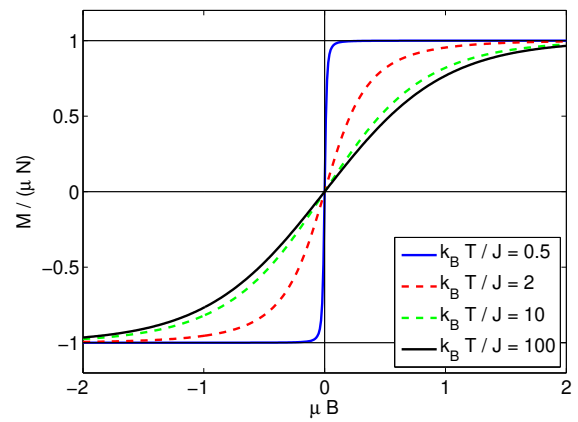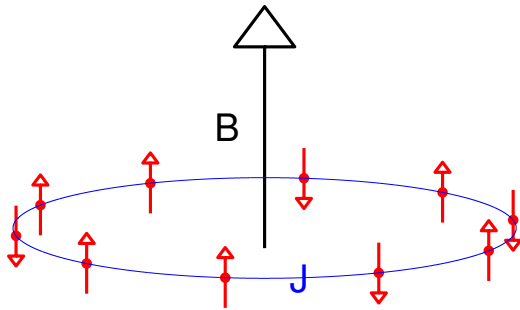# Statistical Physics

Univ. Prof. Dr. Wolfgang von der Linden   (Version 2021)

$$M(T, N, B) = N\mu \frac{\sinh(\mu\beta B)}{\sqrt{\sinh^2(\mu\beta B) + e^{-4J\beta}}}$$

November 24, 2021

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Chapter 1

Introduction

If one examines the behavior of a system of many particles, one finds that it no longer depends on details and initial conditions. Usually a **thermodynamic** equilibrium, which is dependent only on a few macroscopic variables – the so called **state variables** – is achieved after a very short time. The laws and phenomena of systems with macroscopically many particles are different from those at the atomic level. There are organizing principles at work that are largely independent of microscopic properties (emergence). E.g. formation of geometric patterns, collective phenomena, such as magnetism, etc. Another aspect is that time reversal invariance no longer applies. The laws of thermodynamics can be derived from the microscopic equations of motion (classical or quantum mechanical, resp.). Among other things also the irreversability/asymmetry can be derived. However, it is not only impossible, but also nonsensical to solve the equations of motion for 10^{24} particles in order to describe thermodynamic systems. At the end of the day, what is important are average quantities, for which the details of the individual particles are irrelevant. Phenomena of complex systems sometimes need only very little detail at the microscopic level. It would be similarly absurd for a doctor, in order to treat influenza, to solve the Schrödinger equation for the patient with supercomputers.

We will see that in classical thermodynamic systems there is not much left of Newton's equations of motion and the macroscopic behaviour would look very similar if the microscopic laws were different.

1.1 Simple Models

To see how thermodynamic behavior, such as equilibrium or irreversibility,

evolves from Newton's equations of motion for macroscopic particles, we examine simple models.

1.1.1 Ehrenfest-Model (Dog Fleas)

We will consider a (free) gas of N atoms that interact with each other via hard core repulsion. The gas is supposed to be in a cuboidal volume V, which we imagine to be divided by a vertical wall into two partial cubes with volumes V_1 and V_2. The interface between these sub-volumes shall be denoted by A. Accordingly, the dimension perpendicular to the wall is called L_1 or L_2. We define this direction as the x axis.
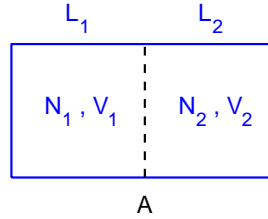
Figure 1.1: Schematic representation of the model system

We now consider an atom in V_1 whose speed in the x-direction shall be v_x. In V_1 it takes the atom the time $T_1 = 2L_1/v_x$ to fly from wall A to the opposite wall of the cuboid and get back to A. Since we do not know where on the x-axis the particle is at any given point in time, the probability that it will cross the wall A within the time interval dt is given by

$$dP_1' = \frac{dt}{T_1} = dt\frac{v_x}{2L_1} = dt\frac{Av_x}{2V_1} \ .$$

At time t there are in total N_1 atoms within volume V_1 with an average velocity of v_x in x-direction. According to the summation rule, the probability for any atom to cross the wall A within dt is

$$dP_1 = N_1 dP_1' = dt\frac{Av_x N_1}{2V_1} = dt\frac{A\rho_1 v_x}{2} \ .$$

It is therefore proportional to the actual density ρ_1 in V_1. In the following we will write this probability as

$$dP_1 = N_1\lambda_1 dt \ .$$

The same applies to V_2 of course. The probability that two atoms cross A simultaneously is a factor dt smaller than the probability that one particle crosses A and can therefore be neglected, if dt is infinitesimally small. Therefore within dt there are only three possibilities:

Process	Probability
1) One particle crosses from V_1 to V_2:	$P_1 = dt\lambda_1 N_1$
2) One particle crosses from V_2 to V_1:	$P_2 = dt\lambda_2 N_2$
3) No particle crosses the wall:	$P = 1 - dt(\lambda_1 N_1 + \lambda_2 N_2)$

We now want to calculate the probabilities $P(\mathcal{N}_1^{(t)} = n)$ that at a given time t the number of particles in V_1 is N_1.

We determine the sought-for probability by deriving a differential equation in time

$$P(\mathcal{N}_1^{(t+dt)} = m) = \sum_{n=0}^{N} P(\mathcal{N}_1^{(t+dt)} = m|\mathcal{N}_1^{(t)} = n) \, P(\mathcal{N}_1^{(t)} = n) \,. \qquad (1.1)$$

In dt there are the following possibilities

$$\begin{aligned}
P(\mathcal{N}_1^{(t+dt)} = m|\mathcal{N}_1^{(t)} = n) &= \delta_{m,n-1} \, \lambda_1 n dt + \delta_{m,n+1} \, \lambda_2(N-n)dt \\
&\quad + \delta_{m,n}[1 - \lambda_1 n dt - \lambda_2(N-n)dt] \\
&= \delta_{n,m+1} \, \lambda_1(m+1)dt \\
&\quad + \delta_{n,m-1} \, \lambda_2[N-(m-1)]dt \\
&\quad + \delta_{m,n}[1 - \lambda_1 m dt - \lambda_2(N-m)dt] \,.
\end{aligned}$$

Plugging this in equation (1.8) [Page 16] yields

$$\begin{aligned}
P(\mathcal{N}_1^{(t+dt)} = m) &= P(\mathcal{N}_1^{(t)} = m) \, [1 - \lambda_1 m dt - \lambda_2(N-m)dt] \\
&\quad + P(\mathcal{N}_1^{(t)} = m+1) \, \lambda_1(m+1)dt + P(\mathcal{N}_1^{(t)} = m-1) \, \lambda_2(N-(m-1))dt \\
\frac{d}{dt} P(\mathcal{N}_1^{(t)} = m) &= P(\mathcal{N}_1^{(t)} = m) \, ((\lambda_2 - \lambda_1)m - \lambda_2 N) \\
&\quad + P(\mathcal{N}_1^{(t)} = m+1) \, \lambda_1(m+1) + P(\mathcal{N}_1^{(t)} = m-1) \, \lambda_2[N-(m-1)] \,.
\end{aligned}$$

We are interested only in the stationary distribution $P(\mathcal{N}_1^{(t\to\infty)} = m)$, the derivation of which can be found in Appendix (A.1) [Page 200]. The resulting stationary distribution reads

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STATIONARY DISTRIBUTION FOR THE EHRENFEST MODEL

$$P(\mathcal{N}_1^{(t \to \infty)} = n) = \binom{N}{n} q_1^n q_2^{N-n}$$

$$q_\alpha = \frac{V_\alpha}{V} \ .$$

This is a very interesting result. A binomial distribution occurs as if the N atoms were distributed at random among the two boxes, with prior probabilities corresponding to the partial volumes.

From the well known formulas for the mean of the binomial distribution we obtain the average number of particles in volume V_1

MEAN VALUES AND DENSITIES IN EQUILIBRIUM

$$\langle N_1 \rangle = N q_1 = \frac{N V_1}{V} = V_1 \, \rho$$

$$\rho_1 = \rho_2 = \rho$$

$$\rho_\alpha := \frac{N_\alpha}{V_\alpha} \ ; \quad \rho := \frac{N}{V} \ .$$

Thus a homogeneous density distribution is achieved in equilibrium. In the stationary state, the probability for a particle to leave V_1 within dt, $P_- = dt A \rho_1 v_x / 2 = dt A \rho v_x / 2 = P_+$, is the same as the probability that one will be added (equilibium!). This situation is called **Detailed Balance**. In equilibrium, the probability that a particle changes sides within the time interval dt (no matter from where to where) is given by

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Fluctuation probability

$$dP = dt \; A\rho v_x = dt \; \frac{N v_x}{L_x} \; .$$

(1.2)

Another important result concerns the relative uncertainty of the mean value for macroscopic systems

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Relative uncertainty of the mean value

$$\frac{\Delta N_1}{\langle N_1 \rangle} = \sqrt{\frac{q_2}{q_1 N}} = O(10^{-12}) \; ; \qquad \text{for } 10^{24} \text{Atome} \; .$$

That means, the macroscopic system tends towards a stationary distribution for which the state variables (N_1, N_2) **are sharply peaked**. The third and most valuable thing we have learned in terms of this model, is the fact that the equilibrium state is the one with the greatest probability. At equal priori probabilities that is the state with the maximum number of micro states.

With a total of N particles, the number of microstates is determined by the binomial coefficient. The maximum is at $N_1 = N/2$. This would be the average number of particles for equal priori probabilities $q_\alpha = 1/2$.

Equilibrium
(*for equal prior prob. of microstates*)

maximum probability of the microstates

Time until significant deviations occur

Let us now consider how long it will take for a system that is already in equilibrium to deviate significantly ($\Delta N_1 = r$) from equilibrium. The mean kinetic energy is $k_B T$, and so the typical velocity is $\vec{v}^{\,2} = 2k_B T/m$.

At room temperature we have $k_B T = 1.38 \cdot 10^{-23} \cdot 300 J = 4.14 \cdot 10^{-21} J$. The mass of a proton is $m_p = 1.67 \cdot 10^{-27} kg$ and the average thermal velocity for atoms with mass number A is then

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<div align="center">

THERMAL VELOCITY

</div>

$$v_x = \sqrt{\frac{2 \cdot 4.14 \cdot 10^{-21}}{A \cdot 1.67 \cdot 10^{-27}} \frac{m}{sec}} = \frac{2.23 \cdot 10^3}{\sqrt{A}} \frac{m}{sec} \; .$$

For air molecules with $A \approx 29$ this is close to the speed of sound. Since we are only interested in the order of magnitude, we consider the special case $V_1 = V_2$. And we assume that deviations from equilibrium are still so small that the probabilities for switching back and forth between the subsystems are equal. Remember that these probabilities in general depend on the actual numbers N_1 and N_2, respectively. As a matter of fact, if we take the real hopping probabilities into account, then it even takes long to reach these deviations.

So we are dealing with a random walk, where the probability for a particle to change sides is given by dP in equation (1.2) [Page 9]. The changes from left to right and vice versa occur with the same probability ($P = 1/2$). The probability for no event to occur in dt is therefor $q = 1 - dP$.

Now let us calculate how many steps it takes until the walker reaches $\Delta N = r$ or $\Delta N = -r$ for the first time when starting from $\Delta N = 0$. This is equivalent to a random walk on the integers $0, 2, \ldots, 2r$ starting in the middle at position r. The random walk ends when the positions 0 or $2r$ are reached for the first time. A detailed treatment of such random walks can be found in the book by Wolfgang Woess, **Denumerable Markov Chains**. Here we shall be content with the simplest variant: We will consider how long it takes a walker on average to reach one of the two ends for the first time. The literature term for this problem is **random walk /markov chain with absorbing walls**.

To do this, we define the average runtime E_n, which indicates how long it takes on average for the walker to reach one of the two boundaries for the first time.

There are two constraints

$$E_0 = E_{2r} = 0 \ , \tag{1.3}$$

as in both cases the goal has already been reached and no further steps are necessary.
We consider the first step:

- With probability $q = 1 - dP$ nothing changes, then after the first step the average runtime is still E_n.

- With probability $dP' = \frac{dP}{2}$ the walker jumps to the left and the remaining average runtime is E_{n-1}.

- With probability $dP' = \frac{dP}{2}$ the walker jumps to the right and the remaining average runtime is E_{n+1}.

Therefore we have

$$E_n = \left[(1 - dP)E_n + \frac{dP}{2}E_{n-1} + \frac{dP}{2}E_{n+1} \right] + 1 \ .$$

The terms in square brackets specify the average runtime after the first step. Furthermore, the time increment for the first step is added. This equation can be simplified to

$$\underbrace{(dP \cdot E_n)}_{:=D_n} = \frac{1}{2}(dP \cdot E_{n-1}) + \frac{1}{2}(dP \cdot E_{n+1}) + 1$$

$$\Rightarrow \qquad -2 = D_{n+1} + D_{n-1} - 2D_n \ . \tag{1.4}$$

In this equation the **waiting times** between hopping processes have been eliminated, and a hopping process occurs at every time step. This difference equation is equivalent to the discretized form of the differential equation

$$D''(x) = -2 \ .$$

For which the solution is $a + b\,x - x^2$. We now show that the ansatz

$$D_n = a + b\,n - n^2$$

also satisfies equation (1.4) .

$$a + b(n+1) - (n+1)^2 + a + b(n-1) - (n-1)^2 - 2\big(a + bn - n^2\big)$$
$$= -(n+1)^2 - (n-1)^2 + 2n^2$$
$$= -\big(n^2 + 2n + 1 + n^2 - 2n + 1 - 2n^2\big)$$
$$= -2 \ .$$

To fulfill the boundary conditions of equation (1.3) [Page 11] we still need

$$a + b \cdot 0 - 0^2 = 0 \ ; \qquad\qquad \Rightarrow \quad a = 0$$
$$b \cdot 2r - (2r)^2 = 0 \ ; \qquad\qquad \Rightarrow \quad b = 2r \ .$$

With that the required average number of steps is

$$D_{n=r} = br - r^2 = 2r^2 - r^2 = r^2 \ .$$

A random walk takes on average r^2 steps to cover a distance of r.
If we take the waiting times into account, we get

$$E_r = \frac{D_r}{dP} = \frac{r^2 \ L_x}{dt \ N v_x} \ .$$

We see that the number of steps diverges with dt. But the average time $\langle t \rangle := E_r dt$ is finite.

AVERAGE TIME UNTIL A FLUCTUATION $\Delta N = \varepsilon N$ OCCURS

$$\langle t \rangle = \frac{\varepsilon^2 N^2 \ L_x}{N v_x} = \frac{\varepsilon^2 N \ L_x \sqrt{A}}{2.23 \cdot 10^3} \frac{sec}{m}$$

We consider one litre of water ($A = 18$, $L_x = 10cm$, $N = 10^{27}$) and a relative particle number fluctuation of $= 10^{-6}$. Then we get

$$\langle t \rangle = \frac{10^{-12} \cdot 10^{27} \cdot 10 \cdot \sqrt{18}}{2.23 \cdot 10^5} sec = 1.9 \cdot 10^{10} sec \ .$$

A year has $a = 366 \cdot 24 \cdot 3600 sec = 3.2 \cdot 10^7 sec$, or $1 sec = 3.16 \cdot 10^{-8} a$, and thus it takes

$$\langle t \rangle = 1.9 \cdot 3.2 \cdot 10^2 \ a = 610a \ ,$$

until a fluctuation occurs.
Let us emphasize again that we have neglected the density-dependent driving force towards equilibrium [1]. With these terms, it would take even longer! From this we can conclude that we will never observe such fluctuations. This is one of the reasons for the stability and universality of thermal equilibrium.

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[1] Changes of $\Delta N_1 = \pm 1$ would be equally likely

Average time until a stationary distribution is reached

We have already shown that a macroscopic system will not leave the state of equilibrium in the sense that fluctuations are negligibly small.

Now we shall consider how long it takes to reach the equilibrium state from an arbitrary starting position. If this would also take so exorbitantly long, there would be no equilibrium thermodynamics. As initial configuration we choose the one which is farthest from equilibrium, i.e. all atoms are in one of the two volumes, say volume 1.

Similar to the previous consideration we determine the mean number of steps required to go from the state $N_1 = 0$ to the state $N_1 = N/2$ for the first time. We assume that there is a total of N particles in the system. Of course, an even numer of particles is assumed.

We define the mean runtime E_n, which is the time it takes on average to reach $N_1 = N/2$, however, here we have a different boundary condition, namely

$$E_{n=N/2} = 0 \ .$$

Again we consider the first step:

- With a probability of $r = 1 - dP$ nothing changes, therefore after the first step the average runtime is still E_n.

- With a probability of $\frac{n}{N} \, dP$ one particle moves from V_1 to V_2, i.e. there are now $n-1$ particles in V_1 and the average runtime is therefore E_{n-1}.

- With a probability of $(1 - \frac{n}{N}) \, dP$ one particle is added to N_1 and therefore the mean runtime is now E_{n+1}.

The result after the first step is given by

$$E_n = \left[(1 - dP) \, E_n + dP \, \frac{n}{N} E_{n-1} + dP \, (1 - \frac{n}{N}) E_{n+1} \right] + 1$$

$$(dP \, E_n) = \frac{n}{N}(dP \, E_{n-1}) + (1 - \frac{n}{N})(dP \, E_{n+1}) + 1 \ .$$

We introduce again the abbreviation $D_n := dP \, E_n$ and obtain

$$D_n = \frac{n}{N}D_{n-1} + (1 - \frac{n}{N})D_{n+1} + 1 \ . \tag{1.5}$$

Again D_n is the average runtime for $dP = 1$ (or $r = 0$), i. e. each step describes a hopping process. The derivation for the result can be found in Appendix (A.2) [Page 203]. The solution of this difference equation reads for

the initial condition $n = 0$

$$D_0 = \frac{N}{4} \ln(N)$$

$$\langle t \rangle = dt E_0 \overset{(1.2)}{=} \frac{L_x D_0}{N v_x}$$

$$= \frac{L_x N \ln(N)}{4 N v_x} = \frac{L_x \ln(N)}{4 v_x} \ .$$

MEAN TIME UNTIL EQUILIBRIUM IS REACHED

$$\langle t \rangle = \frac{t_x \ln(N)}{4}$$

$$t_x := \frac{L_x}{v_x} \ .$$

The quantity t_x is the time it takes an atom at the mean thermal velocity v_x to traverse the length L_x of the volume. If we again take water molecules in a cube with the edge length $L_x = 10 cm$, then this time is

$$t_x = \frac{10 \cdot \sqrt{18}}{2.23 \cdot 10^5} \ sec = 1.9 \cdot 10^{-4} \ sec \ .$$

The crucial difference to the previous result is: The time required to leave the equilibrium is proportional to N while the time to reach equilibrium is merely proportional to $\ln(N)$. Qualitatively, the result can be understood by the fact, that the increase in N_1 in dt is proportional to N_1 and the decrease is proportional to $1 - N_1/N$. As long as N_1 is small, the decrease can be ignored and we have a differential equation

$$\frac{dN_1}{dt} \propto N_1$$

with the solution $t \propto \ln(N_1) \propto \ln(N/2)$. This is not a rigorous proof but just an hand waving argument to understand the logarithmic dependence.

