition function

$$Z(\beta, N, V) = \mathrm{tr}\mathrm{e}^{-\beta H} = \int \mathrm{d}E\omega(E, N, V)\mathrm{e}^{-\beta E} \tag{15.1}$$

may be approximated by the maximum of the integrand with respect to E

$$Z \approx \max_E(\omega(E, N, V)\mathrm{e}^{-\beta E}) \approx \max_E(W(E, N, V)\mathrm{e}^{-\beta E}), \tag{15.2}$$

where E is determined by

$$\frac{\partial}{\partial E}(W\mathrm{e}^{-\beta E}) = 0. \tag{15.3}$$

Because of $\frac{\partial W}{\partial E} = \beta(E)W$ one obtains

$$\beta(E) - \beta = 0. \tag{15.4}$$

Here $\beta(E)$ is the logarithmic derivative of W (inverse temperature of the system), whereas β in Z is introduced as a parameter (inverse temperature of the reservoir). One calls

$$F(T, N, V) = -k_\mathrm{B}T \ln Z(T, N, V) \tag{15.5}$$

the free energy (Helmholtz free energy). Obviously

$$F = -k_\mathrm{B}T \ln(W\mathrm{e}^{-\beta E}) = -k_\mathrm{B}T \ln W + E = E - TS, \tag{15.6}$$

holds, that is $F = E - TS = \mu N - PV$. From $\mathrm{d}E = T\mathrm{d}S + \mu\mathrm{d}N - P\mathrm{d}V$ one obtains

$$\mathrm{d}F(T, N, V) = -S\mathrm{d}T + \mu\mathrm{d}N - P\mathrm{d}V. \tag{15.7}$$

Starting from the definition of Z we consider the derivative $\partial Z/\partial\beta$. From $Z = \sum_n \mathrm{e}^{-\beta E_n}$ one obtains

$$\frac{\partial Z}{\partial \beta} = -\sum_n E_n \mathrm{e}^{-\beta E_n} = -Z\langle H\rangle, \tag{15.8}$$

thus

$$\frac{\partial \ln Z}{\partial \beta} = -\langle H\rangle = -E, \tag{15.9}$$

that is

$$\left.\frac{\partial \ln Z}{\partial T}\right|_{N,V} = \frac{E}{k_\mathrm{B}T^2} = \frac{\partial(-F/k_\mathrm{B}T)}{\partial T}, \tag{15.10}$$

thus

$$E = -k_\mathrm{B}T^2 \frac{\partial(F(T, N, V)/k_\mathrm{B}T)}{\partial T}. \tag{15.11}$$

15.b Canonical partition function and free enthalpy

Analogously to $Z(\beta, V, N)$ we consider $\tilde{Z}(\beta, N, P)$ for a system in thermal contact under pressure P,

$$\tilde{Z}(\beta, N, P) = \frac{1}{a}\int \mathrm{d}z Z(\beta, N, V(z))\mathrm{e}^{-\beta PV(z)}. \tag{15.12}$$

We approximate the integral by the maximum of of the integrand

$$\tilde{Z} \approx \max_V(Z\mathrm{e}^{-\beta PV}) = \max_V(\mathrm{e}^{-\beta F - \beta PV}) \tag{15.13}$$

with V determined by

$$\frac{\partial}{\partial V}(-\beta F - \beta PV)\bigg|_{\beta,N} = \beta(P(V) - P) = 0, \tag{15.14}$$

where $P(V)$ is the pressure of the system, and P the external pressure. We introduce now the free enthalpy (Gibbs' free energy)

$$G = -k_{\mathrm{B}}T \ln \tilde{Z}, \tag{15.15}$$

One obtains for it

$$G = F + PV = I - TS = E - TS + PV = \mu N. \tag{15.16}$$

The relation $G = \mu N$ is called Gibbs-Duhem relation, too. Further one has

$$\mathrm{d}G = -S\mathrm{d}T + \mu \mathrm{d}N + V\mathrm{d}P. \tag{15.17}$$

Taking the derivative of

$$\tilde{Z} = \mathrm{tr}\mathrm{e}^{-\beta(H + P\hat{V})} \tag{15.18}$$

with respect to β and P, one finds that

$$\frac{\partial \ln \tilde{Z}}{\partial \beta}\bigg|_{P,N} = -\langle H + P\hat{V}\rangle = -E - PV = -I \tag{15.19}$$

and

$$\frac{\partial \ln \tilde{Z}}{\partial P}\bigg|_{\beta,N} = -\beta\langle \hat{V}\rangle = -\beta V \tag{15.20}$$

holds.

15.c Grandcanonical partition function and grandcanonical potential

Finally we consider the grandcanonical partition function

$$Y(\beta, \mu, V) = \mathrm{tr}\mathrm{e}^{-\beta(H - \mu\hat{N})} = \sum_N Z(\beta, N, V)\mathrm{e}^{\beta\mu N}. \tag{15.21}$$

If we approximate also here Y by the largest term in the sum, then one obtains

$$Y = \max_N (Z\mathrm{e}^{\beta\mu N}) = \max_N \mathrm{e}^{-\beta F + \beta\mu N} \tag{15.22}$$

with

$$\frac{\partial}{\partial N}(-F + \mu N) = 0. \tag{15.23}$$

To this partition function belongs the grandcanonical potential

$$J = -k_{\mathrm{B}}T \ln Y(\beta, \mu, V). \tag{15.24}$$

One concludes

$$J = F - \mu N = E - TS - \mu N = -PV, \quad \mathrm{d}J = -S\mathrm{d}T - N\mathrm{d}\mu - P\mathrm{d}V. \tag{15.25}$$

15.d Summary of the Potentials

Finally we give a summary of the ensembles and the potentials. Out of each of the three pairs (T, S), (μ, N), and (P, V) we may choose one variable as natural variable. The other ones are obtained as partial derivatives of these variables. However, at least one of the three variables has to be extensive. Thus the combination of the three natural variables T, μ, P is not possible. If one tries to perform the corresponding Legendre-transformation, then one obtains "zero". Indeed any of the three quantities T, μ, P is always determined by the two other ones, whereas the size of the system remains undetermined. The entropy is the natural variable for the first four ensembles. The ensemble is of the form $\Theta(... - H)$, the trace of it (quantum mechanically) is the number W of states, the logarithm thereof is the entropy divided by the Boltzmann constant. However, two of these ensembles are not in use. Temperature is a natural variable of the second four ensembles. They are of the form $\exp(-\beta(H \pm ...))$. Their trace is the partition function, the logarithm thereof multiplied by $-k_{\rm B}T$ the corresponding potential. The various potentials can be obtained by Legendre transformations from one another. The various numbers of quntummechanical states W which are determined for the first four ensembles of the summary and the partition functions of the other ensembles are obtained by appropriate integration or summation from the W of the microcanonical ensemble.

Übersicht über die Potentiale

Summary of the Potentials

Energie Energy	E	$= E$	$= TS + \mu N - PV$	$\mathrm{d}E = T\mathrm{d}S + \mu \mathrm{d}N - P\mathrm{d}V$	$\Theta(E - H)$
Enthalpie Enthalpy	I	$= E + PV$	$= TS + \mu N$	$\mathrm{d}I = T\mathrm{d}S + \mu \mathrm{d}N + V\mathrm{d}P$	$\Theta(I - H - P\hat{V})$
	B	$= E - \mu N$	$= TS - PV$	$\mathrm{d}B = T\mathrm{d}S - N\mathrm{d}\mu - P\mathrm{d}V$	$\Theta(B - H + \mu\hat{N})$
	C	$= E - \mu N + PV$	$= TS$	$\mathrm{d}C = T\mathrm{d}S - N\mathrm{d}\mu + V\mathrm{d}P$	$\Theta(C - H + \mu\hat{N} - P\hat{V})$
Freie Energie Helmholtz free energy	F	$= E - TS$	$= \mu N - PV$	$\mathrm{d}F = -S\mathrm{d}T + \mu \mathrm{d}N - P\mathrm{d}V$	$\exp(-\beta H)$
Freie Enthalpie Gibbs free energy	G	$= E - TS + PV$	$= \mu N$	$\mathrm{d}G = -S\mathrm{d}T + \mu \mathrm{d}N + V\mathrm{d}P$	$\exp(-\beta(H + P\hat{V}))$
Großkanonisches Potential Grandcanonical potential	J	$= E - TS - \mu N$	$= -PV$	$\mathrm{d}J = -S\mathrm{d}T - N\mathrm{d}\mu - P\mathrm{d}V$	$\exp(-\beta(H - \mu\hat{N}))$
"Null" "Zero"	0	$= E - TS - \mu N + PV$	$= 0$	$0 = -S\mathrm{d}T - N\mathrm{d}\mu + V\mathrm{d}P$	$\exp(-\beta(H - \mu\hat{N} + P\hat{V}))$

C Ideal Quantum Gases

16 Ideal Monatomic Quantum Gas

16.a Grandcanonical Potential

The simplest way to treat the monatomic quantum gas is by means of the grandcanonical ensemble. The ideal gas is distinguished by the fact, that there is no interaction between the particles. Wie indicate the one-particle states by $|\mathbf{k}, m\rangle$. These states be eigenstates of the Hamiltonian H and of the momentum Operator $\mathbf{P}$,

$$H|\mathbf{k}, m\rangle = \epsilon_{\mathbf{k},m}|\mathbf{k}, m\rangle, \quad \mathbf{P}|\mathbf{k}, m\rangle = \hbar\mathbf{k}|\mathbf{k}, m\rangle. \tag{16.1}$$

Other quantum-numbers as e.g. the z-component of the spin are indicated by m

$$S_z|\mathbf{k}, m\rangle = m|\mathbf{k}, m\rangle, \quad \epsilon_{\mathbf{k},m} = \frac{\hbar^2}{2m}k^2 - \mu_{\mathrm{B}} g m H_z. \tag{16.2}$$

(More precisely one should indicate the splitting into Landau-levels.)
The many-particle state consists of symmetrized (bosons) and antisymmetrized (fermions) wave-functions, which are determined by the occupation numbers $n_{\mathbf{k},m}$ for each one-particle state. Allowed are

$$\begin{array}{ll} n_{\mathbf{k},m} = 0, 1, 2, ... & \text{for bosons} \\ n_{\mathbf{k},m} = 0, 1 & \text{for fermions} \end{array} \tag{16.3}$$

The occupation-numbers $n_{\mathbf{k},m}$, which indicate how many particles are in the corresponding state, can be considered eigenvalues of occupation-number operators $\hat{n}_{\mathbf{k},m}$. Then the particle number operator $\hat{N}$ and the Hamiltonian H read

$$\hat{N} = \sum_{\mathbf{k},m} \hat{n}_{\mathbf{k},m}, \quad H = \sum_{\mathbf{k},m} \epsilon_{\mathbf{k},m}\hat{n}_{\mathbf{k},m}. \tag{16.4}$$

In order to calculate the grandcanonical partition function we have to sum independently over the occupation numbers of the various $\mathbf{k}, m$. This yields a product over all $\mathbf{k}, m$,

$$Y = \mathrm{tr}(\mathrm{e}^{-\beta(H-\mu\hat{N})}) = \sum_{...n_{\mathbf{k},m}...} \mathrm{e}^{-\beta(E(\{n\})-\mu N(\{n\})} = \prod_{\mathbf{k},m}\left(\sum_{n_{\mathbf{k},m}} \mathrm{e}^{-\beta(\epsilon_{\mathbf{k},m}-\mu)n_{\mathbf{k},m}}\right) = \prod_{\mathbf{k},m} y_{\mathbf{k},m} \tag{16.5}$$

with

$$y_{\mathbf{k},m} = \begin{cases} \dfrac{1}{1-\mathrm{e}^{-\beta(\epsilon_{\mathbf{k},m}-\mu)}} & \text{bosons} \\ 1+\mathrm{e}^{-\beta(\epsilon_{\mathbf{k},m}-\mu)} & \text{fermions} \end{cases} \tag{16.6}$$

This yields the grandcanonical potential

$$J(\beta, \mu, V) = -k_{\mathrm{B}}T \ln Y = -k_{\mathrm{B}}T \sum_{\mathbf{k},m} \ln y_{\mathbf{k},m} = \pm k_{\mathrm{B}}T \sum_{\mathbf{k},m} \ln(1 \mp \mathrm{e}^{-\beta(\epsilon_{\mathbf{k},m}-\mu)}), \tag{16.7}$$

where the upper sign applies to bosons, the lower to fermions.

16.b Particle Number

The averaged particle number of the system is obtained from

$$N = -\frac{\partial J}{\partial \mu} = k_\mathrm{B} T \sum_{\mathbf{k},m} \frac{\partial \ln y_{\mathbf{k},m}}{\partial \mu} = \sum_{\mathbf{k},m} \frac{\mathrm{e}^{-\beta(\epsilon-\mu)}}{1 \mp \mathrm{e}^{-\beta(\epsilon-\mu)}} = \sum_{\mathbf{k},m} \frac{1}{\mathrm{e}^{\beta(\epsilon-\mu)} \mp 1}. \tag{16.8}$$

The terms of the sum are the averaged occupation numbers

$$\bar{n}_\mathrm{B} = \frac{1}{\mathrm{e}^{\beta(\epsilon-\mu)} - 1} \qquad \text{Bose-function} \tag{16.9}$$

$$\bar{n}_\mathrm{F} = \frac{1}{\mathrm{e}^{\beta(\epsilon-\mu)} + 1} \qquad \text{Fermi-function} \tag{16.10}$$

The probability that a one-particle state is n times occupied is given by ($q = \mathrm{e}^{-\beta(\epsilon-\mu)}$)

$$\text{bosons} \qquad w_{\hat{n}} = \frac{q^n}{\sum_{n'=0}^{\infty} q^{n'}} = q^n(1-q), \tag{16.11}$$

$$\text{fermions} \qquad w_{\hat{n}} = \frac{q^n}{1+q} \tag{16.12}$$

This allows to determine the averaged occupation number

$$\text{bosons} \qquad \bar{n}_\mathrm{B} = \langle \hat{n} \rangle = (1-q)(q + 2q^2 + 3q^3 + ...) = q + q^2 + q^3 + ... = \frac{q}{1-q}, \tag{16.13}$$

$$\text{fermions} \qquad \bar{n}_\mathrm{F} = \langle \hat{n} \rangle = \frac{q}{1+q}. \tag{16.14}$$

This yields

$$q = \frac{\bar{n}}{1 \pm \bar{n}}. \tag{16.15}$$

The total (averaged) particle number is given by

$$N = \sum_{\mathbf{k},m} \langle \hat{n}_{\mathbf{k},m} \rangle = \sum_{\mathbf{k},m} \bar{n}_{\mathbf{k},m}. \tag{16.16}$$

16.c Entropy

The entropy is obtained from

$$S = -\frac{\partial J}{\partial T} = \mp k_\mathrm{B} \sum \ln(1 \mp q) + \frac{1}{T} \sum \frac{(\epsilon-\mu)q}{1 \mp q}, \tag{16.17}$$

where

$$1 \mp q = \frac{1}{1 \pm \bar{n}}, \qquad \frac{\epsilon - \mu}{T} = -k_\mathrm{B} \ln q = -k_\mathrm{B} \ln \frac{\bar{n}}{1 \pm \bar{n}}. \tag{16.18}$$

Thus one obtains

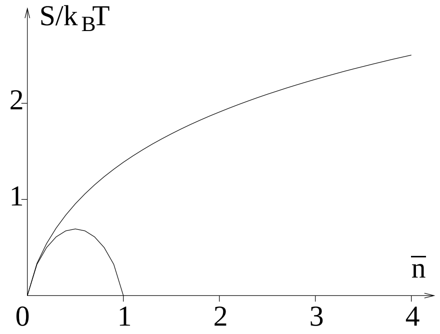
$$S = \pm k_\mathrm{B} \sum \ln(1 \pm \bar{n}) - k_\mathrm{B} \sum \bar{n} \ln \frac{\bar{n}}{1 \pm \bar{n}} \tag{16.19}$$

and therefore

$$S_\mathrm{Bose} = k_\mathrm{B} \sum_{\mathbf{k},m} \left((1 + \bar{n}_{\mathbf{k},m}) \ln(1 + \bar{n}_{\mathbf{k},m}) - \bar{n}_{\mathbf{k},m} \ln \bar{n}_{\mathbf{k},m} \right), \tag{16.20}$$

$$S_\mathrm{Fermi} = k_\mathrm{B} \sum_{\mathbf{k},m} \left(-(1 - \bar{n}_{\mathbf{k},m}) \ln(1 - \bar{n}_{\mathbf{k},m}) - \bar{n}_{\mathbf{k},m} \ln \bar{n}_{\mathbf{k},m} \right). \tag{16.21}$$

Entropy as function of the average particle number $\bar{n}$ for fermions and bosons



16.d Energy

We obtain for the energy

$$
\begin{aligned}
E &= TS + \mu N - PV = TS + \mu N + J \\
&= \mp k_{\mathrm{B}} T \sum \ln(1 \mp q) + \sum \frac{(\epsilon - \mu) q}{1 \mp q} + \sum \frac{\mu q}{1 \mp q} \pm k_{\mathrm{B}} T \sum \ln(1 \mp q) \\
&= \sum \epsilon \frac{q}{1 \mp q} = \sum_{\mathbf{k},m} \epsilon_{\mathbf{k},m} \bar{n}_{\mathbf{k},m}, \qquad (16.22)
\end{aligned}
$$

where we expected the final result anyhow. Each particle with quantum nunbers $\mathbf{k}, m$ contributes $\epsilon_{\mathbf{k},m}$ to the energy.

17 Dilute Ideal Gas: Classical Limit

We have obtained the averaged occupation number of the one-particle states

$$\bar{n}_{\mathbf{k},m} = \frac{1}{\mathrm{e}^{\beta(\epsilon_{\mathbf{k},m}-\mu)} \mp 1}. \tag{17.1}$$

The classical limit is obtained, if the average occupation is small in comparison to 1. Then one has $\mathrm{e}^{\beta(\epsilon-\mu)} \gg 1$ for all $\mathbf{k}, m$. Then the logarithm in (16.7) can be expanded and one obtains for the grandcanonical potential

$$J = \pm k_\mathrm{B} T \sum_{\mathbf{k},m} \ln(1 \mp \mathrm{e}^{-\beta(\epsilon-\mu)}) = -k_\mathrm{B} T \sum_{\mathbf{k},m} \mathrm{e}^{-\beta(\epsilon-\mu)} \mp \frac{k_\mathrm{B} T}{2} \sum_{\mathbf{k},m} \mathrm{e}^{-2\beta(\epsilon-\mu)} - ... \tag{17.2}$$

We assume $\epsilon_k = \hbar^2 k^2/(2m)$. We use $\sum_{\mathbf{k}} \to V/(2\pi)^3 \times \int \mathrm{d}^3 k$ as derived in section 6

$$\begin{aligned} J &= -k_\mathrm{B} T (2S+1) \mathrm{e}^{\beta\mu} \frac{V}{(2\pi)^3} \int \mathrm{d}^3 k \mathrm{e}^{-\beta\hbar^2 k^2/(2m)} \\ &\mp \frac{k_\mathrm{B} T}{2} (2S+1) \mathrm{e}^{2\beta\mu} \frac{V}{(2\pi)^3} \int \mathrm{d}^3 k \mathrm{e}^{-\beta\hbar^2 k^2/m} - ... \\ &= -(k_\mathrm{B} T)^{5/2} V \mathrm{e}^{\beta\mu} (2S+1) \left(\frac{m}{2\pi\hbar^2}\right)^{3/2} \left(1 \pm \frac{\mathrm{e}^{\beta\mu}}{\sqrt{32}} + ...\right) \end{aligned} \tag{17.3}$$

The particle-number is given by

$$N = -\frac{\partial J}{\partial \mu} = (k_\mathrm{B} T)^{3/2} V \mathrm{e}^{\beta\mu} (2S+1) \left(\frac{m}{2\pi\hbar^2}\right)^{3/2} \left(1 \pm \frac{\mathrm{e}^{\beta\mu}}{\sqrt{8}} + ...\right). \tag{17.4}$$

In lowest order one obtains

$$\mathrm{e}^{\beta\mu} = \frac{N\lambda^3}{V(2S+1)} \tag{17.5}$$

with the thermal de Broglie wavelength $\lambda = \left(2\pi\hbar^2/(m k_\mathrm{B} T)\right)^{1/2}$ from eq. (7.7). This yields

$$PV = -J = N k_\mathrm{B} T \left(1 \mp \frac{\mathrm{e}^{\beta\mu}}{\sqrt{32}} + ...\right) = N k_\mathrm{B} T \left(1 \mp \frac{N\lambda^3}{V(2S+1)\sqrt{32}} + ...\right) \tag{17.6}$$