1.2 Model-Based introduction to statistical physics

We now want to learn more about other features of equilibrium thermodynamics. For this purpose, we will consider another simple, particularly suit-

able model. In a volume of size V there are N free classical non-interacting particles. Let the volume shown in Figure 1.2 be divided by an initially fictitious wall A into two chambers with volume V_u and V_l. A micro-state

Figure 1.2: Schematic representation of the model system.

consists of the exact location and velocity of the individual particles. At the beginning, the velocities are randomly distributed.[2] In addition the exact values of the initial conditions are unknown. Although the motion of particles obeys the laws of Newtonian mechanics, the distribution of particles among elementary volumes is random: small, imperceptible changes in initial conditions lead to significant changes in the resulting micro states.

Now we shall divide the space into small sub-volumes (voxels). The volume V_u contains M_u of those voxels and V_l contains M_l. In total there are $M = M_u + M_l$ voxels. We now want to simplify the model further. The dynamics shall cause the particles to be randomly distributed among the M voxels - within which there can only be at most one particle - at different times (i.e. a kind of hardcore interaction). If a particle randomly moves through the volume V with constant speed, the priori probability for the particle to be encountered in an elementary volume at a certain point in time is proportional to its size. For simplicity, we assume that all volumes are of equal size. A micro-state thus consists of the information, in which voxels the particles are located. We now assume that we are interested in a macroscopic measurement observable for our model, which only counts how many particles are located in the two chambers V_u and V_l, which may mimic gravitational or electrostatic effects. This defines the model we want to study.

1.2.1 Isolated chambers

At first, we consider the two chambers V_u and V_l, that shall be isolated from each other, i.e. there is a real impenetrable wall in between. If N_ν particles are located within volume V_ν with M_ν voxels ($\nu \in \{u, l\}$), then the number

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[2]In the case of interacting particles, this is a result of collisions among each other and also with the confining walls.

of micro-states that are compatible is given by

$$L_{N_\nu|M_\nu} := \binom{M_\nu}{N_\nu} = \frac{M_\nu!}{(M_\nu - N_\nu)!N_\nu!} \; .$$

Since both M_ν and N_ν are macroscopic in thermodynamic systems (order of 10^{24} or greater), we can confidently use the Stirling approximation $\ln(N!) \approx N\ln(N) - N$. For the binomial coefficients we obtain

$$\ln(L_{N_\nu|M_\nu}) \approx M_\nu \ln(M_\nu) - \cancel{M_\nu} - N_\nu \ln(N_\nu) + \cancel{N_\nu} \qquad (1.6)$$
$$- (M_\nu - N_\nu)\ln(M_\nu - N_\nu) + \cancel{M_\nu} - \cancel{N_\nu}$$
$$= M_\nu \ln(M_\nu) - N_\nu \ln(N_\nu) - (M_\nu - N_\nu)\ln(M_\nu - N_\nu) \; . \qquad (1.7)$$

Now also $M_\nu \gg N_\nu$ applies. In the classical case, the subdivision is artificial anyways and the voxel size is infinitesimally small. However, also in quantum mechanical systems the voxel size in phase space is very small (there it is given by h^3), so we can assume $M_\nu \gg N_\nu$ to be true. This further simplifies the result

$$\ln(L_{N_\nu|M_\nu}) = M_\nu \ln(M_\nu) - N_\nu \ln(N_\nu) - (M_\nu - N_\nu)\left[\ln(M_\nu) - \frac{N_\nu}{M_\nu}\right]$$

$$= \cancel{M_\nu \ln(M_\nu)} - N_\nu \ln(N_\nu) - \cancel{M_\nu \ln(M_\nu)} + N_\nu \ln(M_\nu) + N_\nu - N_\nu \frac{N_\nu}{M_\nu}$$

$$= -N_\nu\left[\ln\left(\frac{N_\nu}{M_\nu}\right) - 1 + \frac{N_\nu}{M_\nu}\right]$$

The last term is proportional to N/M and therefore negligible compared to the other terms. The prior probability for a particle to end up in volume V_ν is given by

$$q_\nu^0 := \frac{M_\nu}{M}$$

We also define the posterior probability for volume V_ν by

$$q_\nu := \frac{N_\nu}{N} \; .$$

With these definitions lead to

$$\mathcal{S}_\nu(N_\nu) := \ln(L_{N_\nu|M_\nu}) = -Nq_\nu\left[\ln\left(\frac{q_\nu}{q_\nu^0}\right) - 1\right] \qquad (1.8)$$

$$= -N_\nu\left[\ln\left(\frac{N_\nu}{N_\nu^0}\right) - 1\right] \qquad (1.9)$$

$$N_\nu^0 := q_\nu^0 N \; . \qquad (1.10)$$

As a matter of fact, there is an additional term

$$-N_\nu \ln(\frac{M}{N}) \ . \tag{1.11}$$

We will see that it is unimportant. The right hand side of equation (1.8) [Page 16] and equation (1.9) [Page 16] respectively correspond to the relative entropy, which we have again expressed in the particle numbers. Interestingly, it is only important, how the total number of particles is split into the the two chambers. Further details, how the particles are distributed with the chambers do not enter. All that matter from the voxels is the relative number M_ν/M. As we assume equal prior probability for each voxel, this information is equivalent to the relative volume V_ν/V of the chambers.

1.2.2 Particle exchange between both parts

We now want to remove the wall A between the chambers so that the particles can freely change chambers. This is an embryonic model for a grand canonical ensemble. The total number of particles for this system is stil l conserved $N = N_u + N_l$. The number of microstates at fixed N_u and N_l is

$$\Gamma(N_u, N_l) := L_{N_u, N_l | M_u, M_l} = L_{N_u | M_u} L_{N_l | M_l} \ ,$$

because any micro-state of subsystem V_u can be paired with any micro-state of V_l. As long as $N = N_u + N_l$ is fulfilled, we can now arbitrarily distribute the total number of particles on N_ν. The number of micro-states of the total system $\Gamma(N)$ therefore is

$$\Gamma(N) = \sum_{N_u=0}^{N} L_{N_u | M_u} L_{N_l(N_u) | M_l}$$
$$N_l(N_u) := N - N_u \ .$$

First of all, we look at one of the summands and define

$$\mathcal{S}_{12}(N_u, N_l) := \ln\left(L_{N_u | M_1} L_{N_l | M_2}\right) = \sum_{\nu \in \{u,l\}} \ln(L_{N_\nu | M_\nu}) = \sum_{\nu \in \{u,l\}} \mathcal{S}_\nu(N_\nu)$$
$$\tag{1.12}$$

Since all involved numbers are of macroscopic size, we can use the stationary phase approximation, which is explained in Appendix (B) [Page 209]. For this purpose we expand $\mathcal{S}_{12}\big(N_u, N_l(N_u)\big)$ around its maximum in N_u up to quadratic order of the deviations from the maximum. First, we want to determine the maximum as a function of N_u.

We see indeed that here the extra term in equation (1.11) [Page 17], when summed over ν is constant, since N is fixed and it does not contribute to the derivative. Similar observations are made in the next section.

As usual, we determine the maximum from the zero of the derivative. Taking into account that $\frac{dN_l(N_u)}{dN_u} = -1$ we get

$$
\begin{aligned}
\frac{d\mathcal{S}(N_u, N_l(N_u))}{dN_u} &= \frac{\partial S_u(N_u, N_l(N_u))}{\partial N_u} - \frac{\partial S_l(N_u, N_l(N_u))}{\partial N_l} \\
&= -\ln\left(\frac{N_u}{N_u^0}\right) + \ln\left(\frac{N_l}{N_l^0}\right) \stackrel{!}{=} 0 \qquad (1.13) \\
\frac{N_u}{N_u^0} &= \frac{N_l}{N_l^0} = c \ .
\end{aligned}
$$

From this, together with the condition $N_u + N_l = N$, we get

$$
N_\nu = c \cdot N_\nu^0
$$

$$
N = \sum N_\nu = c \sum N_\nu^0 = c \cdot N
$$

$$
\Rightarrow \qquad c = 1
$$

respectively

$$
N_\nu = N_\nu^0 = N\frac{M_\nu}{M} \ ; \qquad \Rightarrow \frac{N_\nu}{M_\nu} = \frac{N}{M}
$$

This means that the equilibrium configuration corresponds to the case where the densities in both chambers are equal. At the same time we conclude that

$$
\frac{\partial S_u(N_u, N_l)}{\partial N_u} = \frac{\partial S_l(N_u, N_l)}{\partial N_l} \ .
$$

The expression $\tilde{\mu} := \frac{\partial S(N_u, N_l)}{\partial N_\nu}$ apparently is an equilibrium quantity. It implies that the entropy changes by $\tilde{\mu}dN$ if the particle number changes by dN. This is identical on both sides. The quantity $\tilde{\mu}$ is proportional to the chemical potential. It follows that at equilibrium, equal densities will be found in both chambers when the system is in the macro-state with the most micro-states.

We now proceed with the stationary phase approximation. To this end we need the second derivative of S at the maximum. From the first derivative in equation (1.13) [Page 18] we obtain

$$
\begin{aligned}
\frac{d^2\mathcal{S}(N_u, N_l(N_u))}{dN_u^2} &= \frac{d}{dN_u}\left(-\ln\left(\frac{N_u}{N_l^0}\right) + \ln\left(\frac{N_l}{N_l^0}\right) \right) \\
&= -\frac{\partial}{\partial N_u}\ln\left(\frac{N_u}{N_u^0}\right) + \frac{\partial}{\partial N_l}\ln\left(\frac{N_l}{N_l^0}\right)\left(\frac{dN_l}{dN_u}\right) \\
&= -\frac{1}{N_u} - \frac{1}{N_l} = -\frac{N_u + N_l}{N_u N_l} = -\frac{N}{N_u N_l}
\end{aligned}
$$

We need this derivation at the maximum $N_\nu = N_\nu^0$. Then the stationary phase approximation for the summands yields

$$L_{N_u|M_u} L_{N_l|M_l} = L_{N_u^0|M_u} L_{N_l^0|M_l} \ exp\left(-\frac{N}{2N_l^0 N_u^0}(N_u - N_u^0)^2\right) .$$

The relative uncertainty for the macroscopic quantity N_u therefore is

$$\varepsilon_{\text{rel}} := \frac{\sigma_{N_u}}{N_u^0} = \sqrt{\frac{2\pi N_u^0 N_l^0}{N(N_u^0)^2}} = \sqrt{\frac{2\pi N_l^0}{N_u^0 N}} \propto \frac{1}{\sqrt{N}} .$$

The relative uncertainty for macroscopic systems is again smaller than 10^{-12}. This means that of all summands, only very few that are in close proximity to the most probable value for N_u actually contribute. We now evaluate the sum in the stationary phase approximation. We can convert the sum into an integral, since the increments of 1 becomes infinitesimal for macroscopic N_u. Because the integrand has an extremely sharp peak, we can also extend the integral over the entire real axis.

$$\Gamma(N) = L_{N_u^0|M_u} L_{N_l^0|M_l} \int_{-\infty}^{\infty} e^{-\frac{1}{2\sigma^2}(N_u - N_u^0)^2} \ dN_u$$

$$= L_{N_u^0|M_u} L_{N_l^0|M_l} \sqrt{2\pi q_u^0 q_l^0/N} .$$

Finally the entropy of the entire system is

$$\mathcal{S}(N) := \ln\left(\Gamma(N)\right) = S_1(N_u^0) + S_2(N_l^0) + \frac{1}{2}\ln(2\pi q_u^0 q_l^0) - \frac{\ln(N)}{2} .$$

Since S_ν is proportional to N, the last two terms are of the order $\frac{\ln(N)}{N}$ and thus negligible in macroscopic systems. Therefore, the following applies:

$$\mathcal{S}(N) := S_u(N_u^0) + S_l(N_l^0) .$$

This is the **extensivity** of the entropy.
Furthermore, the following is valid:

$$\frac{d\mathcal{S}(N)}{dN} = \frac{dS_u(N_u)}{dN_u}\Big|_{N_u=N_u^0}\frac{dN_u^0}{dN} + \frac{dS_l(N_l)}{dN_l}\Big|_{N_l=N_l^0}\frac{dN_l^0}{dN}$$

$$= \tilde{\mu} \ q_u^0 + \tilde{\mu} \ q_l^0 = \tilde{\mu} .$$

This shows that the definition is consistent. The chemical potential of the overall system is identical to that of the two subsystems. As mentioned above, we now calculate a macroscopic model oberservable, e.g. the energy, which should be E_u within the volume V_u and zero in V_l (zero-point of energy!).

Thus we get an energy of $E = E_u N_u$. If we write the energy in units of E_u, the average energy is $\langle E \rangle = \langle N_u \rangle$ and the variance is that of N_u. Thus, the macroscopic observable has a relative uncertainty of $1/\sqrt{N}$.

Another important result of these considerations is that the macro-state with the largest number of micro-states is again attained (the sum is dominating here) with negligibly small uncertainties.

1.2.3   Thermal equilibrium (energy exchange)

We now want to extend the model so that we can investigate what happens when two previously isolated systems $\Sigma^{(1)}$ and $\Sigma^{(2)}$ are brought into thermal contact.
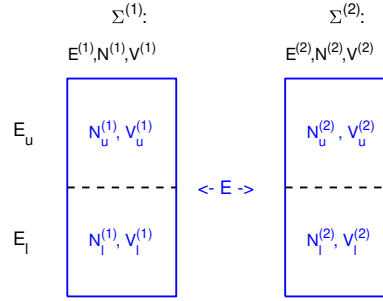
Figure 1.3: Schematic representation of the model system.

System $\Sigma^{(i)}$ has the volume

$$V^{(i)} = V_u^{(i)} + V_o^{(i)}$$

and it contains the folllowing number of particles

$$N^{(i)} = N_u^{(i)} + N_o^{(i)} \ .$$

These quantities should be conserved when thermal contact between the systems is established. This does not hold true for the energies $E^{(1)}$ and $E^{(2)}$. They may differ if the two systems are in thermal contact. Due to the experimental setup, these energies do not necessarily have to correspond to the maximum number of microstates for the isolated systems.

Initially, the two systems are isolated with their individual energies $E^{(\nu)}$.

Now we bring the systems into thermal contact, i.e. they can exchange energy. As already mentioned, the particle numbers and volumes of the two systems remain unchanged. However, the energies $E^{(i)}$ can change, albeit the new overall system shall be isolated from the rest of the world, so that the total energy is conserved

$$E = E^{(1)} + E^{(2)} \ .$$

The change of the energies of the subsystems is achieved by changing the distribution of the particle numbers for the two chambers of each of the two systems.[3] That is to say, the particle numbers in the chambers $N_\nu^{(i)}$ are now variable, albeit under the following constraints:

$$N^{(i)} = N_l^{(i)} + N_u^{(i)} \ ; \qquad\qquad \text{for } i = 1, 2 \ . \qquad (1.14)$$

However, the volumes of the chambers are fixed. For the following calculations we can use the results of the previous sections. However, for the systems $\Sigma^{(i)}$ the particle numbers of the sub-volumes N_ν are now denoted by the conditional particle numbers $N_{\nu|i}$. The total number of particles N of the single system then turns into the particle number $N^{(i)}$ of the system i.

We are now interested in the number of micro-states of the overall system for the macro-state (state variable) $N_u = N_u^{(1)} + N_u^{(2)}$. We define the number of microstates using marginalisation

$$\Gamma(N_u) = \sum_{N_u^{(1)}=0}^{N_u} \underbrace{\Gamma(N_u^{(1)})}_{=\Sigma^{(1)}} \underbrace{\Gamma(N_u^{(2)}(N_u^{(1)}))}_{=\Sigma^{(2)}} \qquad (1.15)$$

$$N_u^{(2)}(N_u^{(1)}) := N_u - N_u^{(1)} \ .$$

With the stationary phase approximation we first simplify the summands in a similar way, as we have done before for a single system. To this end we use equation (1.12) [Page 17].

$$\mathcal{S} := \ln\left(\Gamma(N_u^{(1)})\,\Gamma(N_u^{(2)}(N_u^{(1)}))\right) = \sum_{i=1}^{2} \ln\left(\Gamma(N_u^{(i)})\right)$$

$$\overset{(1.12)}{=} \sum_i \sum_\nu \mathcal{S}_\nu^{(i)}(N_\nu^{(i)})$$

---

[3]We will see that the macrostate with the most microstates (maximum probability) will be achieved again.