The second term in brackets gives the derivation from the classical behavior due to the quantum statistics. It is proportional to $\lambda^3 \propto \hbar^3$. The energy is obtained from the virial theorem (11.22) as

$$E = \frac{3}{2} PV. \tag{17.7}$$

18 Blackbody Radiation

Photons are bosons with spin 1; but there are no longitudinal photons, thus to any wave-vector $\mathbf{k}$ there are only two polarizations ($\mathbf{E}, \mathbf{B} \perp \mathbf{k}$). Thus we have to replace the multiplicity $2S+1$ by 2. For the energy of the photons we have

$$\epsilon_{\mathbf{k}} = \hbar\omega_{\mathbf{k}} = \hbar ck = cp. \tag{18.1}$$

There is no particle-number conservation for photons, they may be absorbed and emmitted. Thus we put $\mu = 0$. Then we obtain

$$\begin{aligned} PV &= k_{\mathrm{B}}T \ln Y = -2k_{\mathrm{B}}T \sum_{\mathbf{k}} \ln(1 - \mathrm{e}^{-\beta\epsilon_{\mathbf{k}}}) \\ &= -\frac{2k_{\mathrm{B}}TV}{(2\pi)^3} \int \mathrm{d}^3k \ln(1 - \mathrm{e}^{-\beta\epsilon_{\mathbf{k}}}). \end{aligned} \tag{18.2}$$

With $x = \beta\hbar ck$ one obtains

$$P = -\frac{2}{(2\pi)^3}(k_{\mathrm{B}}T)^4 \frac{1}{\hbar^3 c^3} \int \mathrm{d}^3x \ln(1 - \mathrm{e}^{-x}). \tag{18.3}$$

The integral can be evaluated (see appendix)

$$-\int \mathrm{d}^3x \ln(1 - \mathrm{e}^{-x}) = -4\pi \int_0^\infty \mathrm{d}x x^2 \ln(1 - \mathrm{e}^{-x}) = \frac{4\pi^5}{45} \tag{18.4}$$

By means of the Stefan-Boltzmann constant

$$\sigma = \frac{\pi^2 k_{\mathrm{B}}^4}{60\hbar^3 c^2} = 5.67 \cdot 10^{-5}\,\mathrm{ergs}^{-1}\,cm^{-2}\,\mathrm{K}^{-4} \tag{18.5}$$

one obtains the pressure

$$P = \frac{4\sigma}{3c} T^4 \tag{18.6}$$

and the energy reads

$$E = -T^2 \frac{\partial(J/T)}{\partial T} = T^2 \frac{\partial(PV/T)}{\partial T} = \frac{4\sigma}{c} VT^4. \tag{18.7}$$

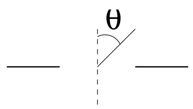
The energy-flux density per solid angle is given by the energy density times velocity of light divided by the total solid angle

$$\frac{\frac{E}{V}}{4\pi} c = \frac{\sigma T^4}{\pi}. \tag{18.8}$$

The energy flux (energy per time) in one direction through an area F is obtained by

$$\int \text{Energy flux density} \times F \cos\theta \mathrm{d}\Omega = \frac{\sigma T^4}{\pi} F \int_0^1 \cos\theta \mathrm{d}\cos\theta \int_0^{2\pi} \mathrm{d}\phi = \sigma T^4 F. \tag{18.9}$$

On energy flux through an area



Actually the Stefan-Boltzmann constant had been introduced for this energy flux. This law is called Stefan-Boltzmann law.
Finally we consider the spectral distribution of the energy density per frequency ω,

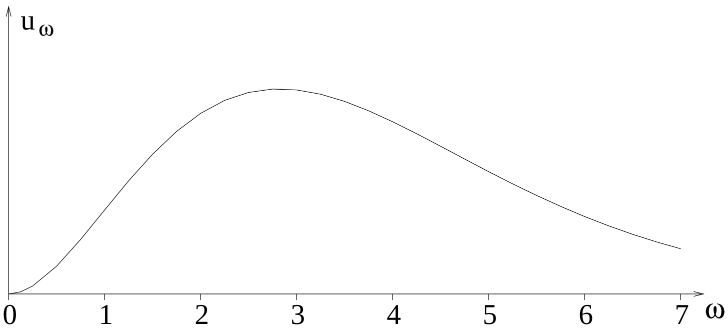
$$\mathrm{d}E = 2\hbar\omega n_{\mathbf{k}} \frac{V}{(2\pi)^3} \mathrm{d}^3k = \frac{V}{4\pi^3} \frac{\hbar\omega \mathrm{d}^3k}{\mathrm{e}^{\beta\hbar\omega} - 1} = \frac{V}{\pi^2} \frac{\hbar\omega k^2 \mathrm{d}k}{\mathrm{e}^{\beta\hbar\omega} - 1} = \frac{V}{\pi^2 c^3} \frac{\hbar\omega^3 \mathrm{d}\omega}{\mathrm{e}^{\beta\hbar\omega} - 1} = V u_\omega \mathrm{d}\omega, \tag{18.10}$$

where

$$u_\omega = \frac{\hbar\omega^3}{\pi^2 c^3 (\mathrm{e}^{\beta\hbar\omega} - 1)} \tag{18.11}$$

is the spectral distribution of the energy density. (Planck 1900)

Spectral energy density of black body radiation.
ω in $k_{\mathrm{B}}T/\hbar$



The maximum of u_ω is at $\hbar\omega_{\mathrm{max}} = 2.82 k_{\mathrm{B}}T$ (Wien's displacement law). If the spectral energy density is related to the wavelength then one obtains a different expression. For small frequencies one obtains the Rayleigh-Jeans-law

$$u_\omega \approx \frac{\hbar\omega^3}{\pi^2 c^3 \beta\hbar\omega} = \frac{k_{\mathrm{B}}T\omega^2}{\pi^2 c^3}, \tag{18.12}$$

which can be obtained classically. For large frequencies one obtains

$$u_\omega = c_1 \omega^3 \mathrm{e}^{-c_2\omega/T}, \tag{18.13}$$

which had been found by Wien in 1896 without explaination of the constants.

19 Phonons in a Solid

We assume that the phonons can be considered in harmonic approximation, that is, the potential is only expanded up to second order in the displacements. (Anharmonicities normally become important at higher temperatures.) One transforms to normal coordinates and obtains in this way decoupled harmonic oscillators. The excitations are the same as in a system of bosons: Phonons are quasi-particles. The Hamiltonian may be written

$$H = E_0 + \sum \hbar\omega_{\mathbf{k},m}(\hat{n}_{\mathbf{k},m} + \frac{1}{2}). \tag{19.1}$$

If there are r atoms per elementary cell of a crystal, then one has $3r$ vibrational modes for each wave-vector $\mathbf{k}$, $m = 1, ...3r$. $3(r-1)$ branches are optical branches, the three other ones are acoustic branches, one longitudinal and two transversal ones.
One obtains for the energy of the system

$$E = E_0 + \sum_{\mathbf{k},m} \hbar\omega_{\mathbf{k},m}\langle\hat{n}_{\mathbf{k},m} + \frac{1}{2}\rangle = E_0 + \sum_{\mathbf{k},m} \hbar\omega_{\mathbf{k},m}\left(\frac{1}{\mathrm{e}^{\beta\hbar\omega_{\mathbf{k},m}} - 1} + \frac{1}{2}\right). \tag{19.2}$$

19.a High Temperatures

For high temperatures, $k_\mathrm{B}T \gg \hbar\omega_\mathrm{max}$ one expands

$$\frac{1}{\mathrm{e}^x - 1} + \frac{1}{2} = \frac{1}{x} + \frac{x}{12} + O(x^3), \quad x \ll 1. \tag{19.3}$$

Thus

$$\begin{aligned} E &= E_0 + \sum_{\mathbf{k},m} \hbar\omega_{\mathbf{k},m}\left(\frac{k_\mathrm{B}T}{\hbar\omega_{\mathbf{k},m}} + \frac{\hbar\omega_{\mathbf{k},m}}{12k_\mathrm{B}T} + ...\right) \\ &= E_0 + 3Nrk_\mathrm{B}T + \frac{1}{12k_\mathrm{B}T}\sum_{\mathbf{k},m}(\hbar\omega_{\mathbf{k},m})^2 + O(T^{-3}). \end{aligned} \tag{19.4}$$

N is the number of elementary cells, Nr the number of atoms.
For the specific heat one obtains

$$C_V = \left.\frac{\partial E}{\partial T}\right|_V = 3Nrk_\mathrm{B} - \frac{1}{12k_\mathrm{B}T^2}\sum_{\mathbf{k},m}(\hbar\omega_{\mathbf{k},m})^2 + ... \tag{19.5}$$

The first term yields the Dulong-Petit law. The second one shows, that the specific heat becomes smaller at lower temperatures.

19.b Low Temperatures

At low temperatures $k_\mathrm{B}T \ll \hbar\omega_\mathrm{max}$ it is sufficient to consider the acoustic branches, since the optical branches (compare 19.d) are frozen. For the acoustic branches we put $\omega_{\mathbf{k},m} \approx c_\mathrm{l}k, c_\mathrm{t}k$ for the longitudinal and transversal acoustic vibrations. We approximate the longitudinal und transversal sound-velocities c_l and c_t as independent of the direction. Then we obtain

$$E = E_0' + \frac{V}{(2\pi)^3}\sum_{m=1}^{3}\int \mathrm{d}^3k \frac{\hbar c_m k}{\mathrm{e}^{\beta\hbar c_m k} - 1}, \tag{19.6}$$

with the groundstate energy $E_0' = E_0 + \frac{1}{2}\sum_{\mathbf{k},m}\hbar\omega_{\mathbf{k},m}$. If we now substitute as for photons in an enclosure $x = \beta\hbar c_m k$, then one obtains

$$E = E_0' + \frac{V}{(2\pi)^3}\sum_m \frac{(k_\mathrm{B}T)^4}{(\hbar c_m)^3}\int \mathrm{d}^3x \frac{x}{\mathrm{e}^x - 1}. \tag{19.7}$$

Since the integral decays rapidly we integrate up to ∞,

$$\int \mathrm{d}^3x \frac{x}{\mathrm{e}^x - 1} = 4\pi \int_0^\infty \mathrm{d}x \frac{x^3 \mathrm{e}^{-x}}{1 - \mathrm{e}^{-x}} = 24\pi\zeta(4) = \frac{4\pi^5}{15} \tag{19.8}$$

This yields the energy

$$E = E_0' + \frac{\pi^2 (k_\mathrm{B}T)^4 V}{30\hbar^3} (\frac{1}{c_\mathrm{l}^3} + \frac{2}{c_\mathrm{t}^3}) \tag{19.9}$$

and a specific heat proportional to T^3.

19.c Debye-Approximation for intermediate temperatures (acoustic vibrations)

One introduces the density of states $z(\omega)$, so that the number of normal modes in the interval $\omega ... \omega + \mathrm{d}\omega$ is $z(\omega)\mathrm{d}\omega$. Then the number of normal modes with $\omega \le \omega_0$ is given by

$$\int_0^{\omega_0} \mathrm{d}\omega z(\omega) = \frac{V}{(2\pi)^3} \frac{4\pi}{3} \left[\left(\frac{\omega_0}{c_\mathrm{l}}\right)^3 + 2\left(\frac{\omega_0}{c_\mathrm{t}}\right)^3 \right] = \frac{C}{3}\omega_0^3, \tag{19.10}$$

since the volumina of the spheres with radii ω_0/c in k-space enter. With the constant

$$C = \frac{V}{2\pi^2} \left(\frac{1}{c_\mathrm{l}^3} + \frac{2}{c_\mathrm{t}^3} \right) \tag{19.11}$$

one obtains

$$z(\omega) = C\omega^2. \tag{19.12}$$

We assume now that this behavior is cut off at a frequency ω_D, which is called Debye-frequency,

$$z(\omega) = \left\{ \begin{array}{cc} C\omega^2 & \omega \le \omega_\mathrm{D}, \\ 0 & \omega > \omega_\mathrm{D}. \end{array} \right. \tag{19.13}$$

Then

$$\int_0^{\omega_\mathrm{D}} z(\omega)\mathrm{d}\omega = 3N = \frac{C}{3}\omega_\mathrm{D}^3 \tag{19.14}$$

must hold, thus

$$\frac{1}{\omega_\mathrm{D}^3} = \frac{C}{9N} = \frac{V}{18\pi^2 N} \left(\frac{1}{c_\mathrm{l}^3} + \frac{2}{c_\mathrm{t}^3} \right), \tag{19.15}$$

since there are in total $3N$ acoustical vibration modes. Then the energy reads

$$E = E_0' + \int_0^{\omega_\mathrm{D}} z(\omega) \frac{\hbar\omega \mathrm{d}\omega}{\mathrm{e}^{\beta\hbar\omega} - 1} = E_0' + \frac{9N}{\omega_\mathrm{D}^3} \int_0^{\omega_\mathrm{D}} \frac{\hbar\omega^3 \mathrm{d}\omega}{\mathrm{e}^{\beta\hbar\omega} - 1}. \tag{19.16}$$

With $x = \beta\hbar\omega$ one obtains

$$E = E_0' + \frac{9N(k_\mathrm{B}T)^4}{\hbar^3\omega_\mathrm{D}^3} \int_0^{\beta\hbar\omega_\mathrm{D}} \frac{x^3 \mathrm{d}x}{\mathrm{e}^x - 1} = E_0' + 3Nk_\mathrm{B}TD(\frac{T}{\Theta_\mathrm{D}}) \tag{19.17}$$

with the Debye-temperature Θ_D, which is determined by $k_\mathrm{B}\Theta_\mathrm{D} = \hbar\omega_\mathrm{D}$, and the Debye-function

$$D(y) = 3y^3 \int_0^{1/y} \frac{x^3 \mathrm{d}x}{\mathrm{e}^x - 1}. \tag{19.18}$$

For small y one finds $D(y) = \pi^4 y^3/5$ and for large y one obtains $D(y) = 1$ in agreement with our estimates for low and high temperatures.

19.d Optical Vibrations

If one assumes that the frequencies $\omega_{\rm opt}$ of the optical phonons are approximately independent of $\mathbf{k}$, then one obtains the contribution

$$\Delta E_{\rm opt} = N \sum_{m({\rm opt})} \hbar\omega_m \frac{1}{{\rm e}^{\beta\hbar\omega_m} - 1} \tag{19.19}$$

to the energy and

$$C_{V,{\rm opt}} = N k_{\rm B} \sum_{m({\rm opt})} \left(\frac{\hbar\omega_m}{k_{\rm B}T}\right)^2 \frac{{\rm e}^{\beta\hbar\omega_m}}{({\rm e}^{\beta\hbar\omega_m} - 1)^2}. \tag{19.20}$$

to the specific heat. The exponential function becomes very large for temperatures $k_{\rm B}T \ll \hbar\omega_m$, so that the contribution to the specific heat vanishes like $Nk_{\rm B}(\hbar\omega_m/(k_{\rm B}T))^2{\rm e}^{-\hbar\omega_m/(k_{\rm B}T)}$. But as soon as $k_{\rm B}T \approx \hbar\omega_m$, then also the optical phonons contribute essentially. For high temperatures $k_{\rm B}T \gg \hbar\omega_m$ one obtains the contribution $k_{\rm B}N$ to the specific heat.
In total all contributions have to be added,

$$E = E_0' + 3Nk_{\rm B}TD(\frac{T}{\Theta_D}) + N \sum_{m({\rm opt})} \hbar\omega_m \frac{1}{{\rm e}^{\beta\hbar\omega_m} - 1}. \tag{19.21}$$

20 Bose Einstein Condensation

Now we consider an ideal Bose-gas at low temperatures. If for simplicities' sake we assume spin 0 for the bosons then its particle number is given by

$$N = \sum_{\mathbf{k}} \frac{1}{\mathrm{e}^{\beta(\epsilon_k - \mu)} - 1}. \tag{20.1}$$

In order that this expression make sense, μ has to be less then ϵ_k for all k. Thus for a dispersion

$$\epsilon_k = \frac{\hbar^2 k^2}{2m} \tag{20.2}$$

μ has to be negative. What happens in the limit $\mu = 0$? First we perform the limit $\sum_k \to V(2\pi)^{-3} \int \mathrm{d}^3k$. Then we obtain for $\mu = 0$

$$N = \frac{V}{(2\pi)^3} \int \mathrm{d}^3k \frac{1}{\mathrm{e}^{\beta\hbar^2k^2/(2m)} - 1} \tag{20.3}$$

The substitution $x = \beta\hbar^2k^2/(2m)$ yields

$$N = \frac{V}{(2\pi)^3} \left(\frac{2mk_\mathrm{B}T}{\hbar^2}\right)^{3/2} \frac{4\pi}{2} \int_0^\infty \mathrm{d}x \frac{x^{1/2}}{\mathrm{e}^x - 1} = \zeta(3/2)V \left(\frac{2\pi m k_\mathrm{B}T}{h^2}\right)^{3/2} = \zeta(3/2)V/\lambda(T)^3 \tag{20.4}$$

with $\zeta(3/2) = 2.612$.
What happens if the particle density becomes larger than $\zeta(3/2)/\lambda^3$? Then μ is so close to 0, that the state $k = 0$ accepts all particles, which do not fit into the particle number calculated above. Then one has a macroscopic occupation for $k = 0$

$$N_0 = N - \zeta(3/2)V/\lambda(T)^3. \tag{20.5}$$

Below a critical temperature T_c, which is determined by

$$N = \zeta(3/2)V/\lambda(T_\mathrm{c})^3 \tag{20.6}$$

one obtains

$$N_0 = N\left(1 - \left(\frac{T}{T_c}\right)^{3/2}\right). \tag{20.7}$$

Thus equation (20.4) yields for $T < T_c$ only the number of excited bosons but not their complete number.
Then one obtains for the energy of the system

$$E = \frac{V}{(2\pi)^3} \int \mathrm{d}^3k \frac{\hbar^2k^2}{2m(\mathrm{e}^{\beta\hbar^2k^2/(2m)} - 1)}. \tag{20.8}$$

The substitution $x = \beta\hbar^2k^2/(2m)$ yields

$$\begin{aligned} E &= \frac{V}{(2\pi)^3} \frac{\hbar^2}{2m} \left(\frac{2m}{\beta\hbar^2}\right)^{5/2} 2\pi \int_0^\infty \mathrm{d}x \frac{x^{3/2}}{\mathrm{e}^x - 1} \\ &= \frac{3}{2} V\zeta(5/2)k_\mathrm{B}T/\lambda^3(T) = 0.770 N k_\mathrm{B} T^{5/2} T_\mathrm{c}^{-3/2}, \end{aligned} \tag{20.9}$$

where the Faktor 0.770 is obtained from $3\zeta(5/2)/(2\zeta(3/2))$. The specific heat at constant volume increases like

$$C_V = 1.926 N k_\mathrm{B} \left(\frac{T}{T_\mathrm{c}}\right)^{3/2} \tag{20.10}$$

The pressure is obtained from the virial theorem

$$P = 2E/(3V) = \zeta(5/2) k_\mathrm{B} T/\lambda^3(T) \tag{20.11}$$

It increases proportional to $T^{5/2}$ independent of the particle density. The reason for this independence is that the particles with momenta 0 do not contribute to the pressure and the particle density of the other particles does not depend on temperature.
For $T > T_\mathrm{c}$ μ becomes negative. Then there is no longer a macroscopic occupation of the state with $k = 0$. A little bit above T_c μ may be calculated from

$$N = \frac{V}{(2\pi)^3} \int \mathrm{d}^3k \frac{1}{\mathrm{e}^{x-\beta\mu} - 1} - \left(\frac{V}{(2\pi)^3} \int \mathrm{d}^3k \frac{1}{\mathrm{e}^x - 1} - \zeta(3/2) \frac{V}{\lambda(T)^3} \right) \tag{20.12}$$

where the expression in parenthesis vanishes. We determine the difference of the particle number at T and that, we would have at $T = T_\mathrm{c}$. Then one obtains

$$N = \zeta(3/2) \frac{V}{\lambda(T)^3} + \frac{V}{(2\pi)^3} \int \mathrm{d}^3k \frac{\mathrm{e}^x (1 - \mathrm{e}^{-\beta\mu})}{(\mathrm{e}^x - 1)(\mathrm{e}^{x-\beta\mu} - 1)}. \tag{20.13}$$

The main contribution of this integral comes from small x. Thus we replace $\mathrm{e}^x = 1$ in the numerator and $\mathrm{e}^x - 1 = x$ and $\mathrm{e}^{x-\beta\mu} - 1 = x - \beta\mu$ in the denominator. Since $\beta\mu$ is small we replace $1 - \mathrm{e}^{-\beta\mu} = \beta\mu$ and obtain

$$N = \zeta(3/2) \frac{V}{\lambda(T)^3} + \frac{V\beta\mu}{(2\pi)^3} \int \frac{\mathrm{d}^3k}{x(x - \beta\mu)} = \frac{V}{\lambda(T)^3} \left(\zeta(3/2) - 2\sqrt{-\pi\beta\mu} \right) \tag{20.14}$$

For constant N and V one obtains for T close to T_c, that $\sqrt{-\mu}$ is proportional to $T - T_\mathrm{c}$, that is $\mu \propto -(T - T_\mathrm{c})^2$. Finally we consider the energy. From

$$\frac{\partial(\beta J)}{\partial\beta} = E - \mu N, \quad \frac{\partial(\beta J)}{\partial\mu} = -\beta N \tag{20.15}$$

one obtains for the mixed derivative

$$\frac{\partial^2(\beta J)}{\partial\beta\partial\mu} = \frac{\partial E}{\partial\mu} - N - \mu \frac{\partial N}{\partial\mu} = -N - \beta \frac{\partial N}{\partial\beta} \tag{20.16}$$

and therefore

$$\frac{\partial E}{\partial\mu} = \mu \frac{\partial N}{\partial\mu} - \beta \frac{\partial N}{\partial\beta}, \tag{20.17}$$

which yields with the approximation above

$$\frac{\partial E}{\partial\mu} = \frac{3}{2} N \tag{20.18}$$

and therefore

$$E = E(T, \mu = 0) + \frac{3}{2} N\mu \tag{20.19}$$

Since $\mu \propto -(T - T_\mathrm{c})^2$, one obtains a deviation of the energy from the behavior (20.9) proportional to $(T - T_\mathrm{c})^2$ and therefore of the specific heat proportional to $T - T_\mathrm{c}$. The specific heat shows a kink at T_c. We note, that a Bose-Einstein condensation is observed in fluid He^4 at approximately 2 K and during the last years also at extremely low temperatures (10^{-7} K) in gases of alkali-atoms. The behavior is, however, considerably modified due to the interaction between the atoms.

21 Diatomic Gases

In a polyatomic gas one has to consider not only translational degrees of freedom but also internal excitations. In molecules these can be rotations and vibrations, that is movements of the atoms against each other. Finally (also in the monatomic case) electronic excitations are possible. They yield additional contributions to energy and entropy in dilute gases.

21.a Rotations

We consider rotations of diatomic molecules. As a model we consider them to constitute of two masses m_1 and m_2 at distanve r_0. Then their moment of inertia is

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2. \tag{21.1}$$

The angular momentum is $\hbar l$, and the corresponding energy

$$\epsilon_l = \frac{\hbar^2 l(l+1)}{2I} = k_{\rm B}\Theta_{\rm rot}\frac{l(l+1)}{2}, \tag{21.2}$$

where $\Theta_{\rm rot}$ is the characteristic temperature for the rotations. For given l one has a $2l+1$-fold degeneracy. Then the partition function of a molecule is

$$z_{\rm rot} = \sum_{l=0}^{\infty}(2l+1)\mathrm{e}^{-l(l+1)\Theta_{\rm rot}/(2T)}. \tag{21.3}$$

For N molecules one has to take the N-th power, since each molecule can assume its rotational states independently of the other molecules, $Z_{\rm rot} = z_{\rm rot}^N$.
If the atoms are distinguishible, then all $l = 0, 1, 2, ...$ are possible. If the atoms are equal, then the appropriate statistics (Bose-Fermi) has to be taken into account.
For Fermions (for example H_2) the spin-function of the spin-singlett ($S = 0$) is antisymmetric and thus the wave-function in real space is symmetric (para-state). Then $l = 0, 2, 4, ...$ applies. In the spin-triplett state ($S = 1$) the wave-function in real space is antisymmetric (ortho-state) and $l = 1, 3, 5, ...$
For bosons with atomic spin $S_1 = S_2 = 0$ the wave-function is symmetric (para-state) with even l. For bosons with atomic spin $S_1 = S_2 = 1$ (e.g. D_2) one obtains para-states for the spin-singulett ($S = 0$) and the spin-quintuplett ($S = 2$) and ortho-states for the spin-triplett ($S = 1$).
Then one obtains at low temperatures, that is for $T \ll \Theta_{\rm rot}$:
For distinguishable atoms

$$\begin{aligned}
Z_{\rm rot} = z_{\rm rot}^N &= \left(1 + 3\mathrm{e}^{-\Theta_{\rm rot}/T} + ...\right)^N && (21.4)\\
E_{\rm rot} = -\frac{\partial \ln Z}{\partial\beta} &= 3Nk_{\rm B}\Theta_{\rm rot}\mathrm{e}^{-\Theta_{\rm rot}/T} + ... && (21.5)\\
C_{V,\rm rot} = \frac{\partial E}{\partial T} &= 3Nk_{\rm B}\left(\frac{\Theta_{\rm rot}}{T}\right)^2 \mathrm{e}^{-\Theta_{\rm rot}/T} + ... && (21.6)
\end{aligned}$$

For para-states one obtains

$$\begin{aligned}
Z_{\rm rot} &= \left(1 + 5\mathrm{e}^{-3\Theta_{\rm rot}/T} + ...\right)^N && (21.7)\\
E_{\rm rot} &= 15Nk_{\rm B}\Theta_{\rm rot}\mathrm{e}^{-3\Theta_{\rm rot}/T} + ... && (21.8)\\
C_{V,\rm rot} &= 45Nk_{\rm B}\left(\frac{\Theta_{\rm rot}}{T}\right)^2 \mathrm{e}^{-3\Theta_{\rm rot}/T} + ... && (21.9)
\end{aligned}$$

and for ortho-states

$$Z_{\rm rot} = \left(3\mathrm{e}^{-\Theta_{\rm rot}/T} + 7\mathrm{e}^{-6\Theta_{\rm rot}/T} + ...\right)^N \tag{21.10}$$

$$E_{\rm rot} = Nk_{\rm B}\Theta_{\rm rot}(1+\frac{35}{3}{\rm e}^{-5\Theta_{\rm rot}/T}+...) \quad (21.11)$$

$$C_{V,\rm rot} = \frac{175}{3}Nk_{\rm B}\left(\frac{\Theta_{\rm rot}}{T}\right)^2 {\rm e}^{-5\Theta_{\rm rot}/T}+... \quad (21.12)$$

At high temperatures the sums can be replaced by integrals $\sum_l \to \int {\rm d}l$. Then one obtains

$$z_{\rm rot} = \int_0^\infty {\rm d}l(2l+1){\rm e}^{-l(l+1)\Theta_{\rm rot}/(2T)} = 2\frac{T}{\Theta_{\rm rot}}\int_0^\infty {\rm d}x{\rm e}^{-x} = 2\frac{T}{\Theta_{\rm rot}}. \quad (21.13)$$

with $x = l(l+1)\Theta_{\rm rot}/(2T)$. This holds for distinguishable atoms. For undistinguishable ones the factor 2 has to be removed. Then one obtains for high temperatures (in all cases)

$$E_{\rm rot} = Nk_{\rm B}T, \quad C_{V,\rm rot} = Nk_{\rm B}. \quad (21.14)$$

For linear polyatomic molecules as e.g. CO_2 one obtains the same result with an appropriate momentum of inertia. Linear molecules are distinguished in so far as one of the principal momenta of inertia vanishes, which is the one around the axis which connects the atoms. For non-linear molecules, like H_2O all the main momenta of inertia are different from zero. In this case there are not $2l+1$, but $(2l+1)^2$ rotational states for given angular momentum $\hbar l$. These states are described by the square of the angular momentum and both a component of the angular momentum in the fixed coordinate system and in the system rotating with the molecule (the Poisson-brackets vanish between these components in classical mechanics). Both components run independently from $-l$ to $+l$. The corresponding wave-functions are the rotation matrix-functions (they describe the transformation of the spherical harmonics under rotation), which depend on the three Eulerian angles. If one of the moments of inertia vanishes then the rotational energy is finite only, if the component of the angular momentum along this axis vanishes. All other rotational energies along this axis become infinite. Generally the states with different z-component of angular momenta in the fixed system of coordinates are degenerate, but not with respect to the angular momentum components in the system rotating with the molecule, which yields multiplicities $2l+1$ (if it is not higher for some other reasons). If all principal moments of inertia are equal (spherical top), as for CH_4, then all states are degenerate and one obtains

$$z_{\rm rot} = \sum_l (2l+1)^2{\rm e}^{-l(l+1)\Theta_{\rm rot}/(2T)} \quad (21.15)$$

and for high temperatures, if we approximate one factor $2l+1$ by $2\sqrt{l(l+1)}$

$$z_{\rm rot} = 4\sqrt{2\pi}\left(\frac{T}{\Theta_{\rm rot}}\right)^{3/2}, \quad (21.16)$$

which yields

$$E_{\rm rot} = \frac{3}{2}Nk_{\rm B}T, \quad C_{V,\rm rot} = \frac{3}{2}Nk_{\rm B} \quad (21.17)$$

Thus at high temperatures we obtain for each rotational degree of freedom a contribution $k_{\rm B}/2$ to the specific heat.

21.b Vibrations

Apart from the rotations there are also vibrational degrees of freedom, where the atoms of the molecules oscillate against each other. A diatomic molecule can vibrate along its axis; thus it has one vibrational degree of freedom. A triatomic linear molecule has two vibrational degrees of freedom in the direction of its axis and two bending degrees of freedom perpendicular to the axis, thus in total four vibrational degrees of freedom. A non-linear triatomic molecule has three vibrational degrees of freedom. The lengths of the sides of the triangle can vary independently. Generally the number of translational degrees of freedom (three) plus the rotational degrees (two or three) plus the number of vibrationall degrees of freedom add up to three times the number of atoms in the molecule.
The vibrations have certain vibrational frequencies ω_{vib} (within harmonic approximation). For these the same holds as for the vibrations of the optical phonons.
Thus we obtain with $k_B\Theta_{\text{vib}} = \hbar\omega_{\text{vib}}$ the contribution to the free energy for one vibrational frequency

$$F_{\text{vib}} = -k_B T N \ln\left(\sum_n \mathrm{e}^{-(n+\frac{1}{2})\Theta_{\text{vib}}/T}\right) = -k_B T N \ln \frac{\mathrm{e}^{-\Theta_{\text{vib}}/(2T)}}{1-\mathrm{e}^{-\Theta_{\text{vib}}/T}} \tag{21.18}$$

and the contribution to the specific heat

$$C_{\text{vib}} = -T\frac{\partial^2 F_{\text{vib}}}{\partial T^2} = k_B N \left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \frac{\mathrm{e}^{\Theta_{\text{vib}}/T}}{(\mathrm{e}^{\Theta_{\text{vib}}/T}-1)^2} \tag{21.19}$$

$$\approx k_B N \left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \mathrm{e}^{-\Theta_{\text{vib}}/T} \text{ für } T \ll \Theta_{\text{vib}}, \tag{21.20}$$

$$\approx k_B N \text{ für } T \gg \Theta_{\text{vib}}. \tag{21.21}$$

Characteristic temperatures for diatomic molecules (from the script Statistische Physik by Heinz Horner)

	Θ_{rot}	Θ_{vib}	Θ_{el} [K]
H_2	85	5958	129 000
D_2	43	4210	129 000
O_2	2.1	2228	11 300
I_2	0.05	305	17 000

Usually the electronic excitations are so high in energy, that the molecules dissociate before they would really contribute.

22 Metal Electrons

Electrons are fermions with spin 1/2. We consider the metal electrons approximately without interaction. However, the Hartree-Fock interaction may be incorporated into the one-particle energies. The averaged particle number be fixed. We introduce the chemical potential. Then with the Fermi-function

$$f(\epsilon-\mu)=\frac{1}{\mathrm{e}^{\beta(\epsilon-\mu)}+1} \tag{22.1}$$

we obtain the expressions for particle number, energy and entropy

$$\begin{aligned} N &= \langle\hat{N}\rangle=\sum_{\mathbf{k},m} f(\epsilon_{\mathbf{k},m}-\mu), &(22.2)\\ E &= \langle H\rangle=\sum_{\mathbf{k},m}\epsilon_{\mathbf{k},m} f(\epsilon_{\mathbf{k},m}-\mu), &(22.3)\\ S &= -k_{\mathrm{B}}\sum_{\mathbf{k},m}(f\ln f+(1-f)\ln(1-f)). &(22.4)\end{aligned}$$

Now we introduce the density of states $z(\epsilon)$; by $Vz(\epsilon)\mathrm{d}\epsilon$ we denote the number of one-particle states with energies between ϵ and $\epsilon+\mathrm{d}\epsilon$. For the ground-state that is at temperature $T=0$ all one-particle states are occupied up to an energy ϵ_{F}, which is called Fermi-energy. In the isotropic case the corresponding momentum $p_{\mathrm{F}}=\hbar k_{\mathrm{F}}$ is called Fermi momentum. For free electrons one finds

$$\begin{aligned} V\int_0^{\epsilon_{\mathrm{F}}} z(\epsilon')\mathrm{d}\epsilon' &= \frac{2V}{(2\pi)^3}\frac{4\pi}{3}k_{\mathrm{F}}^3 &(22.5)\\ &= V\left(\frac{2m\epsilon_{\mathrm{F}}}{\hbar^2}\right)^{3/2}/3\pi^2=N. &(22.6)\end{aligned}$$

Daraus folgt dann

$$\int_0^{\epsilon} z(\epsilon')\mathrm{d}\epsilon'=\frac{N}{V}\left(\frac{\epsilon}{\epsilon_{\mathrm{F}}}\right)^{3/2},\quad z(\epsilon)=\frac{N}{V\epsilon_{\mathrm{F}}}\frac{3}{2}\sqrt{\frac{\epsilon}{\epsilon_{\mathrm{F}}}},\quad \epsilon>0. \tag{22.7}$$

In general $z(\epsilon)$ is given by the band-structure. Generally one has

$$\sum_{\mathbf{k},m} g(\epsilon_{\mathbf{k},m})=V\int g(\epsilon)z(\epsilon)\mathrm{d}\epsilon \tag{22.8}$$

and thus

$$\begin{aligned} \frac{N}{V} &= \int f(\epsilon-\mu)z(\epsilon)\mathrm{d}\epsilon, &(22.9)\\ \frac{E}{V} &= \int \epsilon f(\epsilon-\mu)z(\epsilon)\mathrm{d}\epsilon. &(22.10)\end{aligned}$$

The evaluation of the integrals is performed by the method of Sommerfeld for $\beta\mu\gg 1$ ($k_{\mathrm{B}}T\ll\epsilon_{\mathrm{F}}$). Let

$$G(\mu)=\int_0^\infty g(\epsilon)f(\epsilon-\mu)\mathrm{d}\epsilon=\int_0^\mu g(\epsilon)\mathrm{d}\epsilon+\int_0^\infty g(\epsilon)(f_T(\epsilon-\mu)-f_0(\epsilon-\mu))\mathrm{d}\epsilon. \tag{22.11}$$

The main contribution of the second integral comes from $\epsilon\approx\mu$, since $f_T(\epsilon-\mu)-f_0(\epsilon-\mu)$ is there essentially different from zero. One expands therefore $g(\epsilon)$ in a Taylor series around $\epsilon=\mu$ and obtains

$$G(\mu)=\int_0^\mu g(\epsilon)\mathrm{d}\epsilon+\int_{-\infty}^\infty (g(\mu)+(\epsilon-\mu)g'(\mu)+...)\,(f_T(\epsilon-\mu)-f_0(\epsilon-\mu))\mathrm{d}\epsilon. \tag{22.12}$$

In the second integral we have replaced the lower bound by $-\infty$, which is allowed as long as $\mu\gg k_{\mathrm{B}}T$, since then $f_T(x)-f_0(x)$ is very small. Since $f_T(x)-f_0(x)$ is an odd function in x, only odd powers of $\epsilon-\mu$ contribute to the Taylor expansion of g

$$G(\mu) = \int_0^\mu g(\epsilon)\mathrm{d}\epsilon + 2g'(\mu)\int_0^\infty x f_T(x)\mathrm{d}x + ... \tag{22.13}$$

With $x = \epsilon - \mu = k_\mathrm{B}Ty$ one obtains

$$\int_0^\infty x f_T(x)\mathrm{d}x = (k_\mathrm{B}T)^2\int_0^\infty \frac{y\mathrm{d}y}{\mathrm{e}^y+1} = (k_\mathrm{B}T)^2\frac{\zeta(2)}{2} = \frac{\pi^2}{12}(k_\mathrm{B}T)^2 \tag{22.14}$$

and

$$G(\mu) = \int_0^\mu g(\epsilon)\mathrm{d}\epsilon + \frac{\pi^2}{6}(k_\mathrm{B}T)^2 g'(\mu) + O(T^4). \tag{22.15}$$

For the particle density one obtains

$$\frac{N}{V} = \int_0^\mu z(\epsilon)\mathrm{d}\epsilon + \frac{\pi^2}{6}(k_\mathrm{B}T)^2 z'(\mu) + ... = \underbrace{\int_0^{\epsilon_\mathrm{F}} z(\epsilon)\mathrm{d}\epsilon}_{N/V} + (\mu-\epsilon_\mathrm{F})z(\epsilon_\mathrm{F}) + \frac{\pi^2}{6}(k_\mathrm{B}T)^2 z'(\epsilon_\mathrm{F}) + ... \tag{22.16}$$

Since the particle number is conserved, one obtains

$$\mu(T) = \epsilon_\mathrm{F} - \frac{\pi^2(k_\mathrm{B}T)^2 z'(\epsilon_\mathrm{F})}{6z(\epsilon_\mathrm{F})} + O(T^4) \tag{22.17}$$

One obtains for the energy

$$\begin{aligned}\frac{E}{V} &= \int_0^\mu \epsilon z(\epsilon)\mathrm{d}\epsilon + \frac{\pi^2}{6}(k_\mathrm{B}T)^2(\mu z(\mu))' + ... \\ &= \underbrace{\int_0^{\epsilon_F} \epsilon z(\epsilon)\mathrm{d}\epsilon}_{E_0/V} + \underbrace{(\mu-\epsilon_\mathrm{F})z(\epsilon_\mathrm{F})\epsilon_\mathrm{F} + \frac{\pi^2}{6}(k_\mathrm{B}T)^2\epsilon_\mathrm{F} z'(\epsilon_\mathrm{F})}_{0} + \frac{\pi^2}{6}(k_\mathrm{B}T)^2 z(\epsilon_\mathrm{F}) + ...\end{aligned} \tag{22.18}$$

Thus we are left with the energy

$$E = E_0 + \frac{\pi^2}{6}(k_\mathrm{B}T)^2 V z(\epsilon_\mathrm{F}) + O(T^4) \tag{22.19}$$

and a specific heat

$$C_V = \left.\frac{\partial E}{\partial T}\right|_V = \frac{\pi^2}{3}k_\mathrm{B}^2 T V z(\epsilon_F) \tag{22.20}$$

linear in T. This contribution is larger then the phononic contribution for metals up to approximately 10 K. The behavior for semiconductors and superconductors is different due to an energy gap in the excitation spectrum.

D Thermodynamics and entropy

23 Thermodynamic averages

23.a Generalized grandcanonical ensembles

Until now we have worked with the canonical ensemble, but also allowed that the particle number is not fixed, but is allowed to fluctuate. By adding a term $-\mu\hat{N}$ to the Hamiltonian we obtained the grandcanonical ensemble described by $\rho = \mathrm{e}^{-\beta(H-\mu\hat{N})}/Y$. Similarly one may add other quantities to H as we already did by introducing a canonical ensemble with given pressure instead of volume. One obtains generally

$$\rho = \mathrm{e}^{-\beta(H-\sum_i f_i\hat{Q}_i)}/Y \tag{23.1}$$

or if we introduce the generalized potential K by

$$\mathrm{e}^{-\beta K} = Y = \mathrm{tr}\,\mathrm{e}^{-\beta(H-\sum_i f_i\hat{Q}_i)} \tag{23.2}$$

then we may write

$$\rho = \mathrm{e}^{-\beta(H-\sum_i f_i\hat{Q}_i-K)} \tag{23.3}$$

Note, that K is a function of T or β and of the f_is. Examples of such external forces f_i and their corresponding conjugate operators $\hat{Q}_i$ are

f_i	$\hat{Q}_i$
External forces	operators (conjugate quantities)
chem. potential	particle number
− pressure	volume
stress tensor	$V\cdot$ strain tensor
velocity	momentum
frequency	anguar momentum
magnetic field	magnet. moment
electric field	electr. moment

Taking the derivative with respect to f_i we obtain $Q_i = \langle\hat{Q}_i\rangle$ from K,

$$\frac{\partial K}{\partial f_i} = -k_{\mathrm{B}}T\frac{\partial \ln Y}{\partial f_i} = -k_{\mathrm{B}}T\frac{1}{Y}\beta\mathrm{tr}(\hat{Q}_i\mathrm{e}^{-\beta(H-\sum_i f_i\hat{Q}_i)}) = -\mathrm{tr}(\hat{Q}_i\rho) = -\langle\hat{Q}_i\rangle = -Q_i. \tag{23.4}$$

One can show by means of the cyclic invariance of the trace, that this does not only hold for oerators $\hat{Q}_i$ which commute with $H-\sum_i f_i\hat{Q}_i$. Thus one obtains generally the expectation values of the operators $\hat{Q}_i$ from the derivatives of K. Finally we consider what we obtain from the derivative of K with respect to β,

$$\begin{aligned}\frac{\partial K}{\partial\beta} &= -\frac{\partial}{\partial\beta}\left(\frac{1}{\beta}\ln Y\right) = \frac{1}{\beta^2}\ln Y - \frac{1}{\beta Y}\frac{\partial Y}{\partial\beta} \\ &= \frac{1}{\beta^2}\mathrm{tr}((\beta(H-\sum_i f_i\hat{Q}_i)+\ln Y)\rho)\end{aligned} \tag{23.5}$$

This expression may be written

$$\frac{\partial K}{\partial\beta} = \frac{1}{\beta}(E-\sum_i f_iQ_i - K) \tag{23.6}$$

as well as

$$\frac{\partial K}{\partial \beta} = -\frac{1}{\beta^2}\langle \ln \rho \rangle \tag{23.7}$$

since $\ln \rho = -\beta(H - \sum_i f_i \hat{Q}_i - K)$. Thus we obtain

$$\mathrm{d}K = -\sum_i Q_i \mathrm{d}f_i + k_\mathrm{B}\langle \ln \rho \rangle \mathrm{d}T. \tag{23.8}$$

23.b Entropy

We have found for the canonical and the generalized canonical ensembles

$$\begin{array}{llllll}
\text{Ensemble} & Y & K & f & Q & \mathrm{d}K \\
\text{canonical} & Z & F & - & - & \mathrm{d}F = -S\mathrm{d}T \\
\text{canonical} & \tilde{Z} & G & -P & V & \mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P \\
\text{grandcanonical} & Y & J & \mu & N & \mathrm{d}J = -S\mathrm{d}T - N\mathrm{d}\mu.
\end{array} \tag{23.9}$$

From (23.8) it follows that the entropy for these ensembles should be defined as

$$S = -k_\mathrm{B}\langle \ln \rho \rangle. \tag{23.10}$$

For the microcanonical ensemble we had

$$\rho_i = \left\{ \begin{array}{cc} 1/W & E_i \le E, \\ 0 & E_i > E. \end{array} \right. \tag{23.11}$$

This yields with the definition (23.10)

$$S = -k_\mathrm{B}\sum_i \rho_i \ln \rho_i = k_\mathrm{B} \ln W \tag{23.12}$$

in accordance with the original definition. Note, that

$$\lim_{\rho \to 0} \rho \ln \rho = 0. \tag{23.13}$$

Then we may define the entropy operator

$$\hat{S} = -k_\mathrm{B} \ln \rho \tag{23.14}$$

which reads for our generalized canonical ensembles

$$\hat{S} = \frac{1}{T}(H - \sum_i f_i \hat{Q}_i - K) \tag{23.15}$$

Then we obtain

$$\mathrm{d}K = -S\mathrm{d}T - \sum_i Q_i \mathrm{d}f_i \tag{23.16}$$

and

$$E = K + TS + \sum_i f_i Q_i. \tag{23.17}$$

For classical systems ρ under the logarithm has to be multiplied by $N!h^{3N}$,

$$S = -k_\mathrm{B}\int \mathrm{d}^{3N}p\mathrm{d}^{3N}x \rho \ln(N!h^{3N}\rho). \tag{23.18}$$

First we know, that only one quantum state fits into $\Delta p \Delta x = h$. The probability that it is occupied is obtained by multiplying ρ by the corresponding phase space, that is by the appropriate power of h.