It should be noted noted that for the particle-number arguments, the constraints of equation (1.14) [Page 21] have to be fulfilled. For a single summand we now use equation (1.9) [Page 16] and obtain

$$\mathcal{S} = \sum_i \underbrace{\left\{ -\sum_{\nu \in \{u,l\}} N_\nu^{(i)} \left[\ln(\frac{N_\nu^{(i)}}{N_\nu^{0(i)}}) - 1 \right] \right\}}_{\mathcal{S}_i} \tag{1.16}$$

$$= \mathcal{S}_1(N_u^{(1)}, N_l^{(1)}(N_u^{(1)})) + \mathcal{S}_2(N_u^{(2)}, N_l^{(2)}(N_u^{(2)})) \tag{1.17}$$

$$\text{with:} \qquad N_l^{(i)}(N_u^{(i)}) = N^{(i)} - N_u^i . \tag{1.18}$$

First of all we find that $\mathcal{S} = \mathcal{S}(N_u^{(1)}, N_l^{(1)}, N_u^{(2)}, N_l^{(2)})$ is a function of the numbers of particles in the four chambers. However, only one of these particle numbers can be chosen independently, whereas all the others are dependent via the following constraints

$$N_u^{(1)} + N_u^{(2)} = N_u \Rightarrow \qquad N_u^{(2)} = N_u - N_u^{(1)} \quad \text{(energy conservation)}$$

$$N_u^{(i)} + N_l^{(i)} = N^{(i)} \quad \text{(conservation of the number of particles)} \quad \Rightarrow$$

$$N_l^{(i)} = N^{(i)} - N_u^{(i)}$$

$$N_l^{(2)} = N^{(2)} - N_u^{(2)} = N^{(2)} - N_u + N_u^{(1)}$$

$$N_l^{(1)} = N^{(1)} - N_u^{(1)} .$$

Therefore $N_u^{(1)}$ can be chosen as the independent variable. We summarise the result

---

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given variable : $N_u, N^{(1)}, N^{(2)}$

independent variable : $N_u^{(1)}$

dependant variable :

$$N_u^{(2)} = N_u - N_u^{(1)}$$

$$N_l^{(1)} = N^{(1)} - N_u^{(1)}$$

$$N_l^{(2)} = N^{(2)} - N_u + N_u^{(1)} \tag{1.19}$$

$$\frac{dN_l^{(1)}}{dN_u^{(1)}} = -1$$

$$\frac{dN_u^{(2)}}{dN_u^{(1)}} = -1$$

$$\frac{dN_l^{(2)}}{dN_u^{(1)}} = 1 \ .$$

</div>

Now we determine the value of the independant state variable $(N_u^{(1)})$, for which the number of microstates (same as $\mathcal{S}$) becomes maximal. For this we need the zero of the derivation of $\mathcal{S}$ with respect to $N_u^{(1)}$

$$\frac{d\mathcal{S}}{dN_u^{(1)}} = \frac{d\mathcal{S}^{(1)}}{dN_u^{(1)}} + \frac{d\mathcal{S}^{(2)}}{dN_u^{(1)}} = \frac{d\mathcal{S}^{(1)}}{dN_u^{(1)}} + \frac{d\mathcal{S}^{(2)}}{dN_u^{(2)}} \underbrace{\frac{dN_u^{(2)}}{dN_u^{(1)}}}_{-1} \tag{1.20}$$

$$= \frac{d\mathcal{S}^{(1)}}{dN_u^{(1)}} - \frac{d\mathcal{S}^{(2)}}{dN_u^{(2)}} \overset{!}{=} 0 \tag{1.21}$$

This relation defines inn the present context a new equilibrium quantity. We have to recall that the energy in system $\Sigma^{(i)}$ is given by $E^{(i)} = E_u N_u^{(i)}$, where E_u is the energy unit, then in equilibrium (where the number of micro-states is maximal) the following applies:

THERMAL EQUILIBRIUM AND TEMPERATURE

$$\frac{dS^{(1)}}{dE^{(1)}} = \frac{dS^{(2)}}{dE^{(2)}} =: \frac{1}{k_B T} \tag{1.22}$$

This formula corresponds to the statistical definition of temperature. We further reshape the derivations in equation (1.21) [Page 23]

$$\begin{aligned}
\frac{dS^{(i)}}{dN_u^{(i)}} &= \frac{dS^{(i)}(N_u^{(i)}, N_l^{(i)}(N_u^{(i)}))}{dN_u^{(i)}} \\
&= \frac{\partial S^{(i)}}{\partial N_u^{(i)}} + \frac{\partial S^{(i)}}{\partial N_l^{(i)}} \underbrace{\frac{dN_l^{(i)}}{dN_u^{(i)}}}_{-1} \\
&= \frac{\partial S^{(i)}}{\partial N_u^{(i)}} - \frac{\partial S^{(i)}}{\partial N_l^{(i)}}
\end{aligned}$$

$$\stackrel{(1.16)}{\Rightarrow} \quad \frac{dS^{(i)}}{dN_u^{(i)}} = -\ln\left(\frac{N_u^{(i)}}{N_u^{0(i)}}\right) + \ln\left(\frac{N_l^{(i)}}{N_l^{0(i)}}\right). \tag{1.23}$$

Barometric formula

Now we want to make sure that the temperature introduced in this way has the right properties. On the one hand, the following applies

$$\begin{aligned}
\frac{E_u}{k_B T} = E_u \frac{dS^{(i)}}{dE^{(i)}} &= \frac{dS^{(i)}(N_u^{(i)}, N_l^{(i)}(N_u^{(i)}))}{dN_u^{(i)}} \\
&\stackrel{(1.23)}{=} -\ln\left(\frac{N_u^{(i)}}{N_u^{0(i)}}\right) + \ln\left(\frac{N_l^{(i)}}{N_l^{0(i)}}\right) \\
&= \ln\left(\frac{N_u^{0(i)} N_l^{(i)}}{N_u^{(i)} N_l^{0(i)}}\right).
\end{aligned}$$

Therefore we have

$$\ln\left(\frac{N_u^{0(i)} N_l^{(i)}}{N_u^{(i)} N_l^{0(i)}}\right) = \beta E_u. \tag{1.24}$$

This equation will give us the barometric formula. For the same prior probabilities for lower end upper chamber, i. e. $N_u^{0(i)} = N_l^{0(i)}$, the following applies:

$$\ln\left(\frac{N_l^{(i)}}{N_u^{(i)}}\right) = \beta E_u$$

$$\Rightarrow \qquad \frac{N_u^{(i)}}{N_l^{(i)}} = e^{-\frac{E_u}{k_B T}} = e^{-\beta(E_u - E_l)}$$

$$N_\nu^{(i)} = C^{(i)}\, e^{-\beta E_\nu}\ .$$

The normalisation according to the total particle number gives

$$N^{(i)} = \sum_\nu N_\nu^{(i)} = C^{(i)} \sum_\nu e^{-\beta E_\nu}$$

$$N_\nu^{(i)} = \frac{N^{(i)}}{e^{-\beta E_u} + e^{-\beta E_l}}\, e^{-\frac{E_\nu}{k_B T}}\ .$$

or rather

$$P(E_\nu) = \frac{N_\nu^{(i)}}{N^{(i)}} = \frac{1}{Z} e^{-\beta E_\nu}$$

The probability is independent of the the system $\Sigma^{(i)}$. It only depends on the energy E_ν.

Direction of energy transfer

These model considerations also show in which direction energy flows during thermal contact. For this purpose, we consider an initial state characterized by the occupation numbers $N_u^{*(i)}$ and $N_l^{*(i)}$. The temperatures of the two initially separated systems are defined in equation (1.22) [Page 24].

$$\frac{E_u}{k_B T^{*(i)}} = \ln\left(\frac{N_u^{0(i)} N_l^{*(i)}}{N_u^{*(i)} N_l^{0(i)}}\right)$$

Note that the temperatures are different at the beginning. After thermal contact, the temperature of the entire system is in thermal equilibrium.

$$\frac{E_u}{k_B T} = \ln\left(\frac{N_u^{0(i)} N_l^{(i)}}{N_u^{(i)} N_l^{0(i)}}\right)\ ; \qquad \text{applies to both } i \text{ equally!}$$

$$= \ln\left(\frac{N_u^{*(i)} N_l^{(i)}}{N_u^{(i)} N_l^{*(i)}}\right) + \underbrace{\ln\left(\frac{N_u^{0(i)} N_l^{*(i)}}{N_u^{*(i)} N_l^{0(i)}}\right)}_{E_u/k_B T^{*(i)}}$$

$$\frac{E_u}{k}\left(\frac{1}{T} - \frac{1}{T^{*(i)}}\right) = \ln\left(\frac{N_u^{*(i)} N_l^{(i)}}{N_u^{(i)} N_l^{*(i)}}\right) = \ln\left(\frac{N_u^{*(i)}(N^{(i)} - N_u^{(i)})}{N_u^{(i)}(N^{(i)} - N_u^{*(i)})}\right)\ .$$

If the initial temperature (before contact) in the system $\Sigma^{(i)}$ was higher than the final temperature $T^{*(i)} > T$, then the left hand side is positive and the right hand side yields

$$N_u^{*(i)}(N^{(i)} - N_u^{(i)}) > N_u^{(i)}(N^{(i)} - N_u^{*(i)})$$

$$N_u^{*(i)}N^{(i)} - \overbrace{N_u^{*(i)}N_u^{(i)}}^{(1)} > N_u^{(i)}N^{(i)} - \overbrace{N_u^{(i)}N_u^{*(i)}}^{(1)}$$

$$N_u^{*(i)}N^{(i)} > N_u^{(i)}N^{(i)}$$

$$N_u^{*(i)} > N_u^{(i)} \ .$$

This means, that after contact the energy in $\Sigma^{(i)}$ decreases if its initial temperature was higher than the final temperature.

Additivity of entropy

So far we have only calculated the maximal contribution to the sum in equation (1.15) [Page 21]. We now continue with the stationary phase approximation. For this purpose we need the second derivative at the maximum. First, we transform the first derivative which we determined in equation (1.20) [Page 23]

$$\frac{d\mathcal{S}}{dN_u^{(1)}} = \frac{d\mathcal{S}^{(1)}}{dN_u^{(1)}} - \frac{d\mathcal{S}^{(2)}}{dN_u^{(2)}}$$

$$\stackrel{(1.23)}{=} -\left(\ln\left(\frac{N_u^{(1)}}{N_u^{0(1)}}\right) - \ln\left(\frac{N_l^{(1)}}{N_l^{0(1)}}\right) - \ln\left(\frac{N_u^{(2)}}{N_u^{0(2)}}\right) + \ln\left(\frac{N_l^{(2)}}{N_l^{0(2)}}\right) \right)$$

$$\frac{d^2\mathcal{S}}{d\left(N_u^{(1)}\right)^2} = -\frac{d}{dN_u^{(1)}}\left(\ln\left(\frac{N_u^{(1)}}{N_u^{0(1)}}\right) - \ln\left(\frac{N_l^{(1)}}{N_l^{0(1)}}\right) - \ln\left(\frac{N_u^{(2)}}{N_u^{0(2)}}\right) + \ln\left(\frac{N_l^{(2)}}{N_l^{0(2)}}\right) \right)$$

$$= -\left(\frac{1}{N_u^{(1)}} + \frac{1}{N_l^{(1)}} + \frac{1}{N_u^{(2)}} + \frac{1}{N_l^{(2)}} \right)$$

$$= O(\frac{1}{N})$$

The sign changes originate from $\frac{dN_l^{(1)}}{dN_u^{(1)}} = -1, \frac{dN_u^{(2)}}{dN_u^{(1)}} = -1, \frac{dN_l^{(2)}}{dN_u^{(1)}} = 1$ from equation (1.19) [Page 23].
Now we can again transform the sum in equation (1.15) [Page 21] into a gaussian integral and eventually we get the additivity of entropy

$$\mathcal{S} = S^{(1)} + S^{(2)} \ .$$

The correction terms are again of the order $O(\ln(N))$. This means, that the relative uncertainty is – omitting the correction terms – of order $O(\ln(N)/N)$ and vanishes in the thermodynamic limit.

Consistency of the temperature definition

Finally, we want to check whether the temperature definition leads to a consistent result for the entire system as well.

$$\frac{E_u}{k_B T_{ges}} = \frac{d\mathcal{S}}{dN_u} \ .$$

In equation (1.19) [Page 23] we found that

$$N_u^{(2)} = N_u - N_u^{(1)}$$
$$\frac{dN_u^{(2)}}{dN_u} = 1 - \frac{dN_u^{(1)}}{dN_u} \tag{1.25}$$

The dependency on N_u is given explicitly in $N_u^{(2)}$ and $N_l^{(2)}$ and also implicitly via the optimal $N_u^{(1)}$, which of course is a function of N_u. We, therefore, have

$$\frac{E_u}{k_B T_{ges}} = \frac{d\mathcal{S}^{(1)}(N_u^{(1)}, N_l^{(1)}(N_u^{(1)}))}{dN_u} + \frac{d\mathcal{S}^{(2)}(N_u^{(2)}, N_l^{(2)}(N_u^{(2)}))}{dN_u}$$

$$= \underbrace{\frac{d\mathcal{S}^{(1)}(N_u^{(1)}, N_l^{(1)}(N_u^{(1)}))}{dN_u^{(1)}}}_{\frac{E_u}{k_B T^{(1)}}} \frac{dN_u^{(1)}}{dN_u} + \underbrace{\frac{d\mathcal{S}^{(2)}(N_u^{(2)}, N_l^{(2)}(N_u^{(2)}))}{dN_u^{(2)}}}_{\frac{E_u}{k_B T^{(2)}}} \underbrace{\frac{dN_u^{(2)}}{dN_u}}_{\overset{(1.25)}{=} 1 - \frac{dN_u^{(1)}}{dN_u}}$$

$$= \left(\frac{E_u}{k_B T^{(1)}} - \frac{E_u}{k_B T^{(2)}} \right) \frac{dN_u^{(1)}}{dN_u} + \frac{E_u}{k_B T^{(2)}} \ .$$

Now in equilibrium $T^{(1)} = T^{(2)} = T$ applies and therefore we indeed have a consistent result

$$T_{tot} = T \ .$$

1.2.4 Entropy

So far, we have used the expression $\mathcal{S} = \ln(\Gamma)$ for entropy, i.e., the logarithm of the number of microstates. How does this actually relate to the definition we used in probability theory? With p_l as the probability of the l-th microstate, the (Shanon) entropy we used in probability theory is

$$S = - \sum_{l=1}^{\Gamma} p_l \ln(p_l) \ .$$

The principle of maximum entropy states that this entropy has to be maximized taking the constraints into account. If there are no constraints other

than normalisation, then the maximum entropy solution is $p_l = 1/\Gamma$. If we plug this into the entropy, we get

$$S^{ME} = -\sum_{l=1}^{\Gamma} \frac{1}{\Gamma} \ln\left(\frac{1}{\Gamma}\right)$$
$$= \ln(\Gamma) = \mathcal{S}$$

So the entropy (Boltzmann entropy) as log-number of microstates is the Shannon/ Gibbs entropy at the maximum. Entropy as a measure of uncertainty or disorder is uniquely defined except for a proportionality constant, which has no influence on the maximum entropy probabilities of the various states. According to Boltzmann, in thermodynamics entropy is defined as

$$\mathcal{S} := k_B \ln(\Gamma) \ .$$

ENTROPY

The Boltzmann entropy corresponds to the maximum value for entropy from probability theory

---

1.2.5   Increase in entropy

Entropy increases when two previously separated systems are brought into contact, as this decreases the number of constraints. An example for such forms of contact would be thermal contact. At first $N_u^{(1)}$ and $N_u^{(2)}$ are individually predefined. Thus, the number of microstates in the overall system is given by the product of the numbers of micro-states for fixed $N_u^{(1)}$ and $N_u^{(2)}$. Afterwards only the sum is given and a summation over all $N_u^{(1)}$ is performed. The previous value is only one contribution to the sum over. Therefore also the number of micro-states and the entropy increase.

1.3 Summary of the model based considerations

1.3.1 Dynamics in Ehrefest model
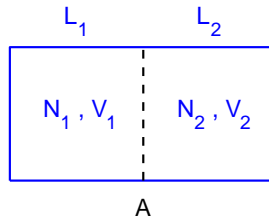
- Dynamics leads to quickly equilibrium

- the system never gets out of equilibrium

- Micro: detailed position of all particles

- Macro: N_1, N_2

- Dynamics unimportant, purely probabilistic

- equilibrium state: that with most microstates

- Equilibrium quantity: $\rho_1 = \rho_2$

- micro: NO time arrow

- macro: time arrow

1.3.2   Particle fluctuations in terms of microstates

- Counting microstates

- Micro: Detailed distribution of particles into voxels

- Macro: N_u, N_l

- Definition of statistical entropy: $S = \ln(\Gamma)$

- Equilibrium (Maximum number of micro states w.r.t. N_u) $\Rightarrow$ new equilibrium quantity:

$$\mu_\nu = \frac{\partial S_\nu}{\partial N_\nu} \ .$$

- in equilibrium: chemical potential is constant in space and time

1.3.3   Energy transfer in terms of microstates
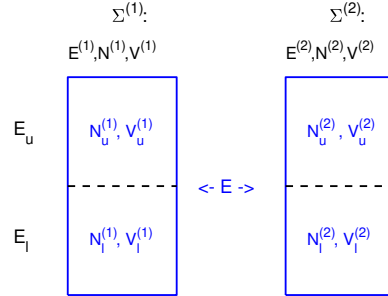
- Counting microstates

- Micro: Detailed distribution of particles into voxels

- Macro: $N_u^{(i)}$, N_l but only $N_u^{(1)}$ is independent

- Equilibrium (Maximum number of micro states w.r.t. N_u) $\Rightarrow$ new equilibrium quantity: statistical def. of temperature: $\frac{1}{k_B T_\nu} = \frac{\partial S_\nu}{\partial E_\nu}$

- in equilibrium: temperature is constant in space and time

- $S_{total} = S_1(N_u^*) + S_2(N_u^*)$ (additivity)

- entropy never decreases

- energy flows from warmer to colder areas

1.4   Various averages

It is observed experimentally that in the thermodynamic limit – that is, when a great number of particels is involved (typically $N > 10^{24}$) and time as well as spatial resolution are not too detailed – macroscopic observables[4] are time-independent. Furthermore, it can be determined that such observables dependent only on very few state variables (such as temperature, pressure, volume, density, ...) and are reversible. This means that no matter how the system was prepared once it reaches equilibrium, the state variables always have the same values.
We will now try to understand this behaviour stating from the microscopic Hamiltonian equations of motion.

1.4.1   Hamiltonian equation of motion

From theoretical mechanics we know that in the Hamilton formalism, the trajectory of a particle is given by the time dependence of a generalised coordinate $x(t)$ and the associated generalised (canonical) momentum $p(t) = \frac{\partial \mathcal{L}}{\partial \dot{x}}$. We now consider the phase space for N particles. In a d-dimensional physical space, the phase space for N particles is $2dN$-dimensional. The coordinates of a point π in phase space are defined as follows

$$\pi = \left(x_1, x_2, \ldots, x_{\mathcal{N}}, p_1, p_2, \ldots, p_{\mathcal{N}} \right) \tag{1.26}$$

$$\mathcal{N} := N \cdot d . \tag{1.27}$$

The Hamilton equations read

$$\frac{dx_\nu}{dt} = \frac{\partial H}{\partial p_\nu} \tag{1.28a}$$

$$\frac{dp_\nu}{dt} = -\frac{\partial H}{\partial x_\nu} \qquad \text{for } \nu \in \{1, \ldots \mathcal{N}\} \tag{1.28b}$$

We can now also define a $2dN$-dimensional Nabla operator as

$$\nabla_\pi = \left(\frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}, \ldots, \frac{\partial}{\partial x_{\mathcal{N}}}, \frac{\partial}{\partial p_1}, \frac{\partial}{\partial p_2}, \ldots, \frac{\partial}{\partial p_{\mathcal{N}}} \right)^T . \tag{1.29}$$

Two important comments:

- (1.28) is an ordinary first order differential equation. Specifying the initial value (point in phase space) uniquely determines how the trajectory continues. Most importantly this means that trajectories cannot intersect!! However, they can form closed paths.

---

[4]this of course implies spatial averaging

- Of course, at a later point in time the trajectory depends on its starting location. However, How it proceeds does not depend on it, but only on the current position (like a markov process).

On the right hand sides of (1.28) momentum and coordinate are reversed in the derivatives in contrast to the left hand side. Therefore, we introduce a $2dN$-dimensional matrix T, which performs the swapping of ∇_π and it also contains the extra minus sign, such that we can write

$$\frac{d}{dt}\pi = T\nabla_\pi H$$

The matrix has a 2×2 block form, with each of the 4 blocks being a $dN \times dN$ matrix, reads

$$T = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} .$$

The matrix T has the special property that when applied to a $2\mathcal{N}$-dimensional vector, it creates an orthogonal vector. That means: $xTx = 0$. This transformation is called symplectic.

1.4.2 Time average

We now consider the motion of a point in phase space. At an initial time $t = 0$, the system be at the point $\pi_0 = \pi(t = 0)$. According to Hamilton's equations of motion, the point in phase space moves and at a later point in time t it is located at $\pi(t)$. An observable F, which is not explicitly time-dependent then has the value $F(\pi(t))$. As outlined already in the beginning we are not interested in microscopic details. We therefore average over space and time. Of course, if we look closely we will see the individual atoms and their temporal motion and time dependence. The spatial averaging shall be included in the definition of the macroscopic observable $F(\pi)$. Nevertheless, one would still not expect a stationary behaviour. This can only be the case if one also averages over a short period of time. This means, what we observe in "thermodynamic" experiments also contains a time average

$$\overline{F}^Z(t) := \frac{1}{T}\int_{t-\frac{T}{2}}^{t+\frac{T}{2}} F(\pi(t'))dt' = \frac{1}{T}\int_{t-\frac{T}{2}}^{t+\frac{T}{2}} F(\pi(t')) \underbrace{\left(\int \delta(\pi - \pi(t'))\, d^{2\mathcal{N}}\pi\right)}_{=1} dt'$$

$$= \int F(\pi) \underbrace{\left(\frac{1}{T}\int_{t-\frac{T}{2}}^{t+\frac{T}{2}} \delta(\pi - \pi(t'))\, dt'\right)}_{\rho^Z(\pi,t)} d^{2\mathcal{N}}\pi .$$

Here we have transformed the time average into a general form for averages of functions $F(\pi)$ over phase space with the corresponding probability density $\rho^Z(\pi, t)$.

TIME AVERAGE

$$\overline{F}^Z(t) = \int F(\pi)\rho^Z(\pi, t)d\pi$$

$$\rho^Z(\pi, t) := \left(\frac{1}{T}\int_{t-\frac{T}{2}}^{t+\frac{T}{2}} \delta(\pi - \pi(t')) \, dt'\right)$$

The probability density $\rho^Z(\pi, t)$ determines the probability to find the trajectory within the volume $d\pi$ centred around the point π in phase space at time t. This probability density is proportional to the average time spent by the phase space trajectory within the volume $d\pi$ at π in total. The experimental observation that macroscopic observables are stationary in thermal equilibrium implies that $\rho^Z(\pi, t)$ is time independent.

1.4.3   Ensemble average

There is another method for averaging, which is the so called ensemble average. It is impossible to know the exact initial state of a thermodynamic system. This situation can also be described by many points in phase space (ensemble). These points all evolve independently from each other with time according to Hamilton's equations of motion. The trajectory for the n-th point of the ensemble be $\pi^n(t)$. The ensemble average is therefore

$$\overline{F}^S(t) := \frac{1}{N}\sum_{n=1}^{N} F(\pi^n(t))$$

$$= \frac{1}{N}\sum_{n=1}^{N} F(\pi^n(t))\int \delta(\pi - \pi^n(t)) \, d\pi$$

$$= \int F(\pi)\underbrace{\left(\frac{1}{N}\sum_{n=1}^{N}\delta(\pi - \pi^n(t))\right)}_{\rho^S(\pi, t)} \, d\pi \; .$$

This leads to

ENSEMBLE AVERAGE

$$\overline{F}^S(t) = \int F(\pi)\, \rho^S(\pi, t)\, d\pi \ .$$

This expression is formally equal to the time average. However, the density has a completely different meaning. Now it represents the probability density $\rho^S(\pi, t)$ for the members of the ensemble to be found within the volume $d\pi$ at π at time t. For an infinite number of ensemble points we get something like a mass density, which is well known from fluid mechanics. For this density we can derive an equation of motion

$$\frac{\partial}{\partial t}\rho^S(\pi, t) = \frac{\partial}{\partial t}\frac{1}{N}\sum_{n=1}^{N}\delta(\pi - \pi^n(t)) = -\frac{1}{N}\sum_{n=1}^{N}\left(\nabla_\pi \delta(\pi - \pi^n(t))\ \right)\dot{\pi}^n(t)$$

$$= -\frac{1}{N}\sum_{n=1}^{N}\left(\nabla_\pi \delta(\pi - \pi^n(t))\right)\ T\nabla_{\pi'}H(\pi')\bigg|_{\pi'=\pi^n(t)} \ .$$

Because of the delta functional we can freely choose in the last argument $\pi^n(t) = \pi$ and therefore we get

$$\frac{\partial}{\partial t}\rho^S(\pi, t) = -\frac{1}{N}\sum_{n=1}^{N}\nabla_\pi \delta(\pi - \pi^n(t))\ T\nabla_\pi H(\pi)$$

$$= -\nabla_\pi \underbrace{\left(\frac{1}{N}\sum_{n=1}^{N}\delta(\pi - \pi^n(t))\right)}_{\rho^S(\pi, t)}\ T\nabla_\pi H(\pi)$$

$$= -\nabla_\pi \rho^S(\pi, t)\ \dot{\pi}(\pi, t)\ .$$

This results is called

LIOUVILLE EQUATION

$$\frac{\partial}{\partial t}\rho^S(\pi, t) = -\left(\nabla_\pi \rho^S(\pi, t)\right)\dot{\pi}(\pi, t)\ . \qquad (1.30)$$

It has almost the form of a continuity equation, as we can identify $\dot{\pi}$ with the velocity field in phase space.

Put differently we have

$$0 = \frac{\partial}{\partial t}\rho^S(\pi, t) + \dot{\pi}(\pi, t)\left(\nabla_\pi \rho^S(\pi, t)\right)$$

$$= \frac{d}{dt}\rho(\pi(t), t)$$

That is to say that the density is constant along a trajectory. By the way, this derivative is also called the material derivative in continuums physics.

1.4.4   Derivation from probability theory

We can also argue that, since we do not and cannot exactly know the initial state (because of $N > 10^{24}$), we have to describe it by means of a probability density $\rho(\pi, t = 0) = p(\pi(t = 0) = \pi)$. The probability density at the time t is then $\rho(\pi, t) := p(\pi(t) = \pi)$. According to the rules of probability theory (marginalization rule) for times $t > 0$ we get

$$p(\pi(t) = \pi') = \int p(\pi(t) = \pi'|\pi(0) = \pi_0)\, p_0(\pi_0)\, d\pi_0 \ .$$

However, if we know the initial condition π_0, then Hamilton's equations of motion clearly define the phase space point at the time t, i.e.

$$p(\pi(t)) = \pi'|\pi(0) = \pi_0) = \delta(\pi' - \pi(t|\pi_0)) \ .$$

Here $\pi(t|\pi_0)$ is the phase space point of the trajectory at the time t, having started at the time $t = 0$ at π_0.

how do

Now we will reformulate the notation a little bit. We define

$$\rho(\pi', t) := p(\pi_t = \pi'|\pi_0 = \pi_0) \ .$$

This is similar to the mass density in fluid mechanics. Trajectories can neither be lost nor created out of nothing, so the continuity equation must apply here as well. Nevertheless, we shall explicitly show that this is true.

$$\frac{\partial \rho(\pi', t)}{\partial t} = \int \frac{\partial}{\partial t}\, \delta(\pi' - \pi(t|\pi_0))\ p_0(\pi_0)\, d\pi_0$$

$$= -\int \sum_j \frac{\partial}{\partial \pi'_j}\, \delta(\pi' - \pi(t|\pi_0))\ \dot{\pi}_j(t|\pi_0)\, p_0(\pi_0)\, d\pi_0$$

$$= -\int \nabla_{\pi'}\, \delta(\pi' - \pi(t|\pi_0))\ \dot{\pi}(t|\pi_0)\, p_0(\pi_0)\, d\pi_0 \ .$$

Now the rate of change $\dot{\pi}(t|\pi_0)$ (see (1.28)) is – as was already discussed – only dependent on the actual position (in phase space) $\pi(t)$, but not on the initial point. Therefore we have

$$\frac{\partial \rho(\pi', t)}{\partial t} = -\left(\nabla_{\pi'} \int \delta(\pi' - \pi(t|\pi_0)) \; p_0(\pi_0) \; d\pi_0\right) \dot{\pi}(\pi', t)$$

$$= -\left(\nabla_{\pi'} \rho(\pi', t)\right) \dot{\pi}(\pi', t)$$

$$0 = \frac{\partial \rho(\pi', t)}{\partial t} + \left(\nabla_{\pi'} \rho(\pi', t)\right) \dot{\pi}(\pi', t)$$

So formally we have the same result as for the ensemble average.
This means that the approach via the artificial ensemble and the approach via probability theory are formally identical.
Therefore from now on we will use a generic symbol ρ for the density. Since $\rho\dot{\pi} = j$ is the current density, this is the continuity equation, albeit already in a special form, since the derivative only affects the density and not the velocity field $u = \dot{\pi}(\pi', t)$. As the continuity equation has to apply because of the conservation of trajectories, u obviously is divergence-free. We will show this now by using (1.28)

$$\nabla_\pi \dot{\pi}(\pi, t) = \nabla_\pi T \nabla_\pi H = 0 \;, \tag{1.31}$$

as $xTx = 0$ is valid for every vector. Therefore the "fluid" is incompressible, i.e. has constant density along the trajectory. For further verification we need the Euler-Cauchy equation

$$\frac{d}{dt}\rho(\pi(t), t) = \frac{\partial}{\partial t}\rho(\pi, t) + \nabla_\pi \rho(\pi, t)\dot{\pi} \stackrel{(1.30)}{=} 0 \;.$$

The density ρ is constant along a trajectory!

The continuity equation is a consequence of the conservation of the number of trajectories. However, the incompressibility additionally follows from Hamilton's equation of motion (see (1.31)).

1.4.5 Ergodic hypothesis/theorem

Under certain conditions, it is possible to show that in phase space a trajectory of an isolated system gets arbitrarily close to every point on the hypersurface of constant energy.

The **Ergodic hypothesis** states that for an isolated system a trajectory, which starts at an arbitrary initial point π_0 eventually comes arbitrarily close to every other point. The set of points that are not reached this way has a measure of zero.[5] We also know from the Liouville equation that the density ρ is constant along the trajectory. Since the trajectory also comes arbitrarily close to each point, this means that the density on the hypersurface of fixed energy is constant. However, this normalization constant will depend on the energy

$$\rho(\pi) = \frac{1}{Z(E)} \; , \qquad \text{for all } \pi \text{ on the hypersurface} \qquad (1.32)$$

with $Z(E)$ being the area of the hypersurface as a function of energy.

$$Z(E) = \int_{H(\pi)=E} d\pi \;\; = \int \delta(H(\pi) - E)d\pi \; .$$

This quantity is also called **density of states** or **sturcture function**. It determines the probability density for states with energy E. In many cases, it is somewhat easier to calculate the associated distribution function, i.e. the integral up to an energy E

$$F(E) := \int_{-\infty}^{E} Z(E')dE' \; .$$

We will come back to tis aspect later on.

1.4.6   Stationarity

We have already said that at thermal equilibrium a stationary state is reached, characterized by $\rho(\pi, t) = \rho(\pi)$.
According to the above considerations, the density is $\rho_E(\pi) = 1/Z(E)$, for all phase space points on the energy-hypersurface E. Phrasing this statement more elegantly we get

$$\rho(\pi) = \rho(H(\pi)) \; .$$

The density is a function of the Hamilton function and and therefore automatically constant on the energy-hypersurface, resultng in the stationarity

---

[5]Note that trajectories cannot intersect. Constants of motion play an important role in this context.

of $\rho(\pi, t)$. So see this point, we rewrite equation (1.30) into

$$\frac{\partial \rho(\pi', t)}{\partial t} = -\left(\nabla_{\pi'} \rho(\pi', t)\right) \dot{\pi}(\pi', t)$$

$$= -\left(\nabla_{\pi'} \rho(\pi', t)\right) T\nabla_{\pi'} H(\pi')$$

$$= -\{\rho, H\} \qquad \text{(Poisson bracket)}$$

If $\rho(\pi, t)$ depends on π only through H, i. e. $\rho = \rho(H(\pi), t)$, then the Poisson bracket is zero:

$$\{\rho, H\} = \left(\nabla_{\pi'} \rho(\pi', t)\right) T\nabla_{\pi'} H(\pi')$$

$$= \frac{\partial \rho(H, t)}{\partial H} \left(\nabla_{\pi'} H\right) T\left(\nabla_{\pi'} H(\pi')\right) = 0 \,.$$

The last step is a consequence of $xTx = 0$. Therefore we indeed have a stationary density.

1.4.7   Learnings from the Hamiltonian dynamics

- We have learned that the density in phase space is constant along a trajectory

- The trajectory lies in the hyperplane of constant energy

- The ergodic theorem states that the trajectory comes arbitrary close to each point of the hyperplane

- Hence in equilibrium, the density of an isolated system is constant within the hyperplane of a given energy

- How does this fit with the fact that the system could be prepared in a very special initial configuration at the beginning and the density must first develop in time? The result oft he Liouville equation states that the density is constant along the trajectory, but for a very short time after initialization the trajectory has not evolved very far from the initial point and the ergodicity is not reached. So equilibrium is equivalent to ergodicity.

Chapter 2

Classical Statistical Physics

2.1 Introduction

2.1.1 What is a thermodynamic system?

Thermodynamics is an **independent** phenomenological theory based on several fundamental postulates (laws of thermodynamics) that can be regarded to be confirmed by experiment. In thermodynamic systems, such phenomena and physical behavior are observed that arise only from the interaction of a very large number of particles.

Nevertheless, thermodynamic systems consist of well-known components (atoms, molecules, clusters, etc.) whose microscopic behaviour satisfies the laws of classical or quantum mechanics. In **statistical mechanics** the postulates and rules of thermodynamics are deduced from the dynamic behaviour of the components. Since we typically have to deal with 10^{24} or more particles in thermodynamic systems, phenomena can be observed that are not exhibited by the individual particles arise. (Emergence)

The whole is more than the sum of its parts! (Aristoteles)

Nevertheless, it will not be necessary to solve the coupled equations of motion of the individual components, which would not even be possible numerically. Rather, we will develop a formalism based on the microscopic equations of motion, which will allow us to directly determine the macroscopic behaviour of thermodynamic systems.

2.1.2 Terms and definitions

A **thermodynamic system** is a macroscopic system consisting of a great many of components (atoms, electrons, phonons, photons,...). As usual in physics, thermodynamic systems are initially considered isolated from the rest of the world. Based on these results, we will let the system get into

contact with the environment in specific ways. For this we will distinguish between three cases

- **Isolated systems:** The system is perfectly decoupled from the environment. Neither can anything – no particles, no energy, no fields – get into the system from the outside, nor can anything get out.

- **Closed systems:** There is still no transfer of matter or particles, but energy can be exchanged with the environment. This happens mainly in the following two ways:

  1. Heat exchange (**thermal contact**):

     In this process, the temperature between the system and the environment is equalised by exchanging energy in the form of heat. Theoretically we describe this by coupling the system to a **heat bath**.

     If no heat can be exchanged, the system is **thermally insulated**

  2. Work exchange contact

     This exchange of energy can be caused by mechanical, electromagnetic, chemical or other forms of work.

- **Open system:** Systems in which energy as well as particles can be exchanged with the environment

2.1.3   States, equilibrium

Thermodynamic systems are characterized by a few macroscopic quantities, the so called **state variables**.
If all thermodynamic variables of a system can be described unambiguously by a certain number of independent state variables, a **complete set of independent state variables** exists.
We know from thermodynamics as a general rule that only a small number of state variables are sufficient. For example, for the description of gases and liquids one uses pressure, volume, temperature, number of particles, entropy, internal energy....
For magnets, magnetic field, magnetic moment, magnetisation and temperature are relevant variables.
Not all state variables are independent; there are relations between them. Therefore there is a distinction between **dependent** and **independent** state variables. The dependent state variables are called **state functions**.
Fruthermore, the following distinction is made:

1. Extensive state variables

   They are proportional to the substance quantity and therefore add up when the subsystems are merged. Examples are: Volume, mass, number of particles, internal energy, magnetisation, etc.

2. Intensive state variables

   They are independent of quantity. Examples are: Temperature, density, chemical potential, etc.

In thermodynamics, one almost exclusively deals with extensive or intensive state variables.
Other important terms are:

- **State space:** Space that is spanned by a complete set of independent state variables.

- **State:** Values of a complete set of independent state variables; point in state space.

- **Equilibrium:** State in which the values of the basic state variables do not change over time anymore.

Further definitions:

- Experience shows that each isolated system goes over into a steady state (**state of equilibrium**). The time needed for this is called **relaxation time**. It can vary from system to system by orders of magnitude.

- **Change of state, process:** Sequence of states, that the system runs through. If the initial state was a state of equilibrium, a change in state can only be caused by changing the external conditions.

- A change of state is called **quasistatic** if it is very slow in comparison to the relaxation times, so that it can be said to consist of a series of equilibrium states.

- A change of state is called **reversible** if it is a reversible sequence of equilibrium states. Thus, if the process is invariant to time inversion it is called reversible.

- The opposite is an **irreversible** change of state. A prime example would be the mixing of two gases. Furthermore, real processes are usually neither quasistatic nor reversible.

- A function of state variables is called **thermodynamic potential**, if it completely defines the equilibrium behaviour of the system and all its derivatives directly yield the dependent state variables.

- **Natural variables** are state variables, as a function of which a variable becomes a thermodynamic potential.

  For example the grand canonical potential can be reshaped into the form $\Omega = -pV$. The variables p and V however, are no natural variables, since partially deriving w.r.t. them does not yield other variables. Likewise the internal energy $U(T, V, N)$ is no thermodynamic potential, because its derivations alone do not allow a complete calculation of all other state variables, e.g. p and S.

2.2 Microcanonical ensemble

First of all, we investigate isolated systems. Investigations on the model systems and considerations of the motion in phase space, together with the assumption that the ergodic hypothesis applies, have shown that thermodynamic systems strive for a stationary equilibrium, which depends only on a few state variables such as volume, number of particles, energy etc. This equilibrium is also unique and independent from the history of how the system reached the current state.