Since equal particles are indistinguishable all $N!$ permutations of the coordinates (p_i, x_i) contribute to the state. Therefore the phase-space for an N-particle state (of equal particles) has to be multiplied by $N!$. One may object, that for bosons one and the same state can be occupied multiply, and that then the factor $N!$ is an overestimate. This is correct. If however, the occupation probability is that large, that this plays a role, then the classical calculation is no longer valid. Similar is the argument, that those regions of the phase-space, in which two fermions have practically the same coordinates should not be taken into account. Here, too, the following applies: If the occupation is so large that this plays a role for the final result, then one has to perform a quantum mechanical calculation. The first quantum correction had been calculated in section 17.

24 Second derivatives of thermodynamic potentials and fluctuations

24.a The Derivatives

We now consider the second derivatives of the thermodynamic potentials with respect to their natural variables. The first derivative was

$$-\frac{\partial K}{\partial f_i} = Q_i = \mathrm{tr}(\hat{Q}_i \underbrace{\mathrm{e}^{-\beta(H-\sum_j f_j \hat{Q}_j - K)}}_{\rho}). \tag{24.1}$$

The second turns out to be

$$\begin{aligned} \frac{\partial Q_i}{\partial f_j} &= \beta \mathrm{tr}(\hat{Q}_i \hat{Q}_j \rho) + \beta \underbrace{\frac{\partial K}{\partial f_j}}_{-Q_j} \mathrm{tr}(\hat{Q}_i \rho) \\ &= \frac{1}{k_\mathrm{B} T} \left(\langle \hat{Q}_i \hat{Q}_j \rangle - Q_i Q_j \right) = \frac{1}{k_\mathrm{B} T} \langle \Delta \hat{Q}_i \Delta \hat{Q}_j \rangle \end{aligned} \tag{24.2}$$

with $\Delta\hat{Q}_i = \hat{Q}_i - Q_i$ (section 3). Here we assume that $\hat{Q}_i$ or $\hat{Q}_j$ commutes with $H - \sum_i f_i \hat{Q}_i$. Then we obtain for the grand-canonical ensemble

$$\frac{\partial N}{\partial \mu} = \frac{1}{k_\mathrm{B} T} \langle (\Delta \hat{N})^2 \rangle = \frac{1}{k_\mathrm{B} T} (\Delta N)^2 = O(N^1). \tag{24.3}$$

The estimate $O(N^1)$ is obtained since we take the derivative of an extensive quantity (N) with respect to an intensive one ($\mu = O(N^0)$). Therefore normally the fluctuation of the particle number is of order $O(N^{1/2})$, thus small against the particle number in macroscopic systems. (Normally means: If $\frac{\partial N}{\partial \mu}$ remains finite.)
Further we consider

$$\frac{\partial Q_i}{\partial \beta} = -T \langle \hat{Q}_i \hat{S} \rangle + \beta \frac{\partial K}{\partial \beta} Q_i \tag{24.4}$$

and therefore

$$\frac{\partial Q_i}{\partial T} = -\frac{1}{k_\mathrm{B} T^2} \frac{\partial Q_i}{\partial \beta} = \frac{1}{k_\mathrm{B} T} \langle \hat{Q}_i \hat{S} \rangle + \frac{1}{k_\mathrm{B} T} \underbrace{\frac{\partial K}{\partial T}}_{-S} Q_i = \frac{1}{k_\mathrm{B} T} \langle \Delta \hat{Q}_i \Delta \hat{S} \rangle \tag{24.5}$$

with

$$\hat{S} = \frac{1}{T} \left(H - \sum_i f_i \hat{Q}_i - K \right), \quad \Delta \hat{S} = \frac{1}{T} \left(\Delta H - \sum_i f_i \Delta \hat{Q}_i \right). \tag{24.6}$$

We observe

$$\frac{\partial S}{\partial T} = \frac{1}{k_\mathrm{B} T} \langle (\Delta \hat{S})^2 \rangle. \tag{24.7}$$

For the canonical ensemble one obtains

$$\frac{\partial S}{\partial T} = \frac{1}{k_\mathrm{B} T^3} \langle (\Delta H)^2 \rangle = O(N^1). \tag{24.8}$$

Thus also the energy fluctuations are normally of order $O(N^{1/2})$ and thus negligible against the average energy for macroscopic systems.

24.b Special second derivatives

We consider now the specific heat. It is the amount of heat which has to be fed into the system divided by the change of temperature. Thus we have

$$C = \frac{\mathrm{d}Q}{\mathrm{d}T} = T\frac{\mathrm{d}S}{\mathrm{d}T}. \tag{24.9}$$

What is obtained in detail depends on the way the process is performed. If volume and particle number are kept fixed then one obtains

$$C_V = T\left.\frac{\partial S}{\partial T}\right|_{V,N}. \tag{24.10}$$

The formulation $\left.\frac{\partial S}{\partial T}\right|_{V,N}$ means that we differentiate S with respect to T at fixed V and N. This is equivalent to the partial derivative of the function $S(T,V,N)$ with respect to T. Since, however, one often changes the variables in thermodynamics, it would be necessary to distinguish different functions for different variables. Instead one prefers to indicate which quantities are kept fixed. If, however, pressure and particle number are fixed, then one obtains

$$C_P = T\left.\frac{\partial S}{\partial T}\right|_{P,N}. \tag{24.11}$$

For an ideal classical monatomic gas one obtains

$$S = k_{\mathrm{B}}N\ln\left(\frac{V}{N}(k_{\mathrm{B}}T)^{3/2}\left(\frac{2\pi m}{h^2}\right)^{3/2}\mathrm{e}^{5/2}\right), \qquad C_V = \frac{3}{2}k_{\mathrm{B}}N, \tag{24.12}$$

$$S = k_{\mathrm{B}}N\ln\left(\frac{1}{P}(k_{\mathrm{B}}T)^{5/2}\left(\frac{2\pi m}{h^2}\right)^{3/2}\mathrm{e}^{5/2}\right), \qquad C_P = \frac{5}{2}k_{\mathrm{B}}N. \tag{24.13}$$

Similarly one distinguishes between adiabatic and isothermal compressibility,

$$\kappa = -\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}P} \tag{24.14}$$

Similarly the magnetic susceptibility $\chi = \frac{\mathrm{d}M}{\mathrm{d}H}$ and the volume expansion coefficient depend on the way the change of the system is performed

$$\alpha = \frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}T}. \tag{24.15}$$

25 Thermodynamic Relations

25.a from the potentials

A number of thermodynamic relations can be obtained by differentiating the potentials. For example one obtains from

$$\begin{aligned} \mathrm{d}E &= T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N, && (25.1)\\ \mathrm{d}I &= T\mathrm{d}S + V\mathrm{d}P + \mu\mathrm{d}N && (25.2) \end{aligned}$$

relations between the specific heats

$$\begin{aligned} \left.\frac{\partial E}{\partial T}\right|_{V,N} &= T\left.\frac{\partial S}{\partial T}\right|_{V,N} = C_V, && (25.3)\\ \left.\frac{\partial I}{\partial T}\right|_{P,N} &= T\left.\frac{\partial S}{\partial T}\right|_{P,N} = C_P, && (25.4)\\ \left.\frac{\partial E}{\partial T}\right|_{P,N} &= T\left.\frac{\partial S}{\partial T}\right|_{P,N} - P\left.\frac{\partial V}{\partial T}\right|_{P,N} = C_P - PV\alpha_P. && (25.5) \end{aligned}$$

25.b from the conditions of integrability

The mixed second derivatives of the potentials have to agree (condition of integrability). Then one obtains from

$$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N \tag{25.6}$$

the condition

$$-\frac{\partial^2 F}{\partial V\partial T} = \left.\frac{\partial S}{\partial V}\right|_{T,N} = \left.\frac{\partial P}{\partial T}\right|_{V,N}. \tag{25.7}$$

Similarly

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}N \tag{25.8}$$

yields

$$-\frac{\partial^2 G}{\partial P\partial T} = \left.\frac{\partial S}{\partial P}\right|_{T,N} = -\left.\frac{\partial V}{\partial T}\right|_{P,N}. \tag{25.9}$$

These relations are called Maxwell-relations.

25.c Functional (Jacobi-) determinant

The Jacobian

$$\frac{\partial(f,g)}{\partial(x,y)} := \frac{\partial f}{\partial x}\frac{\partial g}{\partial y} - \frac{\partial f}{\partial y}\frac{\partial g}{\partial x} \tag{25.10}$$

obeys the chain-rule

$$\frac{\partial(f,g)}{\partial(x,y)} = \frac{\partial(f,g)}{\partial(u,v)}\frac{\partial(u,v)}{\partial(x,y)}. \tag{25.11}$$

Note that

$$\frac{\partial(f,y)}{\partial(x,y)} = \left.\frac{\partial f}{\partial x}\right|_{y} \tag{25.12}$$

and

$$\partial(f,g) = -\partial(g,f) \tag{25.13}$$

holds.

Now we derive a relation between the specific heats and the compressibilities. We transform

$$\begin{aligned}\frac{\partial(P,S,N)}{\partial(V,T,N)} = \frac{\partial(P,S,N)}{\partial(V,S,N)}\frac{\partial(V,S,N)}{\partial(V,T,N)} &= \frac{\partial(P,S,N)}{\partial(P,T,N)}\frac{\partial(P,T,N)}{\partial(V,T,N)} \\ = \left.\frac{\partial P}{\partial V}\right|_{S,N}\left.\frac{\partial S}{\partial T}\right|_{V,N} &= \left.\frac{\partial S}{\partial T}\right|_{P,N}\left.\frac{\partial P}{\partial V}\right|_{T,N} \\ = -\frac{1}{V\kappa_S}\frac{C_V}{T} &= \frac{C_P}{T}\left(-\frac{1}{V\kappa_T}\right),\end{aligned} \tag{25.14}$$

from which we obtain

$$\frac{\kappa_T}{\kappa_S} = \frac{C_P}{C_V} \tag{25.15}$$

We derive another connection between the specific heats

$$C_P = T\left.\frac{\partial S}{\partial T}\right|_{P,N} = T\left.\frac{\partial S}{\partial T}\right|_{V,N} + T\left.\frac{\partial S}{\partial V}\right|_{T,N}\left.\frac{\partial V}{\partial T}\right|_{P,N}. \tag{25.16}$$

We convert further

$$\left.\frac{\partial S}{\partial V}\right|_{T,N} = \left.\frac{\partial P}{\partial T}\right|_{V,N} = \frac{\partial(P,V,N)}{\partial(T,V,N)} = \frac{\partial(P,V,N)}{\partial(P,T,N)}\frac{\partial(P,T,N)}{\partial(T,V,N)} = \left.\frac{\partial V}{\partial T}\right|_{P,N}\cdot\Big(-\left.\frac{\partial P}{\partial V}\right|_{T,N}\Big) \tag{25.17}$$

and therefore

$$C_P = C_V + T(V\alpha_P)^2\frac{1}{V\kappa_T} = C_V + TV\frac{\alpha_P^2}{\kappa_T}. \tag{25.18}$$

The integrability condition (25.7)

$$\left.\frac{\partial P}{\partial T}\right|_{V,N} = \left.\frac{\partial S}{\partial V}\right|_{T,N} \tag{25.19}$$

yields

$$\frac{\partial(P,V,N)}{\partial(T,V,N)} = \frac{\partial(T,S,N)}{\partial(T,V,N)} \tag{25.20}$$

and thus

$$\partial(P,V,N) = \partial(T,S,N) \tag{25.21}$$

and similarly

$$\partial(P,V,\mu) = \partial(T,S,\mu), \quad \partial(P,V,T) = \partial(\mu,N,T). \tag{25.22}$$

25.d Homogeneity

If numerator and denominator of a Jacobian contain the same two intensive variables (T, P, μ) and one extensive variable, then from homogeneity it follows, that the Jacobian determinant is the ratio of the two extensive variables,

$$\frac{\partial(V,P,T)}{\partial(N,P,T)} = \left.\frac{\partial V}{\partial N}\right|_{P,T} = \frac{V}{N}. \tag{25.23}$$

This relation can be used to determine the isothermal compressibility from the grand canonical potential,

$$\begin{aligned}\kappa_T &= -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_{T,N} = -\frac{1}{V}\frac{\partial(V,N,T)}{\partial(P,N,T)} = -\frac{1}{N}\frac{\partial(V,N,T)}{\partial(P,V,T)} = \left(\frac{1}{N}\left.\frac{\partial N}{\partial P}\right|_{T,V}\right) \\ &= -\frac{1}{N}\frac{\partial(V,N,T)}{\partial(\mu,N,T)} = -\frac{V}{N^2}\frac{\partial(V,N,T)}{\partial(\mu,V,T)} = \frac{V}{N^2}\left.\frac{\partial N}{\partial\mu}\right|_{T,V}\end{aligned} \tag{25.24}$$

Considering that $N = -\frac{\partial J}{\partial\mu}$ the compressibility is obtained from the second derivative of the grand canonical potential with respect to μ.

26 Positivity of Entropy: Third Law of Thermodynamics

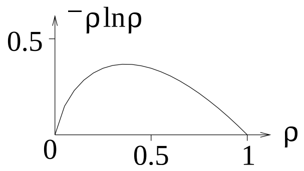
26.a Positivity

For all eigenvalues of the density matrix one has $0 \leq \rho_n \leq 1$ and thus $-\rho_n \ln \rho_n \geq 0$ and therefore

$$S = -k_{\mathrm{B}} \sum_n \rho_n \ln \rho_n \geq 0. \tag{26.1}$$

The entropy is never negative. It can only vanish, if each eigenvalue ρ_n equals either 0 or 1. Since $\sum_n \rho_n = 1$, then one of the eigenvalues equals one and the other ones vanish. Thus the entropy vanishes only for a pure state.

$-\rho \ln \rho$ *versus* ρ



The statement of the positivity requests the quantum nature of the system.
Formally in a part of the phase-space of a classical system ρ can be larger then $1/(N!h^{3N})$, which yields a negative contribution to the entropy. This, however, would violate fundamental principles of quantum mechanics and such a phase-space density cannot be a good description of a physical system.

26.b Third Law of Thermodynamics

We consider a large but finite system with discrete energy levels. The ground-state be g-fold degenerate. At absolute zero only the ground-states are occupied,

$$S(T=0) = k_{\mathrm{B}} \ln g. \tag{26.2}$$

g may even be macroscopically. An isotropic ferromagnet with total spin $\tilde{S} = O(N)$ has the degeneracy $g = 2\tilde{S} + 1$, that is $S(T=0) = k_{\mathrm{B}} \ln(2\tilde{S}+1) = O(\ln N)$. We see, however, that

$$\lim_{N\to\infty} \lim_{T\to 0} \frac{S}{N} = 0. \tag{26.3}$$

This is the statement of the third law of thermodynamics. It is possible to construct theoretical models with $S(T=0) \propto N$. (This can be done e.g. for ice-models. In these models the oxygen atoms are connected by hydrogen bridges, where the hydrogen is closer or remoter to one or the other oxygen. All states in which two hydrogen atoms are close to each oxygen are considered energetically degenerate.) It seems that in reality such high degeneracies are lifted.

27 Extremal Properties of the Entropy

27.a An Inequality

ρ and ρ' be two statistical operators with eigenstates

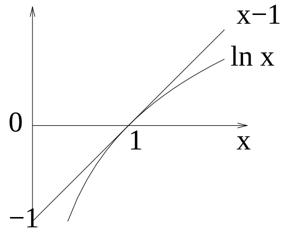
$$\rho|n\rangle = \rho_n|n\rangle, \quad \rho'|\nu\rangle = \rho'_\nu|\nu\rangle. \tag{27.1}$$

Then one has

$$\begin{aligned} \mathrm{tr}(\rho'(\ln\rho - \ln\rho')) &= \sum_{n,\nu} \langle\nu|\rho'|n\rangle\langle n|\ln\rho - \ln\rho'|\nu\rangle \\ &= \sum_{n,\nu} \rho'_\nu\langle\nu|n\rangle\langle n|\nu\rangle(\ln\rho_n - \ln\rho'_\nu). \end{aligned} \tag{27.2}$$

Now one has $\ln x \le x - 1$, which follows from $\ln x = \int_1^x \frac{\mathrm{d}x'}{x'}$ and $\frac{1}{x'} < 1$ for $x' > 1$ and $\frac{1}{x'} > 1$ for $x' < 1$

Graphical representation of the inequality $\ln x \le x-1$



$$\ln\rho_n - \ln\rho'_\nu = \ln\frac{\rho_n}{\rho'_\nu} \le \frac{\rho_n}{\rho'_\nu} - 1 \tag{27.3}$$

and

$$\mathrm{tr}(\rho'(\ln\rho - \ln\rho')) \le \sum_{n,\nu} |\langle\nu|n\rangle|^2(\rho_n - \rho'_\nu) = \sum_n \rho_n - \sum_\nu \rho'_\nu = 1 - 1 = 0, \tag{27.4}$$

that is

$$S' = -k_\mathrm{B}\sum_\nu \rho'_\nu \ln\rho'_\nu \le -k_\mathrm{B}\mathrm{tr}(\rho'\ln\rho). \tag{27.5}$$

The equal-sign holds only, if for each term in (27.4) either $\langle\nu|n\rangle = 0$ or $\rho_n = \rho'_\nu$, from which $\rho = \rho'$ follows.

27.b Microcanonical Ensemble

The statistical operator ρ' be composed from the states $|\nu\rangle$ of the Hilbert-space spanned by the eigenstates $|n\rangle$ of the Hamiltonian in the energy-interval $E - \Delta < E_n \le E$. ρ describes the microcanonical ensemble

$$\rho = \frac{1}{W(E) - W(E-\Delta)} \sum_{n, E-\Delta<E_n\le E} |n\rangle\langle n|. \tag{27.6}$$

Then one obtains

$$S' \le -k_\mathrm{B}\mathrm{tr}(\rho'\ln\rho) = k_\mathrm{B}\mathrm{tr}(\rho'\ln(W(E) - W(E-\Delta)) = S. \tag{27.7}$$

The microcanonical ensemble has the largest entropy of all ensembles which are composed from states in the energy-interval $E - \Delta...E$. A similar statement holds, if energy is replaced by enthalphy.