In the microcanonical case (isolated, E, V, N are fixed) all microstates are equally probable. Such an ensemble is also called **Gibbs ensemble**. This prior probability is a result of physics and cannot be explained apriori.

Therefore, the probability density depends only on the energy, i.e.

PROBABILITY DENSITY OF THE MICROCANONICAL ENSEMBLE

$$p(\pi|E, N, V) = \frac{\delta(H(\pi) - E)}{Z(E, N, V)}$$

$$Z(E, N, V) = \int \delta(H(\pi) - E) d^{2\mathcal{N}} \pi$$

$$\mathcal{N} := N \cdot d \ .$$

The normalisation to this is the phase space volume of the hypersurface of the energy E, or the density of states, also called the number of microstates.

2.2.1   Example: The ideal gas for classical particles

We shall consider a gas of N classical particles, that neither interact with each other nor with a potential. However, they are confined to a cuboid with the edges (L_x, L_y, L_z). The calculation of the hypersurface $Z(E, N, V)$ usually is more difficult than that of the corresponding distribution function – the phase space volume $F(E, N, V)$, form which we can calculate $Z(E, N, V) = \left(\frac{\partial F}{\partial E}\right)\big|_{N,V}$ by differentiation with respect to E:

$$
\begin{aligned}
F_N^{\text{kl}}(E, V) &:= \iint \theta(E - H(\pi))\, d^{\mathcal{N}}p\, d^{\mathcal{N}}x \\
&= \int \theta(E - \frac{p_{ges}^2}{2m})\, d^{\mathcal{N}}p \int d^{\mathcal{N}}x \\
&= V^N\, V_{\mathcal{N}}(\sqrt{2mE})\ .
\end{aligned}
$$

With the volume of the $\mathcal{N}$-dimensional hypersphere from equation (C.2) [Page 211], which has the radius radius $\sqrt{2mE}$, we finally get

$$
F_N^{\text{kl}}(E, V) = V^N\, (2mE)^{\mathcal{N}/2}\, \frac{\pi^{\frac{\mathcal{N}}{2}}}{\Gamma(\frac{\mathcal{N}}{2} + 1)}\ . \tag{2.1}
$$

This result has some weaknesses, which can only be corrected by quantum mechanics, which we will discuss in detail later on.

Quantum correction

It is possible to apply a minimal correction to the equations of classical statistical mechanics, which already takes into account essential quantum properties. To this end we once more consider the same situation, but this time quantum-mechanically. In quantum mechanics, phase space does not exist, since the coordinates of location and impulse cannot be specified at the same time. The number of microstates is obviously equal to the number of quantum states. The energies of free non-interacting particles in a box are

$$
E_{\vec{l}} = \frac{1}{2m} \sum_{i=1}^{d} \left(\frac{2\pi\hbar l_i}{L_i}\right)^2 = \frac{1}{2m} \sum_{i=1}^{d} \left(\frac{h l_i}{L_i}\right)^2\ ,
$$

with $l_i \in 0, \ldots, \infty$. The distribution function **for one particle** then is

$$
F_{\mathbf{1}}{}^{\text{qm}}(E) = \sum_{\vec{l}} \theta(E - E_{\vec{l}})\, \triangle^d l
$$

With the quantised momenta $p_i(l_i) = \frac{h l_i}{L_i}$ we get

$$
\begin{aligned}
F_1^{\mathrm{qm}}(E) &= \frac{L_1 L_2 L_3}{h^3} \sum_{\vec{p}(\vec{l})} \theta(E - E_{\vec{l}}) \, \triangle^3 p \\
&= \frac{V}{h^3} \sum_{\vec{p}(\vec{l})} \theta(E - E_{\vec{p}(\vec{l})}) \, \triangle^d p \; .
\end{aligned}
$$

Now the difference in the energies of neighbouring values of the momentum is very small and in the thermodynamic limit $V \to \infty$, because of $\triangle p_i = \frac{h}{L_i}$ it goes to zero. Therefore the sum over p becomes an integral.

$$
F_1^{\mathrm{qm}}(E) = V \int \theta(E - \frac{p^2}{2m}) \, \frac{d^3 p}{h^3} \; .
$$

Obviously, the only difference to the classical case is the factor $\frac{1}{h^3}$ in the integration measure, that originates from the momentum-quantization. For N particles we therefore obtain

$$
F_N^{\mathrm{qm}}(E) = V \int \theta(E - \frac{p^2}{2m}) \, \frac{d^{\mathcal{N}} p}{h^{\mathcal{N}}} \; .
$$

This is the number of microstates / quantum states. In this expression the particles are treated as indistinguishable. That is, however, not correct for identical particles. For the correct number of microstates of indistinguishable particles we have to introduce the factor $1/N!$. Then we obtain

$$
F_N^{\mathrm{qm}}(E) = V \int \theta(E - \frac{p^2}{2m}) \, \frac{d^{\mathcal{N}} p}{h^{\mathcal{N}} N!} \; .
$$

Because of quantization and indistinguishability, there is an additional factor $1/(h^{\mathcal{N}} N!)$ that does not come into play in most cases, but is essential in some situations for the correct description of experiments. Without this factor, the classical calculations lead to the so-called Gibbs paradox, which we will discuss in more detail later on 4.1.3.

One can consider the quantum correction as a modified integration measure, instead of $d^{2\mathcal{N}} \pi$ we use

---

MEASURE IN PHASE SPACE FOR CLASSICAL PROBLEMS
(*including quantum correction*)

$$\mathcal{D}_\pi^{\mathcal{N}} := \frac{d^{2\mathcal{N}}\pi}{h^{\mathcal{N}}N!}$$
$$\mathcal{N} := Nd \,.$$

Summarising the results we got so far:

NUMBER OF MICROSTATES AND BOLTZMANN ENTROPY

$$Z(E, N, V, d) := \int \delta(H(\pi) - E)\, \mathcal{D}_\pi^{\mathcal{N}} = \frac{1}{h^{\mathcal{N}}N!} \int \delta(H(\pi) - E)\, d^{2\mathcal{N}}\pi$$
$$S^B(E, N, V) := k_B \ln\left[Z(E, N, V)\right] . \tag{2.2}$$

These expressions are applicable to a system with only one type of particle, i.e. indistinguishable objects.

Before proceeding with another type of ensemble, let us calculate various physical properties of the ideal gas in the microcanonical ensemble described in section section (4.1.1) [Page 90].

2.3   Thermally coupled subsystems

We will consider, in a very general way, two isolated systems, which we describe with the two state variables z_j. These state variables can be the energy, the number of particles, the volume, etc.

As in the model example, we now connect the two isolated systems, where the values of the state variables before contact are $z_j^{(1/2)}$. The entire system is still to be isolated. Depending on the coupling of the two systems, some of the state variables remain fixed. For example, in the case of thermal contact, we only allow the exchange of energy and no exchange of particles or volume. We now split the set of state variables in those that remain fixed – $\vec{f}$ – and those that are variable – $\vec{v}$. So, before the contact there are the state variables $(\vec{f}^{(1)}, \vec{v}^{(1)})$ and $(\vec{f}^{(2)}, \vec{v}^{(2)})$ and after the contact the individual

values $\vec{f}^{(1/2)}$ remain, but the variable state variables change, but with the following constraints

$$\vec{v} = \vec{v}^{(1)} + \vec{v}^{(2)} \ .$$

In other words, after the contact the variable quantities in system 1 can have the values $\vec{v}^{(1)}$ and in turn the values for system 2 are $\vec{v} - \vec{v}^{(1)}$. The final state is characterised by $(\vec{v}^{(1)}, \vec{v}, \vec{f}^{(1)}, \vec{f}^{(2)})$. According to the previous considerations, the new stationary equilibrium state will be the one with the maximal number of micro-states or the largest phase space volume (compatible with the specified macroscopic state variables). Moreover, the two systems are not supposed to interact, and therefore the number of microstates or phase space volumes is the same as the product of the two subsystems, i.e.

$$Z(\vec{v}^{(1)}|\vec{v}, \vec{f}^{(1)}, \vec{f}^{(2)}) = Z^{(1)}(\vec{v}^{(1)}|\vec{f}^{(1)}) \ Z^{(2)}(\vec{v} - \vec{v}^{(1)}|\vec{f}^{(2)})$$

The maximum for this results from the partial derivative w.r.t. $v_j^{(1)}$, while all other variables are fixed.

$$\frac{\partial}{\partial v_i^{(1)}} Z = \left(\frac{\partial}{\partial v_i^{(1)}} Z^{(1)}(\vec{v}^{(1)}|\vec{f}^{(1)}) \right) Z^{(2)}(\vec{v} - \vec{v}^{(1)}|\vec{f}^{(2)})$$

$$- Z^{(1)}(\vec{v}^{(1)}|\vec{f}^{(1)}) \left. \left(\frac{\partial}{\partial v_i^{(2)}} Z^{(2)}(\vec{v}^{(2)}|\vec{f}^{(2)}) \right) \right|_{\vec{v}^{(2)} = \vec{v} - \vec{v}^{(1)}} \overset{!}{=} 0 \ .$$

Dividing by Z yields

$$\frac{\partial}{\partial v_i^{(1)}} \ln \left(Z^{(1)}(\vec{v}^{(1)}|\vec{f}^{(1)}) \right) = \left. \frac{\partial}{\partial v_i^{(2)}} \ln \left(Z^{(2)}(\vec{v}^{(2)}|\vec{f}^{(2)}) \right) \right|_{\vec{v}^{(2)} = \vec{v} - \vec{v}^{(1)}}$$

$$\frac{\partial}{\partial v_i^{(1)}} S^{(1)} = \left. \frac{\partial}{\partial v_i^{(2)}} S^{(2)} \right|_{\vec{v}^{(2)} = \vec{v} - \vec{v}^{(1)}} \ .$$

So, depending on the type of contact, certain equilibria are established, which we will discuss one after the other.

Energy exchange

Only energy shall be exchanged, i.e. $v = E$. Thus, the condition for equilibrium is

$$\frac{\partial}{\partial E^{(1)}} S^{(1)} = \left. \frac{\partial}{\partial E^{(2)}} S^{(2)} \right|_{E^{(2)} = E - E^{(1)}} \ .$$

In thermodynamics the variable $\frac{\partial S^{(1)}}{\partial E^{(1)}}$ is defined as the inverse temperature $1/T_1$. Energy and temperature are in a certain sense conjugated variables.

<div style="border:1px solid">

DEFINITION OF TEMPERATURE

$$\frac{1}{T} = \left(\frac{\partial S(E, V, N)}{\partial E} \right) \bigg|_{V,N} \tag{2.3}$$

</div>

In terms of statistical physics, temperature thus corresponds to the relative change of entropy w.r.t. energy, that occurs in an otherwise isolated system. Alternatively, it is valid that two subsystems of an isolated overall system in thermal equilibrium have the same temperature. The two subsystems have not been specified at any point in the derivation in any way. We can therefore generalize:

In equilibrium, in an isolated system the temperature is the same in the whole system.

The variable T that we just defined is, in fact, the absolute temperature of thermodynamics. We will find formally equal relations between temperature, entropy and (internal) energy as in phenomenological thermodynamics.

With the microscopic approach, we have thus shown that in thermally coupled systems, the temperatures of both systems adapt to each other. Since the division into the two subsystems was chosen arbitrarily, the same temperature will be maintained in an isolated system in all sub-volumes (everywhere). Of course, the sub-volumes considered must still be of macroscopic size. Otherwise fluctuations would have an effect.

Particle exchange

Now we will also allow particle exchange, i.e. $v^{(1)} = E, v^{(2)} = N$. Therefore the conditions for equilibrium are

$$\frac{\partial}{\partial E^{(1)}} \, S^{(1)} \; = \frac{\partial}{\partial E^{(2)}} \, S^{(2)} \bigg|_{E^{(2)}=E-E^{(1)}}$$

$$\frac{\partial}{\partial N^{(1)}} \, S^{(1)} \; = \frac{\partial}{\partial N^{(2)}} \, S^{(2)} \bigg|_{N^{(2)}=N-N^{(1)}} .$$

The first condition again requires that the temperatures in both systems be the same. The second condition contains the quantity $\frac{\partial S^{(1)}}{\partial N^{(1)}}$ which is defined in thermodynamics as $(-\mu_1/T_1)$. The microscopic approach has thus confirmed that for systems with energy and particle exchange the temperature and the chemical potential will be the same in both systems.

DEFINITION OF THE CHEMICAL POTENTIAL

$$\mu = -T \left(\frac{\partial S(E, V, N)}{\partial N} \right) \Bigg|_{E,V}$$

Accordingly, N and μ are conjugated to each other. The same applies here as well:

In an isolated system all macroscopic subvolumes (everywhere) have the same chemical potential.

Variable volume

Finally, we look at what the formalism yields when the partition wall is movable. The two volumes and the two energies shall therefore be variable. The numbers of particles on the other hand are fixed. Therefore $v^{(1)} = E, v^{(2)} = V$ applies. These are the conditions for equilibrium:

$$\frac{\partial}{\partial E^{(1)}} S^{(1)} = \frac{\partial}{\partial E^{(2)}} S^{(2)} \Bigg|_{E^{(2)}=E-E^{(1)}}$$

$$\frac{\partial}{\partial V^{(1)}} S^{(1)} = \frac{\partial}{\partial V^{(2)}} S^{(2)} \Bigg|_{V^{(2)}=V-V^{(1)}} .$$

The first condition again returns that the temperature has to be equal in both systems. The second condition contains the quantity $\frac{\partial S^{(1)}}{\partial V^{(1)}}$. Mechanics already defines the meaning of this, which we now will work out.

What have we learned so far? The entropy of a (sub-)system depends – in the simplest case – on[1] E, N, V, i.e.

$$S = S(E, V, N)$$

$$dS = \left(\frac{\partial S}{\partial E} \right) \Bigg|_{V,N} dE + \left(\frac{\partial S}{\partial N} \right) \Bigg|_{E,V} dN + \left(\frac{\partial S}{\partial V} \right) \Bigg|_{E,N} dV$$

$$= \frac{1}{T} dE - \frac{\mu}{T} dN + \left(\frac{\partial S}{\partial V} \right) \Bigg|_{E,N} dV$$

$$\text{bzw.} \quad dE = TdS + \mu dN - T \left(\frac{\partial S}{\partial V} \right) \Bigg|_{E,N} dV . \tag{*}$$

---
[1]Of course, other state variables are also conceivable, e.g. when electromagnetic fields are present or the system is composed of different types of particles.

The equation $S = S(E, V, N)$ can be inverted to $E = E(S, V, N)$. From this follows

$$dE = \left(\frac{\partial E}{\partial S}\right)\bigg|_{V,N} dS + \left(\frac{\partial E}{\partial N}\right)\bigg|_{S,V} dN + \left(\frac{\partial E}{\partial V}\right)\bigg|_{S,N} dV .$$

Comparison with (*) yields

$$\left(\frac{\partial E}{\partial S}\right)\bigg|_{V,N} = T$$

$$\left(\frac{\partial E}{\partial N}\right)\bigg|_{S,V} = \mu$$

$$\left(\frac{\partial E}{\partial V}\right)\bigg|_{S,N} = -T \left(\frac{\partial S}{\partial V}\right)\bigg|_{E,N} .$$

If we move the wall by dx, the volume changes by $dV = Adx$, with A representing the surface of the wall. Hereby, work amounting to $dW = Fdx = pAdx = pdV$ is performed. Since the system loses energy as the volume increases, $dE = -pdV$ is defined. With this we have

---

PRESSURE

$$p = T \left(\frac{\partial S(E, V, N)}{\partial V}\right)\bigg|_{E,N} \tag{2.4}$$

The same applies here as well:

In an isolated system, the pressure of all macroscopic partial volumes (everywhere) is the same.

According to this, V and p are conjugated to each other too, i.e. one variable can be transformed into the other via Legendre transformation. Interestingly, always one of the two Legendre partners is extensive (E, N, V) and the other one is intensive (T, μ, p).

2.3.1   Is the statistical entropy the same as the thermodynamic one?

To show that the statistical entropy can be identified with the thermodynamic entropy, two essential statements have to be checked.

1. S is extensive (additive).

2. S fulfills the second law of thermodynamics: In all processes possible in an isolated system the entropy does not decrease ($dS \geq 0$)!

The first condition is checked easily. When connecting two systems, the fixed variables $\vec{f}^{(\alpha)}$ are conserved individually and for the variable state variables $\vec{v}$, the sum $\vec{v} = \vec{v}^{(1)} + \vec{v}^{(2)}$ is given. The number of microstates is given by the convolution

$$Z(\vec{v}, \vec{f}^{(1)}, \vec{f}^{(2)}) = \sum_{v^{(1)}} Z^{(1)}(\vec{v}^{(1)}, \vec{f}^{(1)}) \, Z^{(2)}(\vec{v} - \vec{v}^{(1)}, \vec{f}^{(2)}) \, . \qquad (2.5)$$

As was already shown by means of the model system, for systems of macroscopic size, basically only one state $\vec{v}^{*(1)}$ contributes to the sum and we have

$$Z(\vec{v}, \vec{f}^{(1)}, \vec{f}^{(2)}) = Z^{(1)}(\vec{v}^{*(1)}, \vec{f}^{(1)}) Z^{(2)}(\vec{v} - \vec{v}^{*(1)}, \vec{f}^{(2)}) \, .$$

It is shown easily that this result becomes exact for any system in the thermodynamic limit. Therefore, the following applies for entroppy:

ADDITIVITY

$$S = k_B \ln[Z] = k_B \ln\left[Z^{(1)}\right] + k_B \ln\left[Z^{(2)}\right]$$

2.3.2 Second law of thermodynamics

In order to be able to actually identify the statistical entropy with the thermodynamic entropy, we still have to prove the validity of the second law of thermodynamics. It remains to be proven that entropy does not decrease for any processes within an isolated system. After the preparations of the last section the proof is no longer very difficult.

Again, we consider two initially isolated systems 1 and 2, whose associated microcanonical ensembles occupy the phase volumes

$$Z^{(\alpha)}(E^{(\alpha)}, N^{(\alpha)}, V^{(\alpha)})$$

The complete system, consisting of the still separated systems, then has the phase volume

$$Z(E, N, V) = \prod_{\alpha=1}^{2} Z^{(\alpha)}(E^{(\alpha)}, N^{(\alpha)}, V^{(\alpha)}) \, ,$$

with an entropy of

$$S(E, N, V) = \sum_{\alpha=1}^{2} S^{(\alpha)}(E^{(\alpha)}, N^{(\alpha)}, V^{(\alpha)}) \ .$$

When the two systems are connected, as described in context of equation (2.5) [Page 51] the entropy becomes

$$S(\vec{v}, \vec{f}^{(1)}, \vec{f}^{(2)}) = k_B \ln \left[\sum_{\tilde{v}^{(1)}} Z^{(1)}(\tilde{v}^{(1)}, \tilde{f}^{(1)}) \, Z^{(2)}(\tilde{v} - \tilde{v}^{(1)}, \tilde{f}^{(2)}) \right] \ .$$

The condition before contact represents one of the summands. Since the summands are all non-negative, the entropy is definitely not going to decrease. As we have already discussed, in the thermodynamic limit one of the summands dominates the sum. This is the largest of all summands, the one by which the new equilibrium is determined. As long as the macrostates in both systems change due to the contact, this means that another summand is larger than the one belonging to the initial state. The entropy therefore increases.

Direction of the energy flow

After having verified the validity of the second law of thermodynamics, we shall consider in which direction energy resp. particles are exchanged between systems.
Again, the situation, in which certain state variables are conserved individually and others only as a sum, is considered in general. Before contact, the following applies:

$$S(\vec{f}^{(1)}, \vec{f}^{(2)}, \vec{v}) = S^{(1)}(\vec{f}^{(1)}, \vec{v}^{(1)}) + S^{(2)}(\vec{f}^{(2)}, \vec{v} - \vec{v}^{(1)}) \ .$$

After contact in thermal equilibrium, the following applies in the thermodynamic limit:

$$S(\vec{f}^{(1)}, \vec{f}^{(2)}, \vec{v}) = S^{(1)}(\vec{f}^{(1)}, \vec{v}^{*(1)}) + S^{(2)}(\vec{f}^{(2)}, \vec{v} - \vec{v}^{*(1)}) \ .$$

Thus, the change in entropy is

$$\Delta S(\vec{f}^{(1)}, \vec{f}^{(2)}, \vec{v}) = \Delta S^{(1)}(\vec{f}^{(1)}, \vec{v}^{*(1)}) + \Delta S^{(2)}(\vec{f}^{(2)}, \vec{v} - \vec{v}^{*(1)}) \ .$$

We expand around the initial state and get

$$\Delta S = \left(\nabla_{\vec{v}^{(1)}} S^{(1)}(\vec{f}^{(1)}, \vec{v}^{(1)}) - \nabla_{\vec{v}^{(2)}} S^{(2)}(\vec{f}^{(2)}, \vec{v}^{(2)}) \Big|_{\vec{v}^{(2)} = \vec{v} - \vec{v}^{(1)}} \right) \triangle \vec{v}^{(1)} \stackrel{!}{\geq} 0 \ .$$

This inequation is generally valid. For example we can look at thermal contact where only energy can be exchanged. Then the inequation is

$$\left(\frac{\partial S^{(1)}}{\partial E_1} - \frac{\partial S^{(2)}}{\partial E_2}\right)(E_1^* - E_1^0) = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)(E_1^* - E_1^0) \qquad \overset{!}{\geq} 0 \; .$$

For $T_1 > T_2$ before contact, $\Delta E_1 \leq 0$ follows. The energy of the first system – whose initial energy was the higher one – decreases.

One can also consider what will happen if particle exchange is allowed for the two systems that are already in thermal equilibrium.

$$\begin{aligned}
\Delta S &= \left(\frac{\partial S^{(1)}}{\partial N_1} - \frac{\partial S^{(2)}}{\partial N_2}\right)(N_1^* - N_1^0) \\
&= \left(\frac{\mu_1}{T} - \frac{\mu_2}{T}\right)\Delta N_1 \\
&= \left(\mu_1 - \mu_2\right)\frac{\Delta N_1}{T} \\
&\overset{!}{\geq} 0 \; .
\end{aligned}$$

As a result, particles from the system with higher chemical potential flow into the system with lower chemical potential. Similarly, it can be shown that two systems that are already in thermal contact move the separating wall between them so that the same pressure is applied on both sides. This occurs in such a way that the volume increases in the subsystem where the pressure was previously greater.

2.3.3 The first law and the basic relations of thermo-dynamics

Equally important for thermodynamics as for the statistical physics of equilibrium is the concept of **quasi-stationary changes of state**. In statistical physics, this means a steady and slow variation of the state variables, so that a microcanonical ensemble can be defined at any moment. The process can always be designed to be slow enough for the system to be considered isolated and in equilibrium at any moment. Therefore, an entropy can be defined at any time during a quasi-stationary change. For this infinitesimal change of entropy the following must apply:

$$dS(E, N, V) = \left(\frac{\partial S}{\partial E}\right)\bigg|_{N,V} dE + \left(\frac{\partial S}{\partial N}\right)\bigg|_{E,V} dN + \left(\frac{\partial S}{\partial V}\right)\bigg|_{E,N} dV \quad (2.6)$$

$$= \frac{1}{T}dE - \frac{\mu}{T}dN + \frac{p}{T}dV \; . \quad (2.7)$$

From this we can also read, that entropy is the thermodynamic potential of the microcanonical ensemble,

$$
\begin{array}{c}
\textsc{Entropy } S(E, N, V) \\
\textit{(Differentials)}
\end{array}
$$

$$
dS = \frac{1}{T}dE - \frac{\mu}{T}dN + \frac{p}{T}dV
$$

$$
\left(\frac{\partial S(E,V,N)}{\partial E}\right)\bigg|_{V,N} = \frac{1}{T}
$$

$$
\left(\frac{\partial S(E,V,N)}{\partial N}\right)\bigg|_{E,V} = -\frac{\mu}{T} \tag{2.8}
$$

$$
\left(\frac{\partial S(E,V,N)}{\partial V}\right)\bigg|_{E,N} = \frac{p}{T} \,,
$$

because the derivation with respect to the natural variables E, N, V yields the conjugated variables T, μ, p.

Alternatively, we can also reshape equation (2.7) into

$$
dE = TdS - pdV + \mu dN, \tag{2.9}
$$

so that the energy $E(S, N, V)$ becomes a function of S, N, V with the derivatives

$$
\left(\frac{\partial E}{\partial S}\right)\bigg|_{V,N} = T
$$

$$
\left(\frac{\partial E}{\partial N}\right)\bigg|_{S,V} = \mu \tag{2.10}
$$

$$
\left(\frac{\partial E}{\partial V}\right)\bigg|_{S,N} = -T\left(\frac{\partial S}{\partial V}\right)\bigg|_{E,N} = -p \,.
$$

equation (2.7) is equivalent to the

FIRST LAW OF THERMODYNAMICS

$$dE = TdS - pdV + \mu dN$$

change in energy = change in heat + change in mechanical energy + changes in the particle number

---

which we have deduced specifically for a gas of N particles of the same kind within the volume V. When adding the validity of the second law of thermodynamics, we get the basic relation of thermodynamics, which corresponds to a summary of the first two laws of thermodynamics.

BASIC RELATION OF THERMODYNAMICS

$$TdS \geq dE + pdV - \mu dN$$

The third law of thermodynamics remains to be proven. However, this proof can only be carried out within the framework of quantum statistics.
Thus the basic relation and therefore the whole macroscopic thermodynamics are statistically justified. All measurement quantities can be traced back to the microscopic interactions via the phase volume and the Hamilton function.

Effects of homogeneity

The natural variables of entropy (E, N, V) are all extensive quantities. As a result of homogeneity the following has to apply

$$S(\lambda E, \lambda N, \lambda V) = \lambda S(E, N, V) \ .$$

We take the derivative of both sides and get

from the left hand side:

$$\frac{d}{d\lambda} S(\lambda E, \lambda N, \lambda V) = \frac{\partial}{\partial E'} \Big(S(E', \lambda N, \lambda V) \Big) \Big|_{E'=\lambda E} E + \frac{\partial}{\partial N'} \Big(S(\lambda E, N', \lambda V) \Big) \Big|_{N'=\lambda N} N$$
$$+ \frac{\partial}{\partial V'} \Big(S(\lambda E, \lambda N, V') \Big) \Big|_{V'=\lambda V} V \ ,$$

from the right hand side:

$$\frac{d}{d\lambda}S(\lambda E, \lambda N, \lambda V) = S(E, N, V) \ .$$

Both sides together give:

$$S(E, N, V) = \frac{\partial}{\partial E'}\left(S(E', \lambda N, \lambda V)\right)\Big|_{E'=\lambda E} E + \frac{\partial}{\partial N'}\left(S(\lambda E, N', \lambda V)\right)\Big|_{N'=\lambda N} N$$
$$+ \frac{\partial}{\partial V'}\left(S(\lambda E, \lambda N, V')\right)\Big|_{V'=\lambda V} V \ .$$

Since the left hand side does not depend on λ, the same must be true for the right hand side and we can therefore analyze it for $\lambda = 1$. For this we get

$$S(E, N, V) = \underbrace{\left(\frac{\partial S}{\partial E}\right)\Big|_{N,V}}_{\overset{(2.8)}{=}1/T} E + \underbrace{\left(\frac{\partial S}{\partial N}\right)\Big|_{E,V}}_{\overset{(2.8)}{=}-\mu/T} N + \underbrace{\left(\frac{\partial S}{\partial V}\right)\Big|_{T,N}}_{\overset{(2.8)}{=}-p/T} V \ .$$

ENTROPY

$$TS(E, N, V) = E - \mu N - pV \ . \tag{2.11}$$

Now, on the right side there are only the extensive natural variables together with the corresponding conjugated intensive quantities.

Summary

- The natural variables of the microcanonical ensemble are E, N, V.

- The thermodynamic potential is the entropy $S(E, N, V)$, because from it we can calculate all other dependent quantities (p, T, μ) through partial derivation.

- General procedure:

  - Formulating the Hamilton function $H(\pi|\alpha)$, which may not only contain dynamical variables, but also external parameters α like the volume.

- – Calculation of $Z(E, N, V)$.

- – Calculation of the entropy $S(E, N, V) = k_B \ln(Z)$.

- – Determining temperature, chemical potential and pressure by means of the above formulae.

- – Determining the (internal) energy $U = \langle H \rangle$ by means of inverting

$$S(E, N, V) = \mathbf{S} \; ; \Rightarrow \; E = E(\mathbf{S}, N, V) \; .$$

- • Using Legendre transformation, further thermodynamic potentials can be calculated, e.g.

$$
\begin{aligned}
\text{free energy} \quad & F(T, V, N) = U - TS \\
\text{free Gibbs enthalpy} \quad & G(T, p, N) = U + pV - TS
\end{aligned}
$$

2.3.4 Attraction of equilibrium and irreversibility

As shown in the introductory example, a system converges to equilibrium within a very short period of time and it would take infinitely long to escape form the equilibrium. It was shown in terms of the model systzems that the great number of degrees of freedom in macroscopic systems introduces novel behaviour. All of the conclusions derived from a very abstract and simple model in this section are validated by all models that can be calculated exactly. Even the assumption of them being universally valid has not yet led to any discepancies between theory and experiment.

Nevertheless, the microscopic equations of motion are invariant to time reversal and at first the same applies to macroscopic systems: We prepare a system in a thermodynamically extremely unlikely state π^{**} and then let it reach equilibrium. Then we measure location and momentum of all particles at one fixed point in time. Now if we prepare a state with the exact same locations, but reversed momenta the system is certain to shortly reach the extremely unlikely state π^{**}. Now it is certainly not easy to prepare 10^{24} particles with absolutely exact locations and momenta and arbitrarily small changes would suffice for the system to not be able to leave equilibrium anymore. This now prompts the question, why the system does not get to the point in phase space, which leads from equilibrium back to π^{**} by itself (as according to the ergodic hypothesis it gets arbitrarily close to any point). The answer here is that the number of states, which lead to the system leaving equilibrium is negligibly small in the thermodynamic limit.

2.4   Canonical ensemble

The microcanonical ensemble describes isolated systems. We will now change this idealized situation and consider only a closed system which can exchange energy with its environment. This system shall be temporarily called **reference system**. The environment (**heat bath**) is much larger than the reference system. The whole system, consisting of heat bath and reference system, shall be isolated again. This situation was already discussed in the last section, where it was found that the system will reach an equilibrium in which the temperatures of both reference system and heat bath are the same. As the heat bath shall be of infinite size its temperature will not change when it is in contact with the reference system, i.e. the reference system will assume the temperature of the heat bath. The statistical ensemble describing this situation is called **canonical ensemble**.

2.4.1   Probability density

Now we shall derive the probability density $p(\pi_R | N_R, N_B, V_R, V_B, E)$ of the reference system. Here the index R stands for the reference system and B for the heat bath. For the whole system the following applies

$$N = N_R + N_B$$
$$V = V_R + V_B$$
$$E = H_R(\pi_R) + H_B(\pi_B) \ .$$

The last equation requires that the interaction between the two subsystems, which must exist in order to make energy exchange possible, is still small enough for the energy of the whole system to be equal to the sum of the energies of its parts. Marginalisation yields

$$p(\pi_R | N_R, N_B, V_R, V_B, E) = \int p(\pi_R, \pi_B | N_R, N_B, V_R, V_B, E) \ \mathcal{D}_{\pi_B}^{\mathcal{N}_B} \ .$$

The integrand is the probability density for the whole system and therefore we have

$$p(\pi_R | N_R, N_B, V_R, V_B, E) = \int_{V_B} \frac{\delta(H(\pi_R, \pi_B) - E)}{Z(E, N, V)} \ \mathcal{D}_{\pi_B}^{\mathcal{N}_B}$$
$$= \frac{1}{Z(E, N, V)} \int_{V_B} \delta(H_B(\pi_B) - (E - H_R(\pi_R))) \ \mathcal{D}_{\pi_B}^{\mathcal{N}_B} \ .$$

The remaining integral is the area of the bath's hypersuface at the energy $E - H_R(\pi_R)$. This leads to

$$p(\pi_R | N_R, N_B, V_R, V_B, E) = \frac{Z_B(E - H_R(\pi_R), N_B, V_B)}{Z(E, N, V)} \ .$$

Here only the dependence on π_R is of interest. All other factors can be put into the normalisation constant and, therefore, we get

$$p(\pi_R|N_R, N_B, V_R, V_B, E) = \frac{1}{Z} \, Z_B(E - H_R(\pi_R), N_B, V_B) \;.$$

Now the stationary phase approximation, which becomes exact for $N_B \to \infty$, is used.

$$p(\pi_R|N_R, N_B, V_R, V_B, E) = \frac{1}{Z} \, e^{\ln[Z_B(E - H_R(\pi_R), N_B, V_B)]}$$

$$= \frac{1}{Z} \, e^{\frac{1}{k_B} S_B(E - H_R(\pi_R), N_B, V_B)}$$

$$S_B(E - H_R(\pi_R), N_B, V_B) = S_B(E, N_B, V_B) - \left.\frac{\partial S_B(E_B, N_B, V_B)}{\partial E_B}\right|_{E_B = E} H_R(\pi_R)$$

$$+ \frac{1}{2} \left.\frac{\partial^2 S_B(E_B, N_B, V_B)}{\partial E_B^2}\right|_{E_B = E} H_R^2(\pi_R) + \dots$$

The first order term yields

$$\left.\frac{\partial S_B(E_B, N_B, V_B)}{\partial E_B}\right|_{E_B = E} H_R(\pi_R) = \frac{H_R(\pi_R)}{T_B} \;,$$

where we have to consider that $T_B = T$. The second order term can be approximated as follows: S_B, E_B and H_R are extensive quantities and are therefore proportional to the respective number of particles, i.e.

$$\left.\frac{\partial^2 S_B(E_B, N_B, V_B)}{\partial E_B^2}\right|_{E_B = E} H_R^2(\pi_R) \propto \frac{N_B}{N_B^2} \, N_R^2 = N_R \frac{N_R}{N_B} \;.$$

The first order term is proportional to N_R, while the second order term is a factor N_R/N_B smaller and can be neglected for $N_B \to \infty$.
After having derived the result, we can now omit the indices, since the bath serves only as a temperature source.

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PROBABILITY DENSITY OF THE CANONICAL ENSEMBLE

$$p(\pi|T, N, V, d) = \frac{1}{Z(T, N, V, d)} \, e^{-\beta H(\pi)} \;.$$

</div>

The normalisation $Z(E, N, V, d)$ (number of micro-states) is also called partition function.

CANONICAL PARTITION FUNCTION

$$Z(T, N, V, d) = \int e^{-\beta H(\pi)} \, \mathcal{D}_\pi^\mathcal{N} = \frac{1}{h^{dN} N!} \int e^{-\beta H(\pi)} \, d^{2\mathcal{N}}\pi \; .$$

Before continuing with the formalism, two examples shall be discussed.

a) Ideal gas of classical particles

The ideal gas of classical particles as canonical ensemble is discussed in section Section (4.1.4) [Page 96].

b) Free classical particle in an external potential

Let us now consider the more realistic situation of N noninteracting classical particles in three dimensions, which are influenced by an external potential. The Hamilton function then is

$$H = \sum_{i=1}^{N} \frac{\vec{p_i}^2}{2m} + V(\vec{x}) \; .$$

The vector $\vec{x}$ contains the spatial coordinates of all particles. Likewise the vector $\vec{p}$ contains the momenta of all particles. The canonical partition function is then given by

$$Z(T, N, V) = \frac{1}{h^\mathcal{N} N!} \int e^{-\beta V(\vec{x})} d^\mathcal{N} x \int e^{-\frac{\beta}{2m}\vec{p}^2} d^\mathcal{N} p$$

$$\int e^{-\frac{\beta}{2m}\vec{p}^2} d^\mathcal{N} p = \left(\int e^{-\frac{\beta}{2m} p^2} dp \right)^\mathcal{N}$$

$$\int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} p^2} dp = \left(\frac{2\pi m}{\beta} \right)^{1/2}$$

$$\int e^{-\frac{\beta}{2m}\vec{p}^2} d^\mathcal{N} p = \left(\frac{2\pi m}{\beta} \right)^{\mathcal{N}/2}$$

$$Z(T, N, V) = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\mathcal{N}/2} \int e^{-\beta V(\vec{x})} d^\mathcal{N} x$$

CANONICAL PARTITION FUNCTION FOR FREE CLASSICAL PARTICLES

$$Z(T,N,V) = \frac{\lambda_T^{-\mathcal{N}}}{N!} \int e^{-\beta V(\vec{x})} d^{\mathcal{N}}x$$

$$\lambda_T := \frac{h}{\sqrt{2\pi m k_B T}} \qquad \text{(thermal de Broglie wavelength)} .$$

2.4.2 Connection to thermodynamics

First we calculate the internal energy $U(T,N,V) = \langle H \rangle$.

$$U(T,N,V) = \frac{1}{Z(T,N,V)} \int H(\pi)\, e^{-\beta H(\pi)}\, \mathcal{D}_\pi^{\mathcal{N}} \qquad (2.12)$$

$$= -\frac{\partial}{\partial \beta} \ln[Z] = k_B T^2 \frac{\partial \ln[Z(T,N,V)]}{\partial T} . \qquad (2.13)$$

The microcanonical ensemble is defined by the variables $(E = U), N, V$. These are, as we know already from thermodynamics, the **natural variables** of the **thermodynamic potential** $S = S(U,N,V)$. Thus, the energy $U(S,N,V)$ can be expressed as a function of S,N,V. Therefore, the internal energy is not a thermodynamic potential in the **canonical** variables (T,N,V).