27.c Generalized (grand)canonical Ensemble

ρ be the statistical operator of the generalized canonical ensemble

$$\rho = \mathrm{e}^{-\beta(H - \sum_i f_i \hat{Q}_i - K)} \tag{27.8}$$

and ρ' be an arbitrary statistical operator. Then one obtains

$$S' \le k_{\mathrm{B}} \beta \mathrm{tr}(\rho'(H - \sum_i f_i \hat{Q}_i - K)) = \frac{1}{T}(E' - \sum_i f_i Q'_i - K). \tag{27.9}$$

With $K = E - \sum_i f_i Q_i - TS$ one obtains

$$S' \le S + \frac{1}{T}(E' - E + \sum_i f_i (Q_i - Q'_i)). \tag{27.10}$$

α) Be ρ' an ensemble with given expectation values $E' = E$, $Q'_i = Q_i$. Then one finds: The generalized canonical ensemble has the largest entropy of all ensembles with given expectation value of the energy and of the operators $\hat{Q}_i$. β) From the inequality (27.10) one obtains

$$K \le E' - TS' - \sum f_i Q'_i. \tag{27.11}$$

This allows for a variational principle in order to determine an upper bound for K for given T and f_is: One varies ρ' and looks for that with the lowest $E' - TS' - \sum f_i Q'_i$ as an approximation. This is a generalization of the variational principle to determine the groundstate ($T = 0$), $E \le E'$.

27.d Information entropy

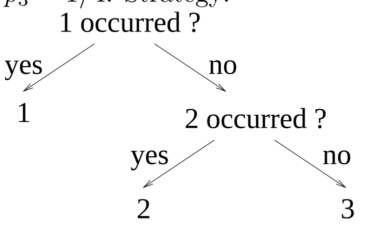
The expression

$$S = -k_{\mathrm{B}} \sum_n \rho_n \ln \rho_n \tag{27.12}$$

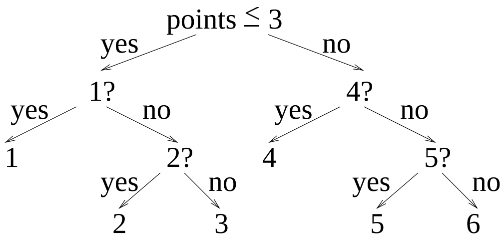
is closely related with the measure for information. For events n with a-priori probabilities ρ_n, $\sum_n \rho_n = 1$ one defines the information, that the event n occurs as $-\mathrm{ld}\rho_n$. Here ld is the logarithm to basis 2, $\mathrm{ld}\rho = ^2\log\rho = \ln\rho/\ln 2$. A rare event carries a larger amount of information, a frequent one only a small amount. Compare the amount of information of the two statements: "I hit the jackpot" and "I have drawn a blank". The averaged information is

$$I = -\sum_n \rho_n \mathrm{ld}\rho_n. \tag{27.13}$$

Obviously the relation is $S = k_{\mathrm{B}} I/\ln 2$. The meaning of I is the following:
α) If one follows an optimal strategy of questions, then one needs *in the average* at least I questions with answers yes or no (bits), in order to find out which event did occur.
β) There is always a strategy, so that *in the average* less than $I+1$ such questions are necessary to find out which event occurred. Example 1: Three events happen with probabilities $p_1 = 1/2$, $p_2 = 1/4$, $p_3 = 1/4$. Strategy:



One obtains $I = 3/2$, the average number of questions is $3/2$.
Example 2: One throws dices. Six possible events with probability $p_i = 1/6$. Strategy:



One finds $I = \mathrm{ld}6 = 2.584$. The average number of questions is $8/3 = 2.667$.
Apart from the factor in front the entropy S is an information entropy. It is characteristic for the microcanonical and the canonical ensembles that the missing information (on the state of the system) is maximal under the conditions given (energy boundaries or energy-expectation value). That is besides these conditions *nothing* is known on the state of the system.

Literatur/literature: Ash, Information Theory (Bibl. Ang. Math.), L. Brillouin, Science and Information Theory.

28 Second Law of Thermodynamics

The second law of thermodynamics says: The thermodynamic entropy of a closed system obeys $\mathrm{d}S/\mathrm{d}t \geq 0$. Thus the thermodynamic entropy of a closed system can only increase or stay constant as a function of time.

28.a Constance of information entropy

First we consider the development of the information entropy of a closed system. We represent $\rho(t)$ by its eigenstates at a certain time

$$\rho(t) = \sum_n |n(t)\rangle \rho_n \langle n(t)|. \tag{28.1}$$

The states $|n(t)\rangle$ need not be eigenstates of the hamiltonian. They develop according to

$$|m(t')\rangle = \mathrm{e}^{-\mathrm{i}H(t'-t)/\hbar}|m(t)\rangle, \quad \langle n(t')| = \langle n(t)|\mathrm{e}^{\mathrm{i}H(t'-t)/\hbar}. \tag{28.2}$$

Thus one obtains, that the states at time t' are also orthonormal

$$\langle n(t')|m(t')\rangle = \langle n(t)|m(t)\rangle = \delta_{n,m}. \tag{28.3}$$

Therefore one has

$$\rho(t') = \sum_n |n(t')\rangle \rho_n \langle n(t')|, \tag{28.4}$$

where $\rho(t')$ is expanded in its eigenstates, too. The eigenvalues ρ_n are unchanged. Then one obtains for the information entropy

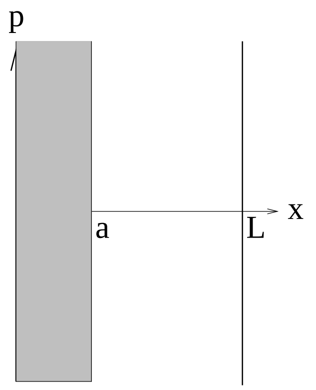
$$S(t') = -k_{\mathrm{B}} \sum_n \rho_n \ln \rho_n = S(t). \tag{28.5}$$

Thus the information entropy of a closed system is constant. This holds for classical systems, too.

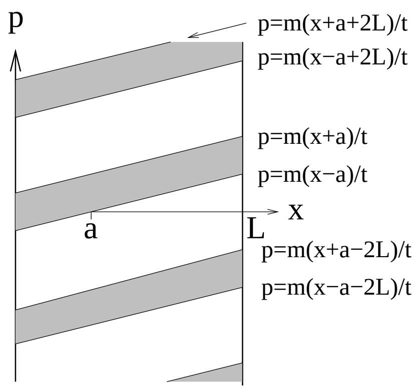
28.b Reversible and irreversible expansion of an ideal classical gas

Let us now consider an ideal classical gas which is heat insulated.
First we consider what happens, if the system undergoes a **slow expansion**. Then the system delivers the energy $P\mathrm{d}V$. Thus one has $\mathrm{d}E = -P\mathrm{d}V$ und thus $T\mathrm{d}S = 0$, that is $S =$const. This is an adiabatic process. The process is reversible, both $\mathrm{d}V/\mathrm{d}t > 0$ and $\mathrm{d}V/\mathrm{d}t < 0$ are possible without change of entropy.
Next we consider a **fast expansion**: The wall should move faster then the average thermal velocity, or we remove suddenly a wall of the vessel. Then the system does (nearly) not deliver energy. The pressure exerted on the wall is much less then the internal pressure, $\mathrm{d}E \approx 0$. Since for fixed energy the entropy increases (in equilibrium) with the volume, we have $\dot{S} > 0$, $\dot{V} > 0$. The process is irreversible, since it is not possible to capture the particles in the original volume without doing work.
Now there is the question: Does the entropy increase? Does the system approach equilibrium?
For this purpose we consider what happens to an ideal gas, if we remove the wall at time $t = 0$. Up to this time all atoms be in the box $0 \leq x \leq a$. For $t > 0$ the atoms can move freely in the larger box $0 \leq x \leq L > a$.

All atoms in the box $0 \leq x \leq a$ at time $t = 0$.



At times $t > 0$ free motion in the box $0 \le x \le L$.



Now a streak structure develops: In the (x,p) space occupied and unoccupied regions change frequently. The information entropy (microscopic entropy) is conserved. For $t \to \infty$ the stripes become smaller and smaller. Then one replaces ρ by an ρ averaged in some region of the Γ-space: coarse graining. The assumption is, that one cannot draw any use out of the streak structure. The situation becomes more apparent, if one takes the interaction into account. Then the averaged one-particle density $\rho_1(p,x)$ does no longer show a streak structure, but the N-particle density ρ.
We have assumed that the particles are reflected ideally at the walls. If this is not the case, then the system is coupled to its surroundings. This induces a fading of the streak structure and consequently an increase of the entropy of the gas in the box. A pure state coupled to another system will not remain in generally a pure state, but develop into a mixture with increasing entropy.

28.c Thermodynamical entropy

The thermodynamical entropy is the maximal information entropy for a system with given expectation values (e.g. for energy, volume, etc.) One replace the actual ρ by an averaged one. This averaging (coarse graining) yields practically no difference for expectation values like $\langle H\rangle$, $\langle \hat{Q}_i\rangle$, but an essential difference for the entropy. Generally one has
information entropy $\le$ thermodynamical entropy
In considering expectation values one need not confine oneself to quantities of the whole system. One may for example introduce space-dependent densities, or as we will show in the following, averaged occupation numbers for particles of different momenta.

28.d Boltzmann-equation

If we now assume, that we can describe the system by the average occupation $\bar{n}$. Then the following picture emerges: The entropy can be expressed in terms of the occupation numbers. It turns out, that again eqs. (16.20, 16.21) hold (for simplicities' sake we leave aside the other quantum numbers)

$$S = k_{\rm B} \sum_{\mathbf{k}} ((\pm(1 \pm \bar{n}_{\mathbf{k}}) \ln(1 \pm \bar{n}_{\mathbf{k}}) - \bar{n}_{\mathbf{k}} \ln \bar{n}_{\mathbf{k}})) \tag{28.6}$$

This is immediately clear for fermions (lower sign), since there the $n_{\mathbf{k}}$ assume only the values 0 and 1. Thus the probabilities w_n for n-fold occupation are given by $w_0 = 1 - \bar{n}$, $w_1 = \bar{n}$ with the contribution

$$-k_{\rm B}(w_0 \ln w_0 + w_1 \ln w_1) = -k_{\rm B}(1-\bar{n}) \ln(1-\bar{n}) - k_{\rm B}\bar{n} \ln \bar{n} \tag{28.7}$$

to the entropy. For bosons we have the contribution to the entropy $-k_{\rm B}\sum_n w_n \ln w_n$. One adds by means of Lagrange parameters κ and λ the conditions for total probability 1 and average occupation $\bar{n}$, so that

$$-k_{\rm B} \sum_n w_n \ln w_n + \kappa(\sum_n w_n - 1) + \lambda(\sum_n n w_n - \bar{n}) \tag{28.8}$$

has to be varied. The variation of w_n yields

$$-k_{\rm B}(1 + \ln w_n) + \kappa + \lambda n = 0. \tag{28.9}$$

If one solves the equation with respect to w_n and determines κ and λ from the auxiliary conditions, then one obtains the distribution (16.11) and evaluates the entropy (16.20).
The change of entropy in the course of time is then given by

$$\dot{S} = k_{\mathrm{B}} \sum_{\mathbf{k}} \dot{\bar{n}}_{\mathbf{k}} \left(\ln(1 \pm \bar{n}_{\mathbf{k}}) - \ln \bar{n}_{\mathbf{k}} \right) \tag{28.10}$$

From Fermi's golden rule we now that the transition probability from a many-particle state n to m is given by

$$\Gamma_{m,n} = \frac{2\pi}{\hbar} \delta(E_n - E_m) |\langle n|V|m\rangle|^2 \tag{28.11}$$

We apply this to a system interacting via two-particle interaction and consider the scattering of two atoms with momenta $\hbar\mathbf{k}_3$ and $\hbar\mathbf{k}_4$ into atoms with momenta $\hbar\mathbf{k}$ und $\hbar\mathbf{k}_2$.
Then we obtain for the average occupation of the one-particle state with momentum $\hbar\mathbf{k}$ die Boltzmann-equation (integrated over local space)

$$\dot{\bar{n}}_{\mathbf{k}} = \frac{1}{2} \sum_{\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} \Gamma_{\mathbf{k},\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} \left(\langle \hat{n}_{\mathbf{k}_3} \hat{n}_{\mathbf{k}_4} (1 \pm \hat{n}_{\mathbf{k}})(1 \pm \hat{n}_{\mathbf{k}_2}) \rangle - \langle \hat{n}_{\mathbf{k}} \hat{n}_{\mathbf{k}_2} (1 \pm \hat{n}_{\mathbf{k}_3})(1 \pm \hat{n}_{\mathbf{k}_4}) \rangle \right) \tag{28.12}$$

The factor $\frac{1}{2}$ has been introduced, since otherwise the scattering from $\mathbf{k}_3$, $\mathbf{k}_4$ and from $\mathbf{k}_4$, $\mathbf{k}_3$ would be counted twice. We note, that Γ contains two δ-factors because of energy conservation and momentum conservation,

$$\Gamma_{\mathbf{k},\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} \propto \delta(\epsilon_{\mathbf{k}} + \epsilon_{\mathbf{k}_2} - \epsilon_{\mathbf{k}_3} - \epsilon_{\mathbf{k}_4}) \delta(\mathbf{k} + \mathbf{k}_2 - \mathbf{k}_3 - \mathbf{k}_4) \tag{28.13}$$

The factors $\hat{n}_{\mathbf{k}_3}\hat{n}_{\mathbf{k}_4}$ in the expectation value in (28.12) are immediately obvious. The rate of the transitions from $\mathbf{k}_3$ and $\mathbf{k}_4$ is of course proportional to the corresponding occupations. There is also a back-scattering from $\mathbf{k}$, $\mathbf{k}_2$. This is described by the second expectation value in (28.12). If the gas is dilute, then one may replace the factors $1 \pm \hat{n}$ in the expectation values by 1. For fermions the factor can easily be understood. If the state with momentum $\hbar\mathbf{k}$ is already occupied, then it is not possible to scatter anything into this state, thus the factor $1 - \hat{n}$. For bosons one obtains instead a factor $1 + \hat{n}$. The process is stimulated, if the state is already occupied.
One assumes, that there is no correlation between the occupations, thus one puts

$$A := \langle \hat{n}_{\mathbf{k}_3} \hat{n}_{\mathbf{k}_4} (1 \pm \hat{n}_{\mathbf{k}})(1 \pm \hat{n}_{\mathbf{k}_2}) \rangle = \bar{n}_{\mathbf{k}_3} \bar{n}_{\mathbf{k}_4} (1 \pm \bar{n}_{\mathbf{k}})(1 \pm \bar{n}_{\mathbf{k}_2}). \tag{28.14}$$

and similarly for the other expectation value

$$B := \bar{n}_{\mathbf{k}} \bar{n}_{\mathbf{k}_2} (1 \pm \bar{n}_{\mathbf{k}_3})(1 \pm \bar{n}_{\mathbf{k}_4}) \tag{28.15}$$

This is an essential approximation. It is called molecular chaos. It assumes that correlations do not play an essential role. Then one obtains

$$\dot{S} = \frac{k_{\mathrm{B}}}{2} \sum_{\mathbf{k},\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} \Gamma_{\mathbf{k},\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} (\ln(1 \pm n_{\mathbf{k}}) - \ln n_{\mathbf{k}})(A - B). \tag{28.16}$$

If we take into account, that Γ and $A - B$ are invariant against interchange of $\mathbf{k}$ and $\mathbf{k}_2$, and that by the exchange of the pair $\mathbf{k}, \mathbf{k}_2$ with the pair $\mathbf{k}_3, \mathbf{k}_4$ again Γ is invariant and $A - B$ changes sign, then we may write

$$\dot{S} = \frac{k_{\mathrm{B}}}{8} \sum_{\mathbf{k},\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} \Gamma_{\mathbf{k},\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} (\ln B - \ln A)(B - A) \tag{28.17}$$

Obviously the entropy S increases until one has $A = B$ or equivalently $\ln B = \ln A$ for all terms with $\Gamma \neq 0$. If $\ln B = \ln A$, then one has

$$\nu_{\mathbf{k}} + \nu_{\mathbf{k}_2} = \nu_{\mathbf{k}_3} + \nu_{\mathbf{k}_4} \text{ with } \nu_{\mathbf{k}} = \ln \frac{\bar{n}_{\mathbf{k}}}{1 \pm \bar{n}_{\mathbf{k}}}. \tag{28.18}$$

Since $\Gamma \neq 0$ holds only for energy-conservation and momentum-conservation and in our case there is also particle-conservation one has $A = B$ for

$$\nu_{\mathbf{k}} = -\beta(\epsilon_{\mathbf{k}} - \mathbf{v}\hbar\mathbf{k} - \mu) \tag{28.19}$$

which yields

$$\bar{n}_{\mathbf{k}} = \frac{1}{\mathrm{e}^{\beta(\epsilon_{\mathbf{k}} - \mathbf{v}\hbar\mathbf{k} - \mu)} \mp 1} \tag{28.20}$$

As long as momentum-conservation is not perturbed (e. g. by the walls of a vessel) the particles can move with an averaged velocity $\mathbf{v}$. For $\mathbf{v} = \mathbf{0}$ this is the Bose- and Fermi-distribution, resp.

29 Carnot Cycle

A Carnot cycle is a process where some medium works reversible between two heat reservoirs and returns to its original state. If the machine works optimally then the total entropy is conserved. If the entropy increases, then one looses reversible (e.g. mechanical) energy to the second-rate heat energy. In reality each periodically working machine produces entropy, the more, the faster it runs. A reversible process is an idealization: It shows the limit of what can be reached.
Principle of the Carnot process: A cycle in four steps α) isothermal change at $T = T_1$. The working medium takes an amount of heat $Q_1 = T_1 \Delta S$ out of the reservoir with temperature T_1. β) The system goes adiabatically (S =const., heat insulated) to the temperature T_2. γ) a second isothermal change, $T = T_2$, the working medium gives to the second reservoir the amount $Q_2 = T_2 \Delta S$. δ) the system goes adiabatically (S =const.) back to temperature T_1.
We consider now the **heat balance** and observe

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}. \tag{29.1}$$

This can be used to determine the temperature scale without ideal gas.
For the **energy balance** one finds: The working medium takes the amount $Q_1 = T_1 \Delta S$ of heat and delivers $Q_2 = T_2 \Delta S$ of heat. Energy conservation requires, that the work A done by this medium is

$$A = Q_1 - Q_2 = (T_1 - T_2)\Delta S. \tag{29.2}$$

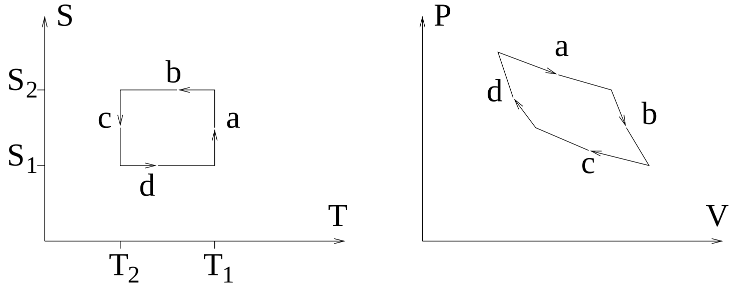
29.a Various Applications

The Carnot cycle can be used in various ways:

29.a.α Heat engines

In the T, S- and the P, V-diagram one obtains the following picture

Carnot cycle of the heat engine in the ST and the PV-diagram



The work delivered is $A = \oint P \mathrm{d}V$. In (25.21) we have shown that $\partial(P, V, N) = \partial(T, S, N)$. Therefore the net heat

$$Q_1 - Q_2 = \oint T \mathrm{d}S = \oint P \mathrm{d}V = A \tag{29.3}$$

fed into the system equals the work A done by the system. The enclosed areas in both figures are equal. The ideal efficiency is the ratio of the obtained work A to the heat Q_1 fed into the machine,

$$\eta = \frac{A}{Q_1} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1} < 1. \tag{29.4}$$

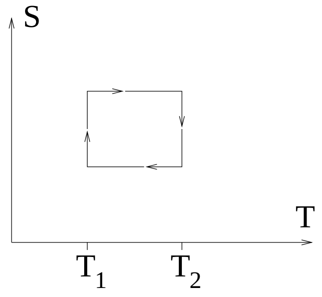
29.a.β Heat Pump

The heat pump works the other way around. One feeds work $-A$ into these machines (mechanical or electrical) and extracts heat at the higher temperature T_2. The ideal efficiency is obtained from the ratio of the heat Q_2 to the work $-A$.

$$\eta = \frac{Q_2}{-A} = \frac{T_2}{T_2 - T_1} = \frac{1}{1 - T_1/T_2} > 1. \tag{29.5}$$

The heat pump does not only convert work into heat, but pumps moreover heat from the cold reservoir to the warm one.

Carnot cycle of the heat pump



29.a.γ Refrigerator

The refrigerator works in the same direction as the heat pump. However, now one is interested in the heat which is extracted from the colder reservoir. Thus the efficiency is now given by the ratio of the heat Q_1 to the work $-A$, in the ideal case

$$\eta = \frac{Q_1}{-A} = \frac{T_1}{T_2 - T_1}. \tag{29.6}$$

For a conventional refrigerator, where $T_2 - T_1 \ll T_1$, one can have $\eta > 1$. For a real low-temperature machine where $T_1 \ll T_2 - T_1$ one has an efficiency $\eta \ll 1$.
Do not forget to insert the temperatures T in kelvin for these calculations.

29.b Exergy

There is much talk about the energy crisis. In reality it is not an energy crisis. After all energy is conserved. However, we know meanwhile that heat is in a certain sense a second class energy. It can only be transformed in a limited amount into an energy of first class like mechanical or electrical energy. Therefore one asks the question: If one has a certain substance in a given environment, how much work can one extract from this substance by bringing it into equilibrium with the environment? This work is called exergy.
We assume, that we work with two species of particles and that the reservoir (environment) has temperature T_0, pressure P_0, and the chemical potentials μ_{a0} and μ_{b0}.
Now we perform several steps, in which the system will deliver mechanical work against the external pressure

$$A = \int (P - P_0)\mathrm{d}V = \int P\mathrm{d}V - P_0(V_0 - V) \tag{29.7}$$

with

$$P\mathrm{d}V = -\mathrm{d}E + T\mathrm{d}S + \mu_a \mathrm{d}N_a + \mu_b \mathrm{d}N_b. \tag{29.8}$$

In a first step we keep S, N_a, and N_b fixed and change V until our substance has the temperature of the environment, $T = T_0$. Then we have

$$P\mathrm{d}V = -\mathrm{d}E, \quad \mathrm{d}S = 0, \quad \mathrm{d}N_a = 0, \quad \mathrm{d}N_b = 0. \tag{29.9}$$

In a second step we keep T_0, N_a, N_b fixed and change the volume of our substance until $\mu_a = \mu_{a0}$. Then we have

$$P\mathrm{d}V = -\mathrm{d}E + T_0\mathrm{d}S, \quad \mathrm{d}N_a = 0, \quad \mathrm{d}N_b = 0. \tag{29.10}$$

In a third step we introduce a semipermeable membrane, which allows particles a to pass but is impermeable to particles b. If we move this membrane, then we have

$$P\mathrm{d}V = -\mathrm{d}E + T_0\mathrm{d}S + \mu_{a0}\mathrm{d}N_a, \quad \mathrm{d}N_b = 0. \tag{29.11}$$

In total the system has done the work

$$
\begin{aligned}
A &= -\int \mathrm{d}E + T_0 \int \mathrm{d}S + \mu_{a0} \int \mathrm{d}N_a - P_0(V_0 - V) \\
&= E - E_0 + T_0(S_0 - S) + \mu_{a0}N_{a0} - \mu_{a0}N_a - P_0V_0 + P_0V. \qquad (29.12)
\end{aligned}
$$

If we consider that the substance b is in equilibrium with the reservoir after the third step, $N_b = N_{b0}$, and that

$$E_0 = T_0S_0 - P_0V_0 + \mu_{a0}N_{a0} + \mu_{b0}N_{b0}, \qquad (29.13)$$

then we obtain for the work, which can maximally be extracted from the substance

$$A = E - T_0S + P_0V - \mu_{a0}N_a - \mu_{b0}N_b. \qquad (29.14)$$

This is the exergy of the substance. It is simultaneously the minimum amount of work required to produce this substance in the given environment.
If we add an index $_0$ to the unprimed quantities in eq. (27.10) and remove the primes from the primed quantities, then we obtain for the potential $K_0 = E_0 - \mu_{a0}N_{a0} + P_0V_0 - T_0S_0 = \mu_{b0}N_{b0}$ the inequality

$$S \leq S_0 + \frac{1}{T}(E - E_0 + \mu_{a0}(N_{a0} - N_a) - P_0(V_0 - V)) \qquad (29.15)$$

and thus $A \geq 0$. As expected this work can never be negative.

E Interacting Systems

30 Virial Expansion

This is an expansion for small densities starting from an expansion in powers of $e^{\beta\mu}$.

30.a Grand canonical potential

We expand the grand canonical partition function by summing the contributions for various particle-numbers

$$Y = \sum_N Z(T,V,N)e^{N\mu/k_BT} = 1 + Z(T,V,1)e^{\mu/k_BT} + Z(T,V,2)e^{2\mu/k_BT} + ... \tag{30.1}$$

This is not a good expansion, since one has to sum up to very large particle numbers. It is much better to expand its logarithm

$$\ln Y = \underbrace{Z(1)e^{\mu/k_BT}}_{\text{one-particle problem}} + \underbrace{(Z(2) - \frac{1}{2}Z^2(1))e^{2\mu/k_BT}}_{\text{two-particle problem}} + ... \tag{30.2}$$

The potential energy be a sum of two-particle interactions,

$$H_{\text{pot}} = \sum_{i<j} W(x_i - x_j). \tag{30.3}$$

Then one obtains for the classical system

$$Z_{\text{kl}}(1) = \frac{V}{\lambda^3}, \tag{30.4}$$

$$Z_{\text{kl}}(2) = \frac{1}{2\lambda^6}\int d^3x_1 d^3x_2 e^{-\beta W(x_1-x_2)} \tag{30.5}$$

$$\begin{aligned} Z_{\text{kl}}(2) - \frac{1}{2}Z^2_{\text{kl}}(1) &= \frac{1}{2\lambda^6}\int d^3x_1 d^3x_2 \left(e^{-\beta W(x_1-x_2)} - 1\right) \\ &= \frac{V}{2\lambda^6}\int d^3x \left(e^{-\beta W(x)} - 1\right). \end{aligned} \tag{30.6}$$

One calls

$$b_{\text{kl}}(T) = -\frac{1}{2}\int d^3x(e^{-\beta W(x)} - 1) \tag{30.7}$$

the second virial coefficient and writes generally (including the quantum case)

$$Z(2) - \frac{1}{2}Z^2(1) = -\frac{V}{\lambda^6}b(T). \tag{30.8}$$

30.b Equation of state

From this expression we can determine the equation of state

$$\frac{PV}{k_B T} = \ln Y = \frac{V e^{\beta\mu}}{\lambda^3} - \frac{V e^{2\beta\mu}}{\lambda^6} b(T) + O(\frac{e^{3\beta\mu}}{\lambda^9}), \tag{30.9}$$

$$N = \frac{1}{\beta}\frac{\partial \ln Y}{\partial \mu} = \frac{V}{\lambda^3} e^{\beta\mu} - 2\frac{V e^{2\beta\mu}}{\lambda^6} b(T) + ... \tag{30.10}$$

$$\frac{V}{\lambda^3} e^{\beta\mu} = N + 2V\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^2 b(T) + ... = N + 2b(T)\frac{N^2}{V} + ... \tag{30.11}$$

and therefore

$$\frac{P}{k_B T} = \frac{N}{V} + b(T)\frac{N^2}{V^2} + O(\frac{N^3}{V^3}) \tag{30.12}$$

This expansion is called virial expansion. We note that we obtained for the ideal quantum gas in eq.(17.3)

$$b_{\text{id.qu.}} = \mp \frac{\lambda^3}{\sqrt{32}(2S+1)} \tag{30.13}$$

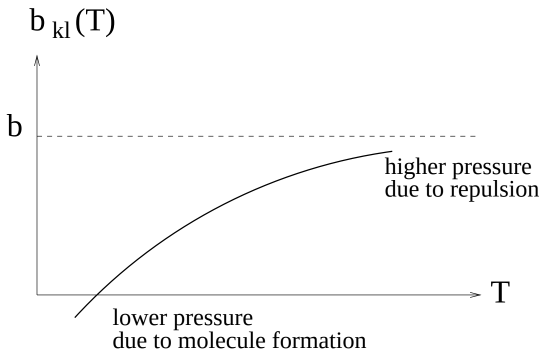
A simple approximation for $b_{\text{kl}}(T)$ is the following: The potential be strongly repelling for $|x_{12}| < c$ and weakly attractive for $|x_{12}| > c$

$$e^{-\beta W(x)} - 1 = \begin{cases} -1 & |x| \leq c, \\ -\beta W(x) & |x| > c. \end{cases} \tag{30.14}$$

Then one obtains

$$b_{\text{kl}}(T) = b - \frac{a}{k_B T}, \tag{30.15}$$

where $b = \frac{1}{2}\frac{4\pi}{3}c^3$ is four times the volume of the hard sphere and $a = -\frac{1}{2}\int_{r>c} d^3 r W(r)$. In case of attraction one has $W < 0$, $a > 0$. $b_{\text{kl}}(T)$ *versus* T.

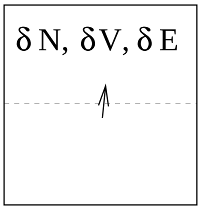


31 Phase Equilibria

31.a One component

The state of a homogeneous body in equilibrium is normally determined by giving the extensive quantities, e.g. energy, volume and particle number. It can happen that given these quantities the body is not homogeneous but consists of two states in touch with each other, which have different properties, as e.g. different density. Such states are called different phases of a component.

These phases have as all substances in equilibrium the same temperature, the same pressure and the same chemical potential. This is due to the fact that the entropy of the total system assumes its maximum.If one increases the energy of one phase by δE, its particle number by δN, and its volume by δV, then the change of the total entropy is



$$\delta S_{\text{tot}} = \underbrace{\left(\frac{1}{T} - \frac{1}{T'}\right)}_{0} \delta E - \underbrace{\left(\frac{\mu}{T} - \frac{\mu'}{T'}\right)}_{0} \delta N + \underbrace{\left(\frac{P}{T} - \frac{P'}{T'}\right)}_{0} \delta V, \tag{31.1}$$

which yields

$$T = T', \quad P = P', \quad \mu = \mu'. \tag{31.2}$$

If one expresses the chemical potentials as function of pressure and temperature, then one obtains the condition of equilibrium

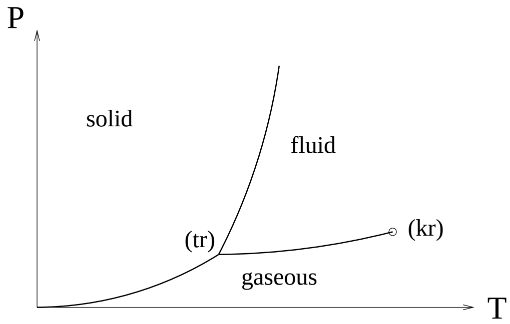
$$\mu(P,T) = \mu'(P,T). \tag{31.3}$$

This equation defines the coexistence curve $P(T)$ of two phases, as for example for the gaseous and the liquid phase. If there are three phases in equilibrium as at the triple point, then one has

$$\mu(P,T) = \mu'(P,T) = \mu''(P,T). \tag{31.4}$$

These two equations define the triple point

Schematic phase diagram



Latent heat We consider the transition of δN particles from the primed phase to the unprimed one. Then the system absorbs the heat

$$\delta Q = T\left(\left.\frac{\partial S}{\partial N}\right|_{P,T} - \left.\frac{\partial S'}{\partial N'}\right|_{P,T}\right)\delta N = T\left(\frac{S}{N} - \frac{S'}{N'}\right)\delta N \tag{31.5}$$

and its volume increases by

$$\delta V = \left(\left.\frac{\partial V}{\partial N}\right|_{P,T} - \left.\frac{\partial V'}{\partial N'}\right|_{P,T}\right)\delta N = \left(\frac{V}{N} - \frac{V'}{N'}\right)\delta N \tag{31.6}$$

Now we have

$$N \mathrm{d}\mu + S \mathrm{d}T - V \mathrm{d}P = 0, \tag{31.7}$$

thus

$$\mathrm{d}\mu = -\frac{S}{N}\mathrm{d}T + \frac{V}{N}\mathrm{d}P = -\frac{S'}{N'}\mathrm{d}T + \frac{V'}{N'}\mathrm{d}P = \mathrm{d}\mu', \tag{31.8}$$

thus

$$\left(\frac{S}{N} - \frac{S'}{N'}\right)\mathrm{d}T = \left(\frac{V}{N} - \frac{V'}{N'}\right)\mathrm{d}P \tag{31.9}$$

along the coexistence curve. From this we obtain the relation of Clausius and Clapeyron

$$\frac{\delta Q}{\delta V} = T\frac{\mathrm{d}P(T)}{\mathrm{d}T}, \tag{31.10}$$

which gives a connection between the latent heat δQ, the volume change δV and the change of pressure along the coexistence curve as the temperature is changed.
Example: We consider the equilibrium of a substance with its vapor. The volume of the solid or liquid state be negligible. If we assume the ideal gas equation $PV = Nk_\mathrm{B}T$ for the vapor phase, which implies for the transition $P\delta V = k_\mathrm{B}T\delta N$, then we obtain with $q = \delta Q/\delta N$

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{q\delta N}{T\delta V} = \frac{qP}{k_\mathrm{B}T^2}. \tag{31.11}$$

If q is approximately constant, then one has

$$P(T) = P_0\mathrm{e}^{-q/(k_\mathrm{B}T)}. \tag{31.12}$$

31.b Several components

For n different substances (components) (with total particle numbers N_1, ... N_n) and m phases, one has

$$\mu_1 = \mu_1' = ... = \mu_1^{(m-1)}, \tag{31.13}$$
$$... \tag{31.14}$$
$$\mu_n = \mu_n' = ... = \mu_n^{(m-1)}. \tag{31.15}$$

These are in total $n(m-1)$ equations. Variables are P and T and the $m(n-1)$ independent concentrations. Then there remain

$$f = 2 + m(n-1) - n(m-1) = 2 + n - m \tag{31.16}$$

free independent variables. (Gibbs' phase rule). For one component ($n = 1$) we already found this. If we consider a saturated solution, that is a solution in equilibrium with its solute, then one has $n = 2$, $m = 2$, $f = 2$; the saturation concentration is a function of the two variables pressure and temperature, $c_\mathrm{s}(P, T)$.

32 Dilute Solutions

32.a Osmotic pressure

Let us denote the particle number and the chemical potential of the solvent by $\bar{N}$ and by $\bar{\mu}$ and those of the solute by N_1 and μ_1 then the grand canonical partition function can be written

$$Y = \sum_{N_1} Y_{N_1}(\bar{\mu}, T, V)\mathrm{e}^{\beta\mu_1 N_1} = Y_0(\bar{\mu}, T, V) + Y_1(\bar{\mu}, T, V)\mathrm{e}^{\beta\mu_1} + ... \tag{32.1}$$

Y_{N_1} is the grand canonical partition function for the solvent with N_1 particles of the solute. Then one obtains

$$\ln Y = \ln Y_0 + V y_1(\bar{\mu}, T)\mathrm{e}^{\beta\mu_1} + O(\mathrm{e}^{2\beta\mu_1}) \tag{32.2}$$

with

$$V y_1 = \frac{Y_1}{Y_0}. \tag{32.3}$$

From this one obtains the particle number of the solute

$$N_1 = \frac{\partial \ln Y}{\beta \partial \mu_1} = V y_1(\bar{\mu}, T)\mathrm{e}^{\beta\mu_1} + O(\mathrm{e}^{2\beta\mu_1}), \tag{32.4}$$

from which one obtains the pressure

$$P(\bar{\mu}, T, N_1) = \frac{k_\mathrm{B}T}{V} \ln Y = P(\bar{\mu}, T, 0) + k_\mathrm{B}T\frac{N_1}{V} + O(\frac{N_1^2}{V^2}) \tag{32.5}$$

Note that the function y_1 does not appear in this order. Thus if two solutions are separated by a semipermeable membrane which is permeable for the solvent, but not for the solute, then the pressure difference

$$\Delta P = k_\mathrm{B}T\frac{\Delta N_1}{V} \tag{32.6}$$

acts on the membrane. This is van't Hoff's formula for the osmotic pressure. In this and the following calculations we take only the terms in lowest order in the concentration of the solute into account. Therefore they are only valid for dilute systems.

32.b Equilibrium shift

Now we will consider how the melting and boiling curve of the solvent is displaced. For this purpose we consider for fixed V and T the change of pressure

$$\mathrm{d}P = \left.\frac{\partial P}{\partial \bar{\mu}}\right|_{V,T,N_1=0} \mathrm{d}\bar{\mu} + \frac{k_\mathrm{B}T}{V}\mathrm{d}N_1 = \frac{\bar{N}}{V}\mathrm{d}\bar{\mu} + \frac{k_\mathrm{B}T}{V}\mathrm{d}N_1 \tag{32.7}$$

Thus one obtains for fixed pressure

$$\mathrm{d}\bar{\mu} = -\frac{k_\mathrm{B}T}{\bar{N}}\mathrm{d}N_1 \tag{32.8}$$

and thus for the chemical potential

$$\bar{\mu}(P, T, N_1) = \bar{\mu}(P, T, 0) - \frac{k_\mathrm{B}T}{\bar{N}}N_1 = \mu(P, T) - k_\mathrm{B}Tc_1, \tag{32.9}$$

where μ is the chemical potential of the pure solvent and $c_1 = N_1/\bar{N}$ the concentration of the solute. For two phases in equilibrium one has $\bar{\mu} = \bar{\mu}'$, thus

$$\mu(P, T) - k_\mathrm{B}Tc = \mu'(P, T) - k_\mathrm{B}Tc'. \tag{32.10}$$

For the shift we introduce

$$P = P_0 + \Delta P, \quad T = T_0 + \Delta T, \tag{32.11}$$

and use

$$\mu(P,T) = \mu(P_0,T_0) + \underbrace{\left.\frac{\partial\mu}{\partial P}\right|_T}_{\frac{V}{N}=v} \Delta P + \underbrace{\left.\frac{\partial\mu}{\partial T}\right|_P}_{-\frac{S}{N}=-s} \Delta T \tag{32.12}$$

and obtain

$$(v - v')\Delta P - (s - s')\Delta T = k_\mathrm{B}T(c - c'). \tag{32.13}$$

As a special case we consider the lowering of vapor pressure. The unprimed phase be the vapor ($c = 0$ is assumed), the primed phase the liquid ($v' \ll v$). With $\Delta T = 0$ one obtains

$$v\Delta P = -k_\mathrm{B}Tc', \quad \rightarrow \quad \frac{\Delta P}{P_0} = -c'. \tag{32.14}$$

This is Raoult's law.
Another special case is the lowering of the freezing point. Now we keep the pressure unchanged, $\Delta P = 0$. The unprimed phase be liquid, the primed solid. The solute be not solved in the solid phase, $c' = 0$. Since $q = T(s - s')$ is the heat disposed at freezing, then one obtains the lowering of the freezing point

$$\Delta T = -\frac{k_\mathrm{B}T^2c}{q}. \tag{32.15}$$

32.c Saturation concentration and the heat of dilution

The solution of a solute be in equilibrium with the solute, so that the solution is saturated. The chemical potential of the solute in the solution is given by

$$\mu_1 = k_\mathrm{B}T \ln \frac{N_1}{V y_1(\mu,T)} = k_\mathrm{B}T \ln c_1 + g_1(P,T) + O(c_1) \tag{32.16}$$

with

$$g_1(P,T) = -k_\mathrm{B}T \ln y_1(\mu(P,T),T) + k_\mathrm{B}T \ln(\bar{n}(P,T)), \tag{32.17}$$

where $\bar{n}$ is the particle density of the solvent. Denoting the chemical potential of the pure solute by $\mu'(P,t)$ we obtain

$$\mu'(P,T) = \mu_1(P,T,c_\mathrm{s}) \tag{32.18}$$

and therefore the saturation concentration c_s is given by

$$c_\mathrm{s} = \mathrm{e}^{(\mu'(P,T) - g_1(P,T))/(k_\mathrm{B}T)}. \tag{32.19}$$

The heat of dilution is the heat which has to be removed from a system, if the pure solute is solved in the solvent at constant pressure and then the system is brought back to the initial temperature. If the energy is initially given by E_a and finally by E_e (at given temperature) and if the volume changes from V_a to V_e (at external pressure P) then the heat to be removed is the energy gain $E_\mathrm{a} - E_\mathrm{e}$ minus the work $P(V_\mathrm{e} - V_\mathrm{a})$ done against the external pressure,

$$\delta Q = (E_\mathrm{a} + PV_\mathrm{a}) - (E_\mathrm{e} + PV_\mathrm{e}) = I_\mathrm{a} - I_\mathrm{e}, \tag{32.20}$$

thus equal to the difference of the enthalpies: Enthalpy of solution (analogously reaction enthalpy). We determine now the enthalpy as function of $\bar{N}$, N_1, P, and T. We begin with the free enthalpy

$$G = \bar{N}\bar{\mu} + N_1\mu_1 = \bar{N}(\mu(P,T) - k_\mathrm{B}T\frac{N_1}{\bar{N}}) + N_1(k_\mathrm{B}T \ln \frac{N_1}{\bar{N}} + g_1(P,T)) = \bar{N}\mu + N_1 g_1(P,T) + k_\mathrm{B}TN_1 \ln \frac{N_1}{\mathrm{e}\bar{N}} \tag{32.21}$$