The variables T,N,V are natural variables of the **free energy**, which therefore takes the place as thermodynamic potential in the canonical ensemble instead of S. To go from a function of the variables (S,N,V) to one of the variables (T,N,V), a Legendre transformation is needed. This leads here to the **free energy**

FREE ENERGY

$$F(T,N,V) = U(T,V,N) - T\, S(T,V,N) . \qquad (2.14)$$

To make sure the transformation of the variables indeed worked, we consider

$$dF = dU - TdS - SdT$$

$$\overset{(2.9)}{=} TdS - pdV + \mu dN - TdS - SdT \; .$$

Thus the following applies:

FREE ENERGY
(*Total differential*)

$$dF(T, N, V) = -SdT - pdV + \mu dN \; . \tag{2.15}$$

Therefore F is indeed a funcion of the canonical variables.
Now we shall establish the connection between $F(T, N, V)$ and $Z(T, N, V)$.
We first consider the total differential of the free energy for constant N

$$dF = -SdT - pdV \; . \tag{2.16}$$

For the pressure the following relation is used

$$p = -\langle \frac{\partial H}{\partial V} \rangle$$

$$p = \frac{1}{\beta} \frac{\partial}{\partial V} \ln \left[Z(T, N, V) \right] \; . \tag{2.17}$$

This can be shown as follows

$$\frac{1}{\beta} \frac{\partial}{\partial V} \ln \left[Z(T, N, V) \right] = \frac{1}{\beta Z} \frac{\partial}{\partial V} \int e^{-\beta H(\pi)} \, \mathcal{D}_\pi^{\mathcal{N}} \; .$$

The volume dependence is put into the Hamilton function via a box shaped potential. Thus the integration limts are independent of V and it is possible to swap differentiation and integration

$$\frac{1}{\beta} \frac{\partial}{\partial V} \ln \left[Z(T, N, V) \right] = \frac{1}{\beta Z} \int \frac{\partial}{\partial V} e^{-\beta H(\pi)} \, \mathcal{D}_\pi^{\mathcal{N}}$$

$$= \frac{1}{\beta Z} \int e^{-\beta H(\pi)} \frac{\partial(-\beta H)}{\partial V} \, \mathcal{D}_\pi^{\mathcal{N}}$$

$$= -\frac{1}{Z} \int e^{-\beta H(\pi)} \frac{\partial H}{\partial V} \, \mathcal{D}_\pi^{\mathcal{N}} = -\langle \frac{\partial H}{\partial V} \rangle = p \; .$$

Now we consider the total differential of $\ln\left[Z(T, N, V)\right]$ (still for constant N)

$$d\ln\left[Z\right] = \underbrace{\left(\frac{\partial\ln\left[Z\right]}{\partial T}\right)\bigg|_{N,V}}_{\overset{(2.13)}{=}\beta U/T} dT + \underbrace{\left(\frac{\partial\ln\left[Z\right]}{\partial V}\right)\bigg|_{T,N}}_{\overset{(2.17)}{=}\beta p} dV$$

$$= \beta\left(\frac{U}{T}dT + pdV\right)$$

$$\overset{(2.14)}{=} \beta\left(\frac{F}{T}dT + SdT + pdV\right)$$

$$\overset{(2.16)}{=} \beta\left(\frac{F}{T}dT - dF\right) = -\left(F\underbrace{\frac{-dT}{k_BT^2}}_{d\beta} + \beta dF\right)$$

$$= -d(\beta F)\ .$$

So we have the sought-for result

FREE ENERGY
(*Partition function*)

$$F(T, N, V) = -k_BT\ln\left[Z(T, N, V)\right]$$
$$Z(T, N, V) = e^{-\beta F}\ .$$

Since the free energy is a thermodynamic potential, all independent variables can be determined by differentiation. In principle, determining the internal energy from F has already been done in equation (2.13) [Page 61]. We obtain an alternative expression as follows

$$U = -\frac{\partial\ln\left[Z\right]}{\partial\beta} \tag{2.18}$$

$$= -\frac{\partial\ln\left[e^{-\beta F}\right]}{\partial\beta} = \frac{\partial(\beta F)}{\partial\beta}\ .$$

Likewise the relation for pressure follows from equation (2.17) [Page 62]

$$p = -\frac{1}{\beta}\frac{\partial(\beta F)}{\partial V} = -\frac{\partial F}{\partial V}\ ,$$

which can also be read off readily from equation (2.15) [Page 62]. From that equation, we also get the following relation for the entropy:

$$S(T, V, N) = - \left(\frac{\partial F}{\partial T} \right) \bigg|_{N,V} = k_B \left(\frac{\partial (T \ln [Z])}{\partial T} \right) \bigg|_{N,V} .$$

This corresponds to the definition used in thermodynamics. Later it will be shown that the entropy defined in this way is equivalent to the microcanonical definition.

Comclusions from homogenity

The natural variables of the free energy are (T, N, V), with the last two being extensive quantities. Because of homogenity the following has to be valid:

$$F(T, \lambda N, \lambda V) = \lambda F(T, N, V) .$$

After taking the derivative of both sides we get

a) from the left side:

$$\frac{d}{d\lambda} F(T, \lambda N, \lambda V) = N \left. \frac{\partial}{\partial N'} F(T, N', \lambda V) \right|_{N'=\lambda N} + V \left. \frac{\partial}{\partial V'} F(T, \lambda N, V') \right|_{V'=\lambda V}$$

b) from the right side:

$$\frac{d}{d\lambda} F(T, \lambda N, \lambda V) = F(T, N, V) .$$

Both sides together yield:

$$F(T, N, V) = N \left. \frac{\partial}{\partial N'} F(T, N', \lambda V) \right|_{N'=\lambda N} + V \left. \frac{\partial}{\partial V'} F(T, \lambda N, V') \right|_{V'=\lambda V} .$$

As the left side is not dependent on λ the same has to apply for the right side. Therefore it can be evaluated at the point $\lambda = 1$. This yields

$$F(T, N, V) = \underbrace{\left(\frac{\partial F}{\partial N} \right) \bigg|_{T,V}}_{\overset{(2.15)}{=} \mu} N + \underbrace{\left(\frac{\partial F}{\partial V} \right) \bigg|_{T,N}}_{\overset{(2.15)}{=} -p} V .$$

FREE ENERGY
(*Alternative form*)

$$F(T, N, V) = \mu N - pV \ .$$

On the right side there are only the natural variables with the corresponding conjugated intensive quantities.

Only when the dependence of a thermodynamic potential on its natural variables is known, all the terhmodynamical quantities can be calculated. The relation $F = -pV - \mu N$ for example is not sufficient, as for the free energy the natural variable T is missing.

Approach

In the frame of the canonical ensemble, on the basis of the Hamilton function, one will at first determine the partition functeion and from this the free energy.

Heat capacity

Now we shall derive the formula for the heat capacity in the canonical ensemble. The heat capacity C_V is defined as

$$C_V = \left(\frac{\partial U}{\partial T} \right) \bigg|_{N,V} = -k_B \beta^2 \left(\frac{\partial U}{\partial \beta} \right) \bigg|_{N,V} \ .$$

As the internal energy is equivalent to the average energy, we get

$$
\begin{aligned}
- \left(\frac{\partial U}{\partial \beta} \right) \bigg|_{N,V} &= - \left(\frac{\partial}{\partial \beta} \frac{\int H e^{-\beta H} \, \mathcal{D}_\pi^{\mathcal{N}}}{Z} \right) \bigg|_{N,V} \\
&= \frac{\int H^2 e^{-\beta H} \, \mathcal{D}_\pi^{\mathcal{N}}}{Z} - \frac{\int H e^{-\beta H} \, \mathcal{D}_\pi^{\mathcal{N}}}{Z^2} \frac{\partial Z}{\partial \beta} \\
&= \langle H^2 \rangle - \langle H \rangle^2 = \langle (\Delta H)^2 \rangle
\end{aligned}
\tag{2.19}
$$

Therefore the heat capacity can be written as follows:

HEAT CAPACITY I

$$C_V = \left(\frac{\partial U}{\partial T} \right) \bigg|_{N,V} = k_B \beta^2 \langle (\Delta H)^2 \rangle \geq 0 \ .$$

On the one hand the heat capacity cannot be negative and on the other hand, with $S(T, N, V) = S(E(T), N, V)$ we get an alternative expression for the heat capacity

$$\left(\frac{\partial S(T, N, V)}{\partial T} \right) \bigg|_{N,V} = \left(\frac{\partial S(E, N, V)}{\partial E} \right) \bigg|_{N,V} \left(\frac{\partial E(T, N, V)}{\partial T} \right) \bigg|_{N,V} = \frac{1}{T} \, C_V$$

and, therefore, also the following is valid

HEAT CAPACITY II

$$C_V = T \left(\frac{\partial S(T, N, V)}{\partial T} \right) \bigg|_{N,V} \ .$$

From this **thermal stability** can be deduced:

$$0 \leq C_V = \frac{T dS}{dT} \bigg|_{V,N} = \frac{dW}{dT} \ .$$

This means that heat transfer with constant volume and particle number increases temperature.

Equation (2.19) [Page 65] can also be used to derive an interesting relation for the calculation of energy fluctuations

$$\langle (\Delta H)^2 \rangle = - \left(\frac{\partial U}{\partial \beta} \right) \bigg|_{N,V} \overset{(2.18)}{=} \left(\frac{\partial^2 \ln [Z(T, N, V)]}{\partial \beta^2} \right) \bigg|_{N,V} \ . \tag{2.20}$$

Furthermore, the expression for the heat capacity can also be used to calculate the relative uncertainty in the energy

$$\frac{\Delta E}{E} := \frac{\sqrt{\langle (\Delta H)^2 \rangle}}{U}$$

$$= \frac{\sqrt{C_V k_B T^2}}{U} = T\frac{\sqrt{C_V k_B}}{U} \ .$$

Now the heat capacity as well as the internal energy are extensive quantities and therefore the relative uncertainty of the energy goes to zero with

$$\frac{\Delta E}{E} \propto T \frac{1}{\sqrt{N}}$$

This means that in the thermodynamic limit the internal energy of the canonical ensemble is equal to that of the microcanonical ensemble at the same temperature. However, we still have to prove that the temperatures really are the same.

Equivalence of microcanonical and canonical ensemble
Supplemental material

In the canonical ensemble the temperature T is an externally defined parameter (natural variable) while in the microcanonical ensemble it is defined by the following formula:

$$\frac{1}{T_{mkG}} := \left(\frac{\partial S(E, N, V)}{\partial E} \right) \Bigg|_{N,V} \tag{2.21}$$

To show the equivalency between canonical and microcanonical ensemble, we shall again consider the expression for the internal energy in the canonical ensemble.

$$\langle H \rangle = \frac{1}{Z} \int H(\pi) e^{-\beta H(\pi)} \, \mathcal{D}_\pi^{\mathcal{N}}$$

$$= \frac{1}{Z} \int E \, \rho(E) \, e^{-\beta E} dE \ ,$$

with $\rho(E)$ representing the density of states. The fact that the uncertainty of the energy goes to zero in the thermodynamic limit results in $\rho(E)e^{-\beta E}$ being a sharply peaked function. Therefore the stationary phase approximation is applicable for solving the integral. For this we expand

$$\Phi := \ln\left[\rho(\mathrm{E})e^{-\beta\mathrm{E}}\right] = -\beta E + \underbrace{\ln\left[\rho(\mathrm{E})\right]}_{S(E,N,V)/k_B}$$

into a Taylor series around the position of the maximum. The maximum is found at the internal energy[2], which we get from the following condition

$$0 = \frac{\partial \Phi}{\partial E} = -\beta + \frac{1}{k_B} \frac{\partial S(E, N, V)}{\partial E}$$

$$\Rightarrow \quad \frac{1}{T} = \frac{\partial S(E, N, V)}{\partial E} = \frac{1}{T_{mkG}} \ .$$

With this the equivalency of the temperatures is proven. Furthermore this equation yields the position $E^* = U$ of the maximum of Φ. Now we shall proceed with the expansion of the Taylor series

$$\Phi = \Phi(E^*) + \frac{\partial \Phi}{\partial E}(E - E^*) + \frac{1}{2} \frac{\partial^2 \Phi}{\partial E^2}(E - E^*)^2 \ .$$

The first derivative vanishes at the maximum. The second derivative at the point $\mathbf{E} = \mathbf{E}^*$ yields

$$\frac{\partial^2 \Phi}{\partial E^2} \overset{(2.21)}{=} \frac{\partial}{\partial E}\left(\frac{1}{k_B} \overbrace{\frac{\partial S}{\partial E}}^{1/T_{mkG}} - \beta \right) = \frac{1}{k_B} \frac{\partial}{\partial E} \frac{1}{T_{mkG}} - \overbrace{\frac{\partial \beta}{\partial E}}^{=0}$$

$$= -\frac{1}{k_B T_{mkG}^2}\left(\frac{\partial T_{mkG}}{\partial E} \right)\bigg|_{N,V}$$

$$= -\frac{1}{k_B T_{mkG}^2}\left(\frac{\partial E}{\partial T_{mkG}} \right)^{-1}\bigg|_{N,V}$$

$$= -\frac{1}{k_B T_{mkG}^2}\left(\frac{\partial U(T, N, V)}{\partial T} \right)^{-1}\bigg|_{N,V}$$

$$= -\frac{1}{k_B T_{mkG}^2} \frac{1}{C_V} \ .$$

We were able to perform the step before the last , because the temperaturs are the same at the maximum of the energy. Therefore the series expansion is

$$\Phi = \Phi(E^*) - \frac{1}{2k_B T^2 C_V}(E - E^*)^2$$

---

[2]As for the stationary phase approximation $\rho(E)e^{-\beta E}$ is approximated with a gaussian function, whose mean value is at the same position as the maximum.

In the framework of the stationary phase approximation we shall now calculate the partition function

$$Z(T, N, V) = \int \rho(E) e^{-\beta E} dE$$

$$= \rho(E^*) e^{-\beta E^*} \int e^{-\frac{(E-E^*)^2}{2k_B T^2 C_V}} \, dE$$

$$= \rho(E^*) e^{-\beta E^*} \sqrt{2\pi k_B T^2 C_V} \; .$$

The terms, which we omittet for the stationary phase approximation vanish in the thermodynamic limit, as we have seen before. Now we can easily calculate the free energy

$$F = -k_B T \ln[\mathrm{Z}]$$

$$= -\underbrace{k_B \ln[\rho(\mathrm{E}^*)]}_{\overset{(2.2)}{=} S_{mkG}} T + k_B T \beta \underbrace{E^*}_{U} + \frac{1}{2} \ln\left[2\pi k_B T^2 C_V\right]$$

$$= U - T S_{mkG} + O(\ln[\mathrm{N}]) \; .$$

In the thermodynamic limit, the last term is negligible in comparison to the other two extensive quantities and a comparison with the free energy in the canonical ensemble

$$F(T, N, V) = U(T, N, V) - T S_{kG}(T, N, V)$$

immediately yields the equivalence of the entropies, meaning

$$k_B \ln[\rho(\mathrm{E, N, V})] \overset{\text{bzw.}}{=} k_B \ln[\mathrm{Z(E, N, V)}] \overset{\text{bzw.}}{=} -\left(\frac{\partial F(T, N, V)}{\partial T}\right)\bigg|_{N,V} \; .$$

2.4.3 Virial theorem and equipartition theorem

Here, we take a closer look at the thermodynamic expectation value of the the following form

$$\langle \pi_i \frac{\partial H(\pi)}{\partial \pi_j} \rangle$$

in the canonical ensemble. The microcanonical ensemble gives the same result, but the calculation is mathematically much more complex.

$$\langle \pi_i \frac{\partial H(\pi)}{\partial \pi_j} \rangle = \frac{1}{Z} \int \underbrace{e^{-\beta H(\pi)} \frac{\partial H}{\partial \pi_j}}_{-\frac{1}{\beta} \frac{\partial}{\partial \pi_j} e^{-\beta H}} \pi_i \, \mathcal{D}_\pi^{\mathcal{N}} \; .$$

Integration by parts finally yields

$$\langle \pi_i \frac{\partial H(\pi)}{\partial \pi_j} \rangle = -\frac{k_B T}{Z} \left(\underbrace{\pi_i e^{-\beta H(\pi)} \Big|_{\pi_{min}}^{\pi_{max}}}_{=0} - \underbrace{\int e^{-\beta H(\pi)} \frac{\partial \pi_i}{\partial \pi_j} \, \mathcal{D}_\pi^{\mathcal{N}}}_{\delta_{ij} \cdot Z} \right) = \delta_{ij} \ k_B T \ .$$

(2.22)

The first term in the integration by parts vanishes at the boundaries of the integration area. The boundaries for the momenta mean $p \to \pm\infty$ and therefore the kinetic energy is infinite. This casues the Boltzmann factor to drop to zero. There are two possibilities for the spatial part. Either there is a finite volume, but then the potential at the boundary must be infinite. Or there is an infinite volume. Here, too, the potential must diverge, as for example with the harmonic oscillator.

The result in equation (2.22) [Page 70] is valid for any Hamiltonian function. Now we shall consider the physical consequences. Leet's first recall that $\pi_i = p_l$ is the canonical momentum for a generalised coordinate q_i. Thus, according to Hamilton's equations of motion, the following is obtained

$$\frac{\partial H(\pi)}{\partial p_l} = \frac{d}{dt} q_l = \dot{q}_l$$

Thus we get $\quad \langle p_l \dot{q}_l \rangle = k_B T$

resp. $\quad \sum_{l=1}^{\mathcal{N}} \langle p_l \dot{q}_l \rangle = \mathcal{N} k_B T \ .$

On the other hand,

$$\sum_{l=1}^{\mathcal{N}} p_l \dot{q}_l = 2 H_{kin} \ , \Rightarrow \qquad \langle H_{kin} \rangle = \mathcal{N} \frac{k_B T}{2} \ .$$

This means that the average kinetic energy per degree of freedom is

$$\frac{\langle K_{kin} \rangle}{\mathcal{N}} = \frac{k_B T}{2} \ .$$

Alternatively, if $\pi_i = q_l$ is chosen as a generalised coordinate, this results in

$$\frac{\partial H(\pi)}{\partial q_l} = \frac{\partial U(\pi)}{\partial q_l}$$

$$\Rightarrow \qquad \langle \sum_{l=1}^{\mathcal{N}} q_l \frac{\partial U(q)}{\partial q_l} \rangle = \mathcal{N} k_B T \ .$$

If the potential is a homogenous function of order α, this results in

$$\langle H_{pot} \rangle = \frac{\mathcal{N} k_B T}{\alpha}$$

and therefore we have

$$\langle H_{kin} \rangle = \frac{\alpha}{2} \langle H_{pot} \rangle \ .$$

In the case of a quadratic potential the average kinetic energy is equal to the average potential energy.