Thus we obtain the entropy

$$S = -\left.\frac{\partial G}{\partial T}\right|_{\bar{N},N_1,P} = -\bar{N}\frac{\partial \mu}{\partial T} - N_1\frac{\partial g_1}{\partial T} - k_{\mathrm{B}}N_1 \ln \frac{N_1}{\mathrm{e}\bar{N}} \tag{32.22}$$

and the enthalpies

$$I_{\mathrm{e}} = G + TS \quad = \quad \bar{N}(\mu - T\frac{\partial \mu}{\partial T}) + N_1(g_1 - T\frac{\partial g_1}{\partial T}), \tag{32.23}$$

$$I_{\mathrm{a}} \quad = \quad \bar{N}(\mu - T\frac{\partial \mu}{\partial T}) + N_1(\mu' - T\frac{\partial \mu'}{\partial T}). \tag{32.24}$$

Here I_{e} is the enthalpy of the solution and I_{a} the enthalpy of solvent plus solute. Then we obtain the heat of dilution (per particle)

$$q = (\mu' - T\frac{\partial \mu'}{\partial T}) - (g_1 - T\frac{\partial g_1}{\partial T}) = -k_{\mathrm{B}}T^2\frac{\partial \ln c_{\mathrm{s}}}{\partial T}. \tag{32.25}$$

Similarly the change of volume can be determined. It is given by the change of the free enthalpy with respect to pressure

$$\delta V = \frac{\partial (G_{\mathrm{e}} - G_{\mathrm{a}})}{\partial P} = N_1\frac{\partial (g_1 - \mu')}{\partial P} = -N_1 k_{\mathrm{B}}T\frac{\partial \ln c_{\mathrm{s}}}{\partial P}. \tag{32.26}$$

33 Chemical Equilibrium

33.a Equilibrium Condition

The particle numbers cannot arbitrarily change in a chemical reaction. Considering the reaction

$$2H_2 + O_2 \leftrightarrow 2H_2O \tag{33.1}$$

the number of particles will change by

$$\delta N_{H_2} = -2\delta n, \quad \delta N_{O_2} = -\delta n, \quad \delta N_{H_2O} = 2\delta n. \tag{33.2}$$

If generally the particle numbers change by

$$\delta N_i = \nu_i \delta n \tag{33.3}$$

then the reaction reads

$$\sum_i \nu_i A_i \leftrightarrow .\text{reaction enthalpy}\, q \tag{33.4}$$

One calls δn the number of elementary reactions,
The equlibrium state has a maximum of entropy for fixed E and V, similarly for fixed I and P. From

$$\sum_i \left.\frac{\partial S}{\partial N_i}\right|_{E,V} \delta N_i = 0 \quad \text{as well as from} \quad \sum_i \left.\frac{\partial S}{\partial N_i}\right|_{I,P} \delta N_i = 0 \tag{33.5}$$

one obtains

$$T\mathrm{d}S = -\sum_i \mu_i \delta N_i = -\sum_i \nu_i \mu_i \delta n = 0. \tag{33.6}$$

Thus the equilibrium condition reads

$$\sum_i \nu_i \mu_i = 0. \tag{33.7}$$

For our example we have $-2\mu_{H_2} - \mu_{O_2} + 2\mu_{H_2O} = 0$. The reaction enthalpy is obtained by

$$\mathrm{d}I = T\mathrm{d}S + \sum_i \mu_i \mathrm{d}N_i + V\mathrm{d}P \tag{33.8}$$

and thus

$$\delta I = \sum_i \nu_i (T\frac{\partial S}{\partial N_i} + \mu_i)\delta n = -T\sum_i \nu_i \frac{\partial \mu_i}{\partial T}\delta n, \tag{33.9}$$

where we have used eq. (33.7) and

$$\left.\frac{\partial S}{\partial N_i}\right|_{P,T,\text{other } N\text{s}} = -\left.\frac{\partial \mu_i}{\partial T}\right|_{P,\text{all } N} \tag{33.10}$$

and consequently we obtain the reaction enthalpy

$$q = -\frac{\delta I}{\delta n} = T\frac{\partial}{\partial T}(\sum_i \nu_i \mu_i). \tag{33.11}$$

33.b Dilute (ideal) gases

For dilute (ideal) gases the grandcanonical partition function Y can be written

$$Y = \prod_i Y_i = \prod_i \left(\sum_{N_i} \frac{1}{N_i!} Z_i^{N_i}(T,V) \mathrm{e}^{\beta\mu_i N_i} \right) \tag{33.12}$$

where Z_i is the partition function for one-particle of component i. It reads

$$Z_i = \frac{V}{\lambda_i^3} Z_i^{\mathrm{in}}(T) \tag{33.13}$$

with the thermal de Broglie-wavelength λ_i. For atoms without spin one has $Z_i^{\mathrm{in}} = 1$, for other atoms the internal degrees of freedom have to be taken into account (spin, rotation and vibration of molecules). One has to sum over all bound states (binding energy!). Then one obtains

$$Y = \exp\left(\sum_i \frac{V}{\lambda_i^3} Z_i^{\mathrm{in}}(T) \mathrm{e}^{\beta\mu_i} \right) \tag{33.14}$$

and therefore

$$N_i = \frac{\partial \ln Y}{\beta \partial \mu_i} = \frac{V}{\lambda_i^3} Z_i^{\mathrm{in}}(T) \mathrm{e}^{\beta\mu_i}, \tag{33.15}$$

$$PV = k_{\mathrm{B}} T \ln Y = k_{\mathrm{B}} T \sum N_i \tag{33.16}$$

thus

$$\mu_i = k_{\mathrm{B}} T \ln\left(P c_i \chi_i(T)\right), \quad \chi_i = \frac{\lambda_i^3}{k_{\mathrm{B}} T Z_i^{\mathrm{in}}(T)}, \quad c_i = \frac{N_i}{\sum_j N_j}. \tag{33.17}$$

Using the equilibrium condition $\sum_i \nu_i \mu_i = 0$ one obtains the the law of mass action

$$\prod_i c_i^{\nu_i} = \frac{A(T)}{P^{\sum_i \nu_i}}, \quad A(T) = \frac{1}{\prod_i \chi_i^{\nu_i}(T)}. \tag{33.18}$$

The heat of reaction is given by

$$q = T \sum_i \nu_i \frac{\partial \mu_i}{\partial T} = T \sum \nu_i \frac{\mu_i}{T} + k_{\mathrm{B}} T^2 \sum_i \nu_i \frac{\mathrm{d} \ln \chi_i}{\mathrm{d} T} = -k_{\mathrm{B}} T^2 \frac{\mathrm{d} \ln A(T)}{\mathrm{d} T}. \tag{33.19}$$

33.c Dilute solutions

The equilibrium condition for dilute solutions reads

$$\bar{\nu}\bar{\mu} + \sum_i \nu_i \mu_i = 0, \tag{33.20}$$

where it is assumed, that the solvent $\bar{A}$ participates in the reaction, $\bar{\nu}\bar{A} + \sum_i \nu_i A_i \leftrightarrow q$. With

$$\bar{\mu} \approx \mu(P,T), \quad \mu_i = k_{\mathrm{B}} T \ln c_i + g_i(P,T) \tag{33.21}$$

one obtains from

$$\mathrm{e}^{(\bar{\nu}\bar{\mu} + \sum_i \nu_i \mu_i)/(k_{\mathrm{B}} T)} = 1 \tag{33.22}$$

the law of mass action

$$\prod_i c_i^{\nu_i} = K(P,T) = \mathrm{e}^{-(\bar{\nu}\mu + \sum_i \nu_i g_i))/(k_{\mathrm{B}} T)}. \tag{33.23}$$

The enthalpy is given by

$$I = \bar{N}(\mu - T\frac{\partial \mu}{\partial T}) + \sum_i N_i (g_i - T \frac{\partial g_i}{\partial T}) \tag{33.24}$$

and thus the heat of reaction by

$$q = -I(\bar{N} = \bar{\nu}, N_i = \nu_i) = -k_{\mathrm{B}} T^2 \frac{\partial \ln K(P,T)}{\partial T}. \tag{33.25}$$

34 Van der Waals Equation

34.a Derivation

In section 30 we have considered a classical gas with an interacting potential

$$W(x) = \begin{cases} +\infty & |x| < c \quad \text{strongly repellend} \\ W_a(x) & |x| \geq c \quad \text{weakly attractive} \end{cases} \tag{34.1}$$

If only the repulsiv interaction is present then the partition function reads approximately

$$Z_0 = \frac{(V - V_0(N))^N}{N!\lambda^{3N}} \tag{34.2}$$

where $V_0 = V_0(N)$ is the excluded volume. Then the pressure reads

$$\frac{P}{k_\mathrm{B}T} = \frac{\partial \ln Z_0}{\partial V} = \frac{N}{V - V_0} = \frac{N}{V} + \frac{NV_0}{V^2} + ... \tag{34.3}$$

Comparison with the virial expansion in sect. 30 yields $V_0 = Nb(T)$. Together with an attractive potential we replace

$$P = k_\mathrm{B}T\frac{N}{V}(1 + b\frac{N}{V}) - \frac{N^2 a}{V^2} + O(\frac{N^3}{V^3}) \tag{34.4}$$

by

$$P = k_\mathrm{B}T\frac{N}{V - Nb} - \frac{N^2 a}{V^2}. \tag{34.5}$$

This is the van der Waals-equation.

34.b Discussion

We will now discuss the pressure as a function of volume at constant temperature (isotherms), $P = P(V, T)$. At first we determine

$$\frac{\partial P}{\partial V} = -k_\mathrm{B}T\frac{N}{(V - Nb)^2} + \frac{2N^2 a}{V^3}, \tag{34.6}$$

$$\frac{\partial^2 P}{\partial V^2} = k_\mathrm{B}T\frac{2N}{(V - Nb)^3} - \frac{6N^2 a}{V^4} \tag{34.7}$$

If both $\frac{\partial P}{\partial V}$ and $\frac{\partial^2 P}{\partial V^2}$ vanish, then the isotherm has a horizontal point of inflection. From both equations one obtains initially $\frac{2}{V - Nb} = \frac{3}{V}$ and then

$$V_\mathrm{c} = 3Nb, \quad k_\mathrm{B}T_\mathrm{c} = \frac{8a}{27b}, \quad P_\mathrm{c} = \frac{a}{27b^2}. \tag{34.8}$$

Thus one has for the critical point $\frac{Nk_\mathrm{B}T_\mathrm{c}}{P_\mathrm{c}V_\mathrm{c}} = \frac{8}{3}$. For spherical molecules one finds experimentally $\approx 3, 4$. For $T > T_\mathrm{c}$ one has always $\frac{\partial P}{\partial V} < 0$, and thus

$$\kappa_T^{-1} = -V\frac{\partial P}{\partial V} = k_\mathrm{B}T\frac{NV}{(V - Nb)^2} - \frac{2N^2 a}{V^2} > 0, \tag{34.9}$$

For $T < T_\mathrm{c}$ there are regions, in which κ_T^{-1} is negative, which is unphysically. For $T < T_\mathrm{c}$ there are two phases, a dilute one which is gaseous and a denser fluid one, which can be in equilibrium. For this equilibrium $\mu_1 = \mu_2$ has to hold with $\mu = (F + PV)/N$. From $N\mathrm{d}\mu = V\mathrm{d}P - S\mathrm{d}T$ one obtains for fixed N and T

$$N(\mu_2 - \mu_1) = \int_{V_1}^{V_2} V\mathrm{d}P = VP|_{V_1}^{V_2} - \int_{V_1}^{V_2} P(T, V, N)\mathrm{d}V = 0, \tag{34.10}$$

thus

$$\int_{V_1}^{V_2} P(T,V,N)\mathrm{d}V = P(V_2 - V_1). \tag{34.11}$$

This is called the Maxwell-construction.
We now consider the coexistence curve in the vicinity of the critical point. For this purpose we write

$$P = P_\mathrm{c}(1+p), \quad V = V_\mathrm{c}(1+v), \quad T = T_\mathrm{c}(1+t). \tag{34.12}$$

Then the equation of state reads

$$p = \frac{8(t+1)}{3v+2} - \frac{3}{(v+1)^2} - 1 = -\frac{3}{2}v^3 + O(v^4) + t(4 - 6v + O(v^2)). \tag{34.13}$$

For the coexisting phases $p_1 = p_2$ must hold,

$$-\frac{3}{2}v_1^3 - 6tv_1 = -\frac{3}{2}v_2^3 - 6tv_2 \tag{34.14}$$

or equivalently

$$\underbrace{(v_1 - v_2)}_{A}\underbrace{(6t + \frac{3}{2}(v_2^2 + v_1v_2 + v_1^2))}_{B} = 0 \tag{34.15}$$

On the other hand one obtains from

$$\int_{v_1}^{v_2} (1+p(v))\mathrm{d}v = (1+p_2)v_2 - (1+p_1)v_1 \tag{34.16}$$

the equation

$$\left(v + 4tv - 3tv^2 - \frac{3}{8}v^4\right)_{v_1}^{v_2} = \left(v + 4tv - 6tv^2 - \frac{3}{2}v^4\right)_{v_1}^{v_2}, \tag{34.17}$$

from which one obtains

$$3t(v_1^2 - v_2^2) + \frac{9}{8}(v_1^4 - v_2^4) = 0 \tag{34.18}$$

or equivalently

$$3\underbrace{(v_1 - v_2)}_{A}\underbrace{(v_1 + v_2)}_{B'}\underbrace{(t + \frac{3}{8}(v_1^2 + v_2^2))}_{C} = 0 \tag{34.19}$$

Both equations can be solved by
α) $A = 0$. This yields $v_1 = v_2$, that is the same phase and thus describes a trivial solution.
β) $B = B' = 0$. Then we have $v_2 = -v_1$, $t + \frac{1}{4}v_1^2 = 0$, thus for $t < 0$.

$$v_1 = -2\sqrt{-t}, \quad v_2 = 2\sqrt{-t}, \quad p = 4t. \tag{34.20}$$

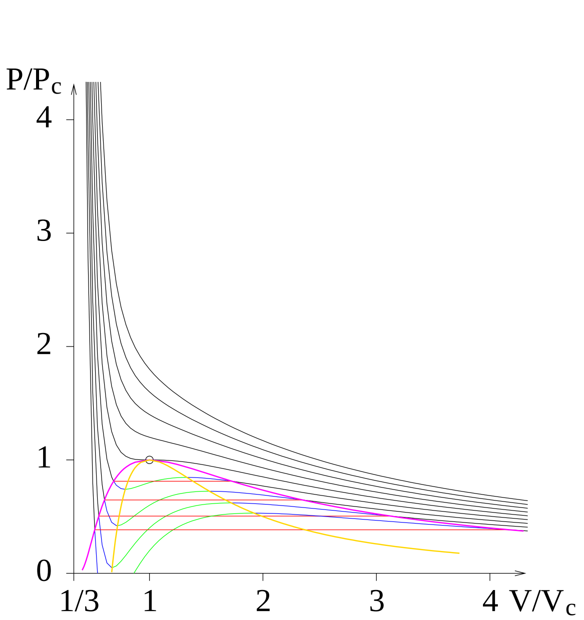
γ) There remains $B = C = 0$. Then one obtains $B - 6C = -\frac{3}{4}(v_1 - v_2)^2 = 0$, which again yields the trivial solution.
Thus we have close to the critical point

$$\delta V = \pm 2V_\mathrm{c}\sqrt{1 - \frac{T}{T_\mathrm{c}}} \quad T < T_\mathrm{c}. \tag{34.21}$$

The system is not stable between these two δV. Instead the system will separate in two phases, the liquid and the gaseous one. One also considers the curves along which κ_T^{-1} vanishes. One obtains for these

$$\frac{\partial p}{\partial v} = -\frac{9}{2}v^2 - 6t = 0, \quad v = \pm\sqrt{-\frac{4}{3}t} \tag{34.22}$$

and calls the curves spinodals. The compressibility is positive between coexistence curve and spinodal curve. In this region the system can be metastable (undercooled, overheated).



Isotherms of the Van der Waals gas: From top to bottom for T/T_c from 1.20 to 0.80 in steps of 0.05. The critical point is indicated by a small circle. The coexistence curve is shown in magenta, the spinodal in light brown. The two-phase region extends below the coexistence curve. In this region part of the system is fluid, the other gaseous. Both coexisting phases are connected by horizontal red lines.

35 Weiss Molecular Field Approximation

35.a Weiss Approximation

In this approximation it is assumed that each magnetic moment ($S = 1/2$)

$$m = \pm\mu_\mathrm{B} \tag{35.1}$$

senses an effective magnetic field (mean field, molecular field)

$$H_\mathrm{eff} = H + WM. \tag{35.2}$$

Here H is the external field, WM an internal field due to the interaction (actually short-range), M is the magnetization, W the Weiss factor. Then one obtains for the energy-levels

$$\epsilon_\pm = \mp\mu_\mathrm{B} H_\mathrm{eff} \tag{35.3}$$

for the magnetic moment and the averaged magnetic moment

$$\langle m\rangle = \mu_\mathrm{B}\frac{\mathrm{e}^{\beta\mu_\mathrm{B}H_\mathrm{eff}} - \mathrm{e}^{-\beta\mu_\mathrm{B}H_\mathrm{eff}}}{\mathrm{e}^{\beta\mu_\mathrm{B}H_\mathrm{eff}} + \mathrm{e}^{-\beta\mu_\mathrm{B}H_\mathrm{eff}}} = \mu_\mathrm{B}\tanh(\beta\mu_\mathrm{B}H_\mathrm{eff}) \tag{35.4}$$

and thus the equation for the magnetization (magnetic moment per volume)

$$M = \frac{N}{V}\langle m\rangle = \frac{N}{V}\mu_\mathrm{B}\tanh(\beta\mu_\mathrm{B}(H + WM)). \tag{35.5}$$

35.b Ising Model

In reality the interaction is short range, e.g. due to the overlapp of the electronic wave-functions

$$\hat{H} = -\frac{1}{2}\sum_{r,r'} I_{r,r'}\frac{m_r m_{r'}}{\mu_\mathrm{B}^2} - H\sum_r m_r \tag{35.6}$$

With the Ising-spins

$$\frac{m_r}{\mu_\mathrm{B}} = S_r = \pm 1 \tag{35.7}$$

one obtains the Ising model

$$\hat{H} = -\frac{1}{2}\sum_{r,r'} I_{r,r'} S_r S_{r'} - H\mu_\mathrm{B}\sum_r S_r. \tag{35.8}$$

35.c Infinitely long-ranged interaction

If one replaces the interaction by an infinitely long-ranged one, where $I_{r,r'} = I/N$ is equal for all pairs m_r, $m_{r'}$ (only division by the number N of spins yields a reasonable limit for $N \to \infty$), then one obtains

$$\hat{H} = -\frac{I}{2N}\sum_{r,r'} S_r S_{r'} = -\frac{I}{2N\mu_\mathrm{B}^2}\sum_{r,r'} m_r m_{r'} = -\frac{IV^2}{2N\mu_\mathrm{B}^2}M^2 \tag{35.9}$$

with the magnetic moment $M = \sum_r m_r/V$. With an external field H the Hamiltonian $\hat{H}$ reads

$$\hat{H} = -I\frac{V^2}{2N\mu_\mathrm{B}^2}M^2 - HMV \tag{35.10}$$

What is the free energy $F(M,T)$ without external field? From this one obtains the partition function

$$Y = \sum_M \mathrm{e}^{-\beta F(M,T) + \beta HMV} \tag{35.11}$$

Then the magnetization is obtained from the maximum

$$\frac{\partial(F - HMV)}{\partial M} = 0, \tag{35.12}$$

from which one obtains

$$H = \frac{1}{V}\frac{\partial F}{\partial M}. \tag{35.13}$$

We have now to calculate F,

$$F(M,T) = E(M) - TS(M), \quad E(M) = -\frac{IV^2}{2N\mu_{\rm B}^2}M^2. \tag{35.14}$$

There remains the determination of the entropy. Thus we have to determine how many spin configurations yield a given magnetization. If N_+ spins are up and N_- spins are down, then one obtains

$$N = N_+ + N_-, \quad MV = \mu_{\rm B}(N_+ - N_-), \tag{35.15}$$

and thus

$$N_\pm = \frac{1}{2}(N \pm \frac{MV}{\mu_{\rm B}}) \tag{35.16}$$

From this we obtain the entropy

$$S = k_{\rm B}\ln W = k_{\rm B}\ln\frac{N!}{N_+!N_-!} = k_{\rm B}\ln\left(\frac{N}{N_+}\right)^{N_+}\left(\frac{N}{N_-}\right)^{N_-}, \tag{35.17}$$

therefore

$$S(M) = -k_{\rm B}\left(\frac{N + \frac{MV}{\mu_{\rm B}}}{2}\right)\ln\left(\frac{1 + \frac{MV}{N\mu_{\rm B}}}{2}\right) - k_{\rm B}\left(\frac{N - \frac{MV}{\mu_{\rm B}}}{2}\right)\ln\left(\frac{1 - \frac{MV}{N\mu_{\rm B}}}{2}\right) \tag{35.18}$$

From $H - \frac{1}{V}\frac{\partial F}{\partial M} = 0$ we obtain

$$H_{\rm eff} = H + \underbrace{\frac{IV}{N\mu_{\rm B}^2}}_{W}M = \frac{k_{\rm B}T}{2\mu_{\rm B}}\ln\frac{1 + \frac{MV}{N\mu_{\rm B}}}{1 - \frac{MV}{N\mu_{\rm B}}} \tag{35.19}$$

from which one obtains

$$M = \frac{N}{V}\mu_{\rm B}\tanh(\beta\mu_{\rm B}(H + WM)), \tag{35.20}$$

and thus the Weiss approximation follows.

35.d Critical Behavior

We consider now the critical behavior, that is the behavior in the vicinity of the Curie-temperature. At this point $T = T_{\rm c}$, $H = 0$, the spontaneous magnetization vanishes. In its vicinity the magnetization is small. Thus we expand in powers of the magnetization

$$E = -\frac{1}{2}WVM^2, \tag{35.21}$$

$$S = k_{\rm B}N\ln 2 - \frac{k_{\rm B}N}{2}[(1+x)\ln(1+x) + (1-x)\ln(1-x)], \tag{35.22}$$

$$x = \frac{MV}{N\mu_{\rm B}} = \frac{M}{n\mu_{\rm B}}, \quad n = \frac{N}{V}, \tag{35.23}$$

$$S = k_{\rm B}N\ln 2 - k_{\rm B}N(\frac{x^2}{2} + \frac{x^4}{12} + ...) \tag{35.24}$$

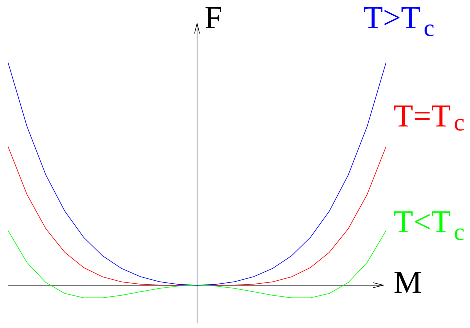
and thus obtain the free energy

$$F = -k_\mathrm{B} T N \ln 2 + V M^2 \left(-\frac{1}{2} W + \frac{k_\mathrm{B} T}{2 n \mu_\mathrm{B}^2} \right) + V M^4 \frac{k_\mathrm{B} T}{12 n^3 \mu_\mathrm{B}^4} + ... \tag{35.25}$$

with $n = N/V$. For temperatures $T > T_\mathrm{c}$ mit $k_\mathrm{B} T_\mathrm{c} = n \mu_\mathrm{B}^2 W$ the minimum of the free energy is at $M = 0$. This is the paramagnetic phase. We may now write

$$F = F_0(T) + \frac{1}{2} a(T) V M^2 + \frac{1}{4} b(T) V M^4 + ..., \quad a(T) = a_0 \cdot (T - T_\mathrm{c}), \quad b(T) \approx b(T_\mathrm{c}) = b_0. \tag{35.26}$$

Sketch of the free energy



We obtain the equation of state from $\frac{\partial F}{\partial M} = HV$

$$a(T) M + b_0 M^3 = H \tag{35.27}$$

This yields ($H = 0$, $T < T_\mathrm{c}$) the spontaneous magnetization

$$M = \pm \sqrt{-\frac{a(T)}{b(T)}} \approx \sqrt{\frac{a_0}{b_0}(T_\mathrm{c} - T)} \tag{35.28}$$

Taking the derivative of the equation of state with respect to the field H we obtain the susceptibility

$$(a(T) + 3b(T) M^2) \underbrace{\frac{\mathrm{d}M}{\mathrm{d}H}}_{\chi_T} = 1 \tag{35.29}$$

and thus

$$\chi_T = \frac{1}{a(T) + 3b(T) M^2}. \tag{35.30}$$

At vanishing external field $H = 0$ one obtains

$$\chi(T) = \begin{cases} \frac{1}{a_0(T - T_\mathrm{c})}, & T > T_\mathrm{c}, \\ \frac{1}{a(T) - 3a(T)} = \frac{1}{2a_0(T_\mathrm{c} - T)}, & T < T_\mathrm{c}. \end{cases} \tag{35.31}$$

For $T = T_\mathrm{c}, H \neq 0$ one obtains

$$H = b_0 M^3, \quad M = \left(\frac{H}{b_0} \right)^{1/3}. \tag{35.32}$$

As one approaches the critical point the susceptibility increases like

$$\chi = \frac{1}{3 b_0 M^2} = \frac{1}{3 b_0} \left(\frac{H}{b_0} \right)^{-2/3}. \tag{35.33}$$

Finally for the specific heat at $H = 0$ one obtains

$$C_{H=0} = T \left. \frac{\partial S}{\partial T} \right|_{H=0} = T \frac{\partial S}{\partial M^2} \left. \frac{\partial M^2}{\partial T} \right|_{H=0} = \begin{cases} 0 & T > T_\mathrm{c}, \\ \frac{T V a_0^2}{2 b_0} & T < T_\mathrm{c}. \end{cases} \tag{35.34}$$

Thus one finds a jump in the specific heat.

36 Landau Theory of Phase Transitions

36.a Landau Theory for critical phenomena

In a more general formulation the free energy is written as a volume integral over a density f

$$F = \int \mathrm{d}^3 r f(r) \tag{36.1}$$

where this density is again expanded in powers of the now local order-parameter $m(r)$,

$$f(r) = f_0(T) - h(r)m(r) + \frac{1}{2}a(T)m^2(r) + \frac{1}{4}b(T)m^4(r) + \frac{1}{2}c(T)(\nabla m(r))^2. \tag{36.2}$$

Here we allow an r-dependent magnetic field $h(r)$. The gradient-term is new in this expression. I t takes into account, that the interaction between spins is of short range and that it is energetically advantegeous, if the magnetization does not vary in space. The most probable state is obtained by taking the minimum of the free energy. If we vary $m(r) \to m(r) + \delta m(r)$, then we obtain in linear order in $\delta m(r)$

$$\delta F = \int \mathrm{d}^3 r \delta m(r)[-h(r) + am(r) + bm^3(r) - c\triangle m(r)] \tag{36.3}$$

where we used partial integration for the gradient term. Thus we obtain for the minimum

$$(a + bm(r)^2 - c\triangle)m(r) = h(r) \tag{36.4}$$

For a homogeneous magnetic field $h(r) = H$ one obtains the same space independent solution $M = \langle m(r)\rangle$ as above. But we may also obtain expressions for the correlations

$$g(r, r') = \langle((m(r) - M)(m(r') - M)\rangle. \tag{36.5}$$

Therefore we consider how the expectation value $\langle A\rangle$ changes if a perturbation δH is added to the Hamiltonian

$$\begin{aligned}
\langle A\rangle &= \frac{\mathrm{tr}(A\mathrm{e}^{-\beta(H_0+\delta H)})}{\mathrm{tr}(\mathrm{e}^{-\beta(H_0+\delta H)})} = \frac{\mathrm{tr}(A\mathrm{e}^{-\beta H_0}) - \beta\mathrm{tr}(A\delta H\mathrm{e}^{-\beta H_0})}{\mathrm{tr}(\mathrm{e}^{-\beta H_0}) - \beta\mathrm{tr}(\delta H\mathrm{e}^{-\beta H_0})} \\
&= \frac{\mathrm{tr}(A\mathrm{e}^{-\beta H_0})}{\mathrm{tr}(\mathrm{e}^{-\beta H_0})} - \frac{\mathrm{tr}(A\delta H\mathrm{e}^{-\beta H_0})}{\mathrm{tr}(\mathrm{e}^{-\beta H_0})} + \frac{\mathrm{tr}(A\mathrm{e}^{-\beta H_0})}{\mathrm{tr}(\mathrm{e}^{-\beta H_0})}\frac{\mathrm{tr}(\delta H\mathrm{e}^{-\beta H_0})}{\mathrm{tr}(\mathrm{e}^{-\beta H_0})} \\
&= \langle A\rangle_0 - \beta(\langle A\delta H\rangle_0 - \langle A\rangle_0\langle\delta H\rangle_0),
\end{aligned} \tag{36.6}$$

where we have kept all contributions linear in δH. We see that the reaction of the system to a perturbation is described by a correlation. One obtains with $A = m(r)$ and $\delta H = -\int \mathrm{d}^3 r'\delta h(r')m(r')$

$$\langle\delta m(r)\rangle = \beta\int \mathrm{d}^3 r'\delta h(r')(\langle m(r)m(r')\rangle - \langle m(r)\rangle\langle m(r')\rangle) = \beta\int \mathrm{d}^3 r'\delta h(r')g(r, r') \tag{36.7}$$

If we perform the variation in (36.4) then we obtain

$$(a + 3bM^2 - c\triangle)\delta m(r) = \delta h(r). \tag{36.8}$$

This differential equation can be solved by means of the Fourier transform

$$(a + 3bM^2 + cq^2)\delta m_q = \delta h_q \tag{36.9}$$

from which one obtains

$$\delta m(r) = \frac{1}{(2\pi)^3}\int \mathrm{d}^3 q\mathrm{d}^3 r'\frac{\mathrm{e}^{-iq(r-r')}}{a + 3bM^2 + cq^2}\delta h(r') = \frac{1}{4\pi}\int \mathrm{d}^3 r'\frac{\exp(-|r - r'|/\xi)}{|r - r'|}\delta h(r') \tag{36.10}$$

with the correlation length

$$\xi = \sqrt{\frac{c}{a+3bM^2}} = \begin{cases} (c/a_0)^{1/2}(T-T_\mathrm{c})^{-1/2} & \text{für for } T > T_\mathrm{c},\ h=0, \\ (c/2a_0)^{1/2}(T_\mathrm{c}-T)^{-1/2} & \text{für for } T < T_\mathrm{c},\ h=0. \end{cases} \tag{36.11}$$

Thus the correlation becomes of long range at the critical point. There it does not decay exponentially but algebraically. The correlation length increases with $\xi \propto 1/\sqrt{|T-T_\mathrm{c}|}$ as one approaches the critical point.

36.b Range of validity of the Landau theory

This theory assumes, that the free energy can be expanded in powers of the order-parameter. This holds for many approximations like the van der Waals equation for a fluid or for the molecular field theory by Weiss. These theories yield normally reasonable results as long as one is not too close to the critical point. In the vicinity of this point they yield wrong results.

Ginzburg has given a criterion when molcular field theory is good. He uses the following argument: There are considerable fluctuations in the order-parameter. However, one may average over some region. The largest distance across which this is reasonable is the correlation-length. Thus one requires, that the correlation is small in comparison to the square of the order-parameter,

$$\langle \delta m(\mathbf{r}) \delta m(\mathbf{r}') \rangle_{|\mathbf{r}-\mathbf{r}'|=\xi} \ll m^2. \tag{36.12}$$

For simplicities' sake we leave now aside pure number factors, but consider the problem for general dimensionality d of space

$$\frac{k_\mathrm{B} T_\mathrm{c}}{c\xi^{d-2}} \ll \frac{|a|}{b}. \tag{36.13}$$

We denote the correlation length at temperature 0 by ξ_0 and introduce the relative temperature difference $\tau = \frac{T-T_\mathrm{c}}{T_\mathrm{c}}$. Then we may write $\xi = \xi_0/|\tau|^{1/2}$ and $a = a_0 T_\mathrm{c} \tau$, so that the inequality reads

$$\frac{k_\mathrm{B} T_\mathrm{c} |\tau|^{d/2-1}}{c\xi_0^{d-2}} \ll \frac{a_0 T_\mathrm{c} |\tau|}{b} \text{ oder } |\tau|^{2-d/2} \gg \frac{k_\mathrm{B} b}{c a_0 \xi_0^{d-2}}. \tag{36.14}$$

We may now eliminate a_0, b, and c, by expressing the correlation length at temperature 0 and the jump ΔC of the specific heat by these quantities,

$$\xi_0 = \sqrt{\frac{c}{a_0 T_\mathrm{c}}}, \quad \Delta C = T_\mathrm{c} \frac{a_0^2}{b}. \tag{36.15}$$

Then we obtain

$$|\tau|^{2-d/2} \gg \frac{k_\mathrm{B}}{\xi_0^d \Delta C}. \tag{36.16}$$

For $d = 3$ one should multiply by a numerical factor. According to the preceeding calculation this would be $1/(16\pi \mathrm{e})$ for $d = 3$. Ginzburg and Levanyuk gave a more careful argument and find, that the Landau-theory should be valid for $|\tau|$ larger then

$$\tau_\mathrm{c} = \frac{1}{32\pi^2} \left(\frac{k_\mathrm{B}}{\Delta C \xi_0^3}. \right)^2 \tag{36.17}$$

The factor ξ_0^6 in the denominator of τ_c indicates that with increasing range of the interaction, which yields a larger correlation length ξ_0, the region inside which Landau theory is invalid can become very small. This holds in particular for conventional superconductors. In tin one finds $\xi_0 = 2300$ Å and $\Delta C = 0.8 \times 10^4$ erg/cm^{3}K, from which $\tau_\mathrm{c} \approx 10^{-14}$ follows. In liquid helium one has a ξ_0, which corresponds to the distance of the atoms. As a result $\tau_\mathrm{c} \approx 1$. The jump of the specific heat in iron is $\Delta C \approx 3 \times 10^7$erg/cm^3 K and $\xi_0 = 2$ Å, from which one obtains $\tau_\mathrm{c} \approx 10^{-2}$. The magnetic fields of the spins in antiferromagnets have the tendency, to cancel each other. Thus τ_c is relatively large.

Ginzburg has estimated $\tau_c \approx 10^{-4}$ for ferroelectrica. For antiferroelectrica one expects larger values of τ_c.
We have performed the calculation for general dimension. This does not only yield an estimate for two-dimensional layers. We realize: If $d > 4$, then on the left hand side of equation (36.16) $|\tau|$ appears with a negative exponent. That is in such high dimensions the immediate vicinity of the critical point is no longer excluded from Landau theory. In four dimensions one has $|\tau|^{2-d/2} = 1$. Since below this dimension the critical phenomena differ from molecular field theory, $d = 4$ is called upper critical dimension.

36.c Power laws and critical exponents

Already at the turn of the century (1900) it was known, that the molecular field behavior as e.g. of the van der Waals equation does not describe the behavior in the vicinity of the critical point correctly. (For the history of critical phenomena see J.M.H. Levelt-Sengers, Physica 73 (1974) 73.) For example one had observed experimentally that the density of a gas or a liquid is not desribed by $\rho - \rho_c \propto (T - T_c)^\beta$ with $\beta = 1/2$, but by $\beta = 0.3434$ (Verschaffelt 1900). Similarly other quantities like susceptibility, specific heat, correlations showed laws with different powers,

$$\begin{array}{ll} \text{specific heat} & C \propto \tau^{-\alpha} \\ \text{order parameter at } h = 0 & m \propto \tau^{\beta} \\ \text{susceptibility} & \chi \propto \tau^{-\gamma} \\ \text{order parameter at } T = T_c & m \propto h^{1/\delta} \\ \text{correlation at } T_c & g(\mathbf{r}, \mathbf{r}') \propto |\mathbf{r} - \mathbf{r}'|^{2-d-\eta} \\ \text{correlation length} & \xi \propto \tau^{-\nu}. \end{array} \tag{36.18}$$

One calls α, β, γ, δ, η, and ν critical exponents. In the following table we show some values of critical exponents

Exponent	molecular field	Ising-M. $d=2$	Ising-M. $d=3$	Heisenberg-M. $d=3$	spherical model $d=3$
α	0(jump)	0(ln)	0.109	−0.116	−1
β	1/2	1/8	0.325	0.365	1/2
γ	1	7/4	1.241	1.387	2
δ	3	(15)	4.82	4.80	5
η	0	1/4	0.031	0.033	0
ν	1/2	1	0.630	0.705	1

(36.19)

First we have given the molecular field values. Next those of the two-dimensional Ising model. Onsager was able to give the solution of the model in 1944. He found, that the specific heat has a logarithmic singularity. Further calculations, in particular those by Yang (1952) determined the spontaneous magnetization and the susceptibility. However, the solution is only known for $h = 0$. One realized from these calculations as well as from those for the spherical model (Berlin and Kac 1952), that the critical exponents can be different from those of molecular field theory. It should be noted, that the values for the three-dimensional Ising model should also apply to liquids at the critical point. One sees, that Verschaffelt's exponent $\beta = 0.3434$, which was actually not measured that precisely, agrees well with $\beta = 0.325$ for the Ising model.
Within this course we cannot derive this behavior. But we would like to indicate shortly, what has to be done: In (36.1, 36.2) we had introduced the free energy for the system. The interpretation given was to simple. Actually it is something intermediate between free energy and Hamiltonian function. If we consider it as a Hamiltonian, then one has to integrate all $m(r)$. These integration may lead to problems with divergencies. In Fourier space one has to confine oneself to the Brillouin zone.
In Fourier space one has to confine oneself to the Brillouin zone. One may proceed in such a way, that one integrates the Fourier components with the largest wave-vectors q. Then there remains an interaction approximately of the same form as in (36.2), only the coefficients a, b and c will change. If one multiplies $m(r)$ with an appropriate factor and rescales the length, so that one again obtains the same region of wave-vectors for those Fourier components, which are not yet integrated, then it

is possible to find a set of interaction constants a, b and c, which stay constant. For these constants the system is self-similar. Upon rescaling it looks similar to itself at all scales. Then it describes the critical point and for example the algebraic decay of the correlation $\langle m(r)m(r')\rangle$.
If one deviates a little bit from these coupling constants, then one can pursue, how these deviations change. They describe the critical behavior with its critical exponents. The procedure of integration over the Fourier components with the largest wave-vectors and the rescaling is called the renormalization group.

A Appendix: Formulae

A.a Γ-function

The Γ-function is defined by

$$\Gamma(n+1) = n! = \int_0^\infty \mathrm{d}x\, x^n \mathrm{e}^{-x} \tag{A.1}$$

One shows by partial integration

$$\Gamma(n+1) = n\Gamma(n), \quad n! = n(n-1)! \tag{A.2}$$

Special values are

$$\Gamma(1) = 0! = 1, \qquad \Gamma(n) = (n-1)! = 1\cdot 2\cdot 3 ... (n-1) \tag{A.3}$$

$$(-1/2)! = \Gamma(1/2) = \sqrt{\pi}, \qquad \Gamma(n+\frac{1}{2}) = \sqrt{\pi}\frac{1\cdot 3\cdot 5 ... (2n-1)}{2^n}. \tag{A.4}$$

For large argument one obtains the Stirling-formula

$$n! = \Gamma(n+1) = \sqrt{2\pi n}\left(\frac{n}{\mathrm{e}}\right)^n. \tag{A.5}$$

A.b Bose- and fermi-integrals with ζ-function

A number of integrals for bosons and fermions can be expressed in terms of the Riemannian ζ-function. It is defined by

$$\zeta(p) = \sum_{n=1}^\infty \frac{1}{n^p} = 1 + \frac{1}{2^p} + \frac{1}{3^p} + \frac{1}{4^p} + ... \tag{A.6}$$

In calculations for bosons one finds

$$\int_0^\infty \mathrm{d}x \frac{x^p}{\mathrm{e}^x - 1} = \int_0^\infty \mathrm{d}x \frac{x^p \mathrm{e}^{-x}}{1-\mathrm{e}^{-x}} = \sum_{n=1}^\infty \int_0^\infty \mathrm{d}x x^p \mathrm{e}^{-nx} = \sum_{n=1}^\infty \frac{1}{n^{p+1}} \int_0^\infty \mathrm{d}y y^p \mathrm{e}^{-y} = \Gamma(p+1)\zeta(p+1), \tag{A.7}$$

where $y = nx$ has been substituted. Similarly one finds

$$-\int_0^\infty \mathrm{d}x x^p \ln(1-\mathrm{e}^{-x}) = \Gamma(p+1)\zeta(p+2). \tag{A.8}$$

For fermions one has similar integrals. By means of

$$\frac{1}{\mathrm{e}^x + 1} = \frac{1}{\mathrm{e}^x - 1} - \frac{2}{\mathrm{e}^{2x} - 1} \tag{A.9}$$

one obtains

$$\int_0^\infty \mathrm{d}x \frac{x^p}{\mathrm{e}^x + 1} = (1 - 2^{-p}) \int_0^\infty \mathrm{d}x \frac{x^p}{\mathrm{e}^x - 1} = (1-2^{-p})\Gamma(p+1)\zeta(p+1) \tag{A.10}$$

and from

$$\ln(1+\mathrm{e}^{-x}) = \ln(1-\mathrm{e}^{-2x}) - \ln(1-\mathrm{e}^{-x}) \tag{A.11}$$

one obtains

$$\int_0^\infty \mathrm{d}x x^p \ln(1+\mathrm{e}^{-x}) = (2^{-p-1} - 1)\int_0^\infty \mathrm{d}x x^p \ln(1-\mathrm{e}^{-x}) = (1-2^{-p-1})\Gamma(p+1)\zeta(p+2). \tag{A.12}$$

Special values are

$$\begin{aligned} &\zeta(3/2) = 2.612, \qquad \zeta(2) = \pi^2/6 = 1.645, \\ &\zeta(5/2) = 1.341, \qquad \zeta(3) = 1.202, \\ &\zeta(7/2) = 1.127, \qquad \zeta(4) = \pi^4/90 = 1.0823. \end{aligned} \tag{A.13}$$

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