The virial as time average was already discussed in analytical mechanics. As time average and manifold average are the same this leads to the already known solution.

Example: Particles in a harmonic potential

Considering N classical particles in a harmonic potential we get

$$\langle H_{kin} \rangle = \langle H_{pot} \rangle = \frac{\mathcal{N} k_B T}{2}$$
$$\Rightarrow \quad \langle H \rangle = \mathcal{N} k_B T \ . \tag{2.23}$$

2.5 Grand canonical ensemble

For the **canonical ensemble** we introduced temperature as a state variable, which is significantly easier to control in experiment than the energy of the system. Now, in most cases it is also difficult to keep the number of particles constant. In addition to that, it may change when changing other state variables. Therefore, the particle number is not a good state variable. Better suited for this purpose is the chemical potential. Thus we shall derive a thermodynamic potential whose natural variables are temperature T, chemical potential μ and the volume V. This will lead to the **grand canonical ensemble**.

For this purpose, we couple the reference system to a heat bath and a particle reservoir. The entire system is still an isolated one. From the previous considerations, we know that the system will settle to a common temperature and a common chemical potential. Both state variables are determined by the heat bath, which is assumed to be infinitely large. Since the number of particles is not fixed, we have to extend the phase space. For this purpose, we define the **fock space**, which is a concatenation of phase spaces for different numbers of particles, starting at zero particles and extending to infinitely many particles.

To illustrate this, let us consider a simple example. We restrict the number of particles to 1 or 2 and consider only one spatial dimension ($d = 1$). We also restrict ourselves to the spatial coordinates of the particles. For one particle we need a one-dimensional "phase space" and for two particles a two-dimensional one. We merge the two to obtain a three-dimensional coordinate system. Let the z-axis describe the phase space of a single particle system and the xy-plane describe the phase space for two particles. Legitimate points in this Fock space are either on the z-axis or on the xy-plane.

For the generalised formalism we need the probability density

$$p(\pi_R^{N_R} | V_R, V_B, N, E)$$

for the phase space point $\pi_R^{N_R}$ of the reference system. Here $\pi_R^{N_R}$ contains not only momentum and spatial coordinate, but also the number of particles N_R, which specifies in which sector of the fock space the point is located. We have now added the number of particles explicitly as an index. If the reference system (R) is in the state $\pi_R^{N_R}$, then the number of particles in the bath has to be $N_B = N - N_R$. Although we are now calculating probability densities for all possible numbers of particles N_R, for every N_R that is to be considered the derivation is as before and via marginalisation we obtain

$$p(\pi_R^{N_R} | V_R, V_B, N, E) \propto Z_B(E_B = E - H_R^{N_R}(\pi_R) | N_B = N - N_R | V_B)$$

$$\propto \exp\left(\frac{1}{k_B} \, S_B(E_B = E - H_R^{N_R}(\pi_R) | N_B = N - N_R | V_B) \right) .$$

Again, we use the stationary phase approximation, where at $N \to \infty$ the terms of higher order vanish completely. This yields the following contributors

$$S_B(E - H_R^{N_R}(\pi_R) | N - N_R | V_B) = S_B(E | N | V_B)$$

$$- \left(\left(\frac{\partial S_B}{\partial E_B} \right) \bigg|_{N_B, V_B} \right) \bigg|_{E_B = E, N_B = N} H_R^{N_R}(\pi_R)$$

$$- \left(\left(\frac{\partial S_B}{\partial N_B} \right) \bigg|_{E_B, V_B} \right) \bigg|_{E_B = E, N_B = N} N_R$$

$$= S_B(E, N, V) - \frac{1}{T_B} \, H_R^{N_R}(\pi_R) + \frac{\mu_B}{T_B} \, N_R .$$

However, now $T_B = T_R = T$ and $\mu_B = \mu_R = \mu$ apply again and the result is therefore

$$p(\pi_R^{N_R} | V_R, V_B, N, E) = \frac{1}{Z} \, e^{-\beta H_R(\pi_R^{N_R}) + \beta \mu N_R} .$$

From now on, we can omit the index R as the bath does not show up explicitly anymore. Also the explicit specification of the number of particles at phase space point π is dropped as it is given implicitly.

PROBABILITY DENSITY FOR THE GRAND CANONICAL ENSEMBLE

$$p(\pi|T,\mu,V) = \frac{1}{Z(T,\mu,V)} \, e^{-\beta H_N(\pi)+\beta\mu N}$$

$$Z(T,\mu,V) = \sum_{N=0}^{\infty} z^N \int e^{-\beta H_N(\pi)} \, \mathcal{D}_\pi^{\mathcal{N}}$$

$$Z(T,\mu,V) = \sum_{N=0}^{\infty} \frac{z^N}{h^{dN}N!} \int e^{-\beta H_N(\pi)} \, d^{2\mathcal{N}}\pi$$

$$= \sum_{N=0}^{\infty} Z(T,N,V) \, z^N \ .$$

Fugacity $z := e^{\beta\mu} \ .$

The fact that the total energy and the total number of particles are conserved for the whole system leads to the fact that the temperature (average energy) and the chemical potential (average number of particles) are determined by the bath.

2.5.1   Connection to thermodynamics

Now we shall express the state variables that are relevant for thermodynamics within the framework of the grand canonical ensemble, i.e. by means of the grand canonical partition function or grand canonical potential. Starting with the average number of particles:

$$\langle N \rangle = \sum_{N=0}^{\infty} \int \mathcal{D}_\pi^{\mathcal{N}} N p(\pi|T,\mu,V)$$

$$= \frac{1}{Z(T,\mu,V)} \sum_{N=0}^{\infty} N z^N \underbrace{\int e^{-\beta H_N(\pi)} \, \mathcal{D}_\pi^{\mathcal{N}}}_{=Z(T,N,V)}$$

AVERAGE NUMBER OF PARTICLES

$$
\langle N \rangle = \frac{\sum_N N z^N Z(T, N, V)}{\sum_N z^N Z(T, N, V)}
$$
$$
= \frac{1}{\beta} \left(\frac{\partial \ln \left[Z(T, \mu, V) \right]}{\partial \mu} \right) \Bigg|_{T,V} . \tag{2.24}
$$

The average number of particles

$$
\langle N \rangle = N(T, \mu, V)
$$

is a function of (T, μ, V). This equation can be inverted with respect to μ and yields

$$
\mu = \mu(T, \langle N \rangle, V) .
$$

Now the grand canonical partition function depends on the chemical potential only through the fugacity. Replacing μ by $\ln(z)/\beta$ in the partition function, we get a function $Z(T, z, V)$ and furthermore we have the relation

$$
\langle N \rangle = z \left(\frac{\partial \ln \left[Z(T, z, V) \right]}{\partial z} \right) \Bigg|_{T,V} . \tag{2.25}
$$

Next we shall calculate the pressure within the framework of the grand canonical ensemble. Analogous to equation (2.17) [Page 62] we have

$$
p = -\langle \frac{\partial H}{\partial V} \rangle = \frac{1}{\beta} \left(\frac{\partial \ln \left[Z(T, \mu, V) \right]}{\partial V} \right) \Bigg|_{T,\mu} . \tag{2.26}
$$

In the derivation it does not make a difference that N is not fixed. For the internal energy the following applies:

$$
U = \langle H \rangle = - \left(\frac{\partial \ln \left[Z(T, \mu, V) \right]}{\partial \beta} \right) \Bigg|_{\mu,V} + \mu \langle N \rangle . \tag{2.27}
$$

The additional term is added because β also appears in the exponent of the probability density as a prefactor of N. If instead of μ, the variable z is used for the partition function and if z is fixed in the derivative this can be avoided and we get the alternative expression

$$
U = - \left(\frac{\partial \ln \left[Z(T, z, V) \right]}{\partial \beta} \right) \Bigg|_{z,V} .
$$

Within the framework of the grand canonical ensemble the **grand canonical potential**, which is the Legendre transformed free energy, takes on the role of the generating functional

$$
\begin{aligned}
\Omega(T, \mu, V) &= F(T, N, V) - \mu N \\
d\Omega &= dF - \mu dN - N d\mu \\
&\overset{(2.15)}{=} -SdT - pdV + \mu dN - \mu dN - N d\mu \\
&= -SdT - pdV - N d\mu \; .
\end{aligned}
$$

Therefore we have

$$
\begin{aligned}
&\textsc{Grand canonical potential} \\[1em]
\Omega(T, \mu, V) &= F(T, N, V) - \mu N \\
d\Omega &= -SdT - pdV - N d\mu \\
\left(\frac{\partial \Omega}{\partial T} \right) \Bigg|_{V,\mu} &= -S \\
\left(\frac{\partial \Omega}{\partial V} \right) \Bigg|_{T,\mu} &= -p \\
\left(\frac{\partial \Omega}{\partial \mu} \right) \Bigg|_{V,T} &= -\langle N \rangle \; .
\end{aligned}
\tag{2.28}
$$

We now calculate the total differential of $\beta\Omega$

$$
\begin{aligned}
d\big(\beta\Omega\big) &= -\frac{\Omega}{k_\beta T^2} dT - \beta \left(SdT + pdV + \langle N \rangle d\mu \right) \\
&= -\frac{\Omega + ST}{k_\beta T^2} dT - \beta \left(pdV + \langle N \rangle d\mu \right) \\
&= -\frac{U - \mu \langle N \rangle}{k_\beta T^2} dT - \beta \left(pdV + \langle N \rangle d\mu \right) \; .
\end{aligned}
$$

The internal energy, the pressure and the average number of particles are then expressed according to equation (2.27) [Page 74], (2.26) and (2.24) by

the derivatives of $\ln(Z)$. Then we find

$$
\begin{aligned}
d(\beta\Omega) &= \frac{1}{k_\beta T^2}\left(\frac{\partial\ln[Z]}{\partial\beta}\right)\Big|_{\mu,V} dT - \left\{\left(\frac{\partial\ln[Z]}{\partial V}\right)\Big|_{T,\mu} dV + \left(\frac{\partial\ln[Z]}{\partial\mu}\right)\Big|_{T,V} d\mu\right\} \\
&= -\left(\frac{\partial\ln[Z]}{\partial T}\right)\Big|_{\mu,V} dT - \left\{\left(\frac{\partial\ln[Z]}{\partial V}\right)\Big|_{T,\mu} dV + \left(\frac{\partial\ln[Z]}{\partial\mu}\right)\Big|_{T,V} d\mu\right\} \\
&= -d\left\{\ln[Z(T,\mu,V)]\right\}
\end{aligned}
$$

Except for a constant that is irrelevant for the thermodynamic potential we therefore get

$$
\ln[Z(T,\mu,V)] = -\beta\Omega\ .
$$

With this we now have a similar relationship between partition function and potential as the one in the case of the canonical ensemble

---

GRAND CANONICAL POTENTIAL
(*Partition function*)

$$
\begin{aligned}
\Omega(T,\mu,V) &= -k_B T\ln[Z(T,\mu,V)] \\
Z(T,\mu,V) &= e^{-\beta\Omega(T,\mu,V)}\ .
\end{aligned}
$$

Conclusions from homogenity

The thermodynamic variables T and μ are intensive quantities and here only V is extensive. This means

$$
\Omega(T,\lambda V,\mu) \overset{!}{=} \lambda\Omega(T,V,\mu)\ . \tag{2.29}
$$

The derivative of this equation with respect to λ is

left side: $\qquad \dfrac{d}{d\lambda}\Omega(T,\lambda V,\mu) = \dfrac{\partial}{\partial V}\Big(\Omega(T,V',\mu)\Big)\Big|_{V'=\lambda V} V$

right side: $\qquad \dfrac{d}{d\lambda}\Omega(T,\lambda V,\mu) = \Omega(T,V,\mu)$

both sides $\quad \dfrac{\partial}{\partial V'}\Big(\Omega(T,V',\mu)\Big)\Big|_{V'=\lambda V} V = \Omega(T,V,\mu)\ .$

As the right side is independent of λ, the same has to be valid for the left side. Therefore, we are able to evaluate the left side at the point $\lambda = 1$. With this we get

$$\Omega(T, V, \mu) = \underbrace{\frac{\partial}{\partial V} \Big(\Omega(T, V, \mu) \Big)}_{\stackrel{(2.28)}{=} -p} V = -pV \ .$$

On the right side there are only the extensive natural variables together with the corresponding conjugated intensive quantities.

With this we have an alternative expression for the grand canonical potential and pressure in the grand canonical ensemble

> GRAND CANONICAL POTENIAL
> (*alternative expression and pressure*)
>
> $$\Omega = -pV \tag{2.30}$$
>
> $$p = -\frac{\Omega}{V} = \frac{k_B T}{V} \ln \left[Z(T, \mu, V) \right] \ . \tag{2.31}$$

Now, if the dependence of a thermodynamic potential on its natural variables is known, one can claculate all thermodynamic quantities of the system. For example the relationship $\Omega = -pV$ for the potential is insufficient, because the natural variables of Ω are not p, V but T, μ, V.

Equivalence of (micro-)canonical and grand canonical ensemle

It is possible to show, that the quantities defined within the framework of the grand canonical ensemble, such as entropy, pressure and average number of particles (see equation (2.28)), match with those of the other ensembles. Details on this can be looked up in the book of W. Nolting, among others.

Compressibility

In this context the (isothermic) compressibility is a quantity of great interest.

$$\kappa_T := - \left(\frac{\partial \ln \left[V \right]}{\partial p} \right) \bigg|_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right) \bigg|_T \ .$$

The negative sign in the definition can be understood as a consequence of the fact that a decrease in volume should be accompanied by an increase in pressure. It is important to note that the temperature is kept constant, but not the chemical potential. Otherwise, starting from the following relation

$$-p = \left. \left(\frac{\partial \Omega}{\partial V} \right) \right|_{T,\mu} = \left. \left(\frac{\partial(-pV)}{\partial V} \right) \right|_{T,\mu} = -p - V \left. \left(\frac{\partial p}{\partial V} \right) \right|_{T,\mu},$$

we would obtain

$$\left. \left(\frac{\partial p}{\partial V} \right) \right|_{T,\mu} = 0.$$

As a **mechanical criterion of stability**, in phenomenological thermodynamics one demands that

$$\kappa_T \geq 0 \ .$$

Note that pressure is that exercised on the walls and in equilibrium it is also the pressure from the outside. Then a negative compressibilty results in

$$\frac{\partial V}{\partial p} \Big|_T > 0$$

and means that decreasing the volume would also decrease the pressure and the system would implode. In the frame of statistical mechanics the following relation can be deduced (see book of W. Nolting). The derivation is similar to that for the heat capacity.

$$\kappa_T = \beta V \, \frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle^2} \ . \tag{2.32}$$

Therefore, the compressibility is correlated with the square of the relative fluctuation of the number of particles and is obviously not negative. Thus, the criterion of stability is proven.

Fluctuation of the number of particles

In equation (2.20) [Page 66] we had seen in the context of the canonical ensemble that one can express energy fluctuations as the second derivative w.r.t. temperature (or β). Analogously, the second derivative of the chemical potential can be related to the fluctuation of the number of particles. Starting from equation (2.28) [Page 75]

$$\left. \left(\frac{\partial \Omega(T,\mu,V)}{\partial \mu} \right) \right|_{T,V} = -\langle N \rangle$$

we get

$$\left(\frac{\partial^2 \Omega(T, \mu, V)}{\partial \mu^2}\right)\bigg|_{T,V} = \left(\frac{\partial \langle N \rangle}{\partial \mu}\right)\bigg|_{T,V}$$

$$= -\left(\frac{\partial}{\partial \mu} \frac{\sum_N N z^N Z(T, N, V)}{\sum_N z^N Z(T, N, V)}\right)\bigg|_{T,V}$$

$$= -\beta \left(\frac{\sum_N N^2 z^N Z(T, N, V)}{\sum_N z^N Z(T, N, V)} - \left(\frac{\sum_N N z^N Z(T, N, V)}{\sum_N z^N Z(T, N, V)}\right)^2\right)$$

$$= -\beta \langle (\Delta N)^2 \rangle .$$

FLUCTUATION OF THE NUMBER OF PARTICLES

$$\langle (\Delta N)^2 \rangle = -k_B T \left(\frac{\partial^2 \Omega(T, \mu, V)}{\partial \mu^2}\right)\bigg|_{T,V} = \beta^{-2} \left(\frac{\partial^2 \ln[Z(T, \mu, V)]}{\partial \mu^2}\right)\bigg|_{T,V} .$$

From equation (2.32) [Page 78] we then get

$$\sqrt{\frac{\langle (\Delta N)^2 \rangle \rangle}{\langle N \rangle^2}} = \sqrt{\frac{\kappa}{\beta V}} .$$

As compressibility and temperature are intensive quantities we get

$$\frac{\sqrt{\langle (\Delta N)^2 \rangle \rangle}}{\langle N \rangle} \stackrel{N \gg 1}{=} \frac{const}{\sqrt{N}} .$$

Therefore, the relative fluctuation of the number of particles also vanishes in the thermodynamic limit and the average number of particles corresponds to the fixed number of particles of the canonical ensemble.

Example: Ideal gas of classical particles

The ideal gas of classical particles in the grand canonical ensemble is discussed in .

Chapter 3

Approach via probability theory

3.1 Gibbs/Shannon entropy

Gibbs already suggested an alternative approach to statistical mechanics, which is nowadays called Bayesian approach.

We assume the Gibbs/Shannon entropy at a predefined particle number, as we already did in the lecture **'Probability theory, Statistics and Data analysis'**

$$S = -k_B \int p(\pi) \ln\left[\mathrm{p}(\pi)\right] \mathcal{D}_\pi^\mathcal{N} = S[p(\pi)]$$

In order to tie in with statistical physics, a proportionality factor, which is irrelevant for MaxEnt, was introduced here. This definition was propagated by Gibbs within the framework of statistical physics and is therefore called **Gibbs entropy** in this context. However, here we considered that the **default model / prior probability density** has to be constant for physical reasons.[1] At first we always have the norming condition

$$\int p(\pi) \, \mathcal{D}_\pi^\mathcal{N} = 1$$

3.2 Microcanonical ensemble

In the case of the microcanonical ensemble the number of particle the volume and the total energy are given. The latter means that we restrict the allowed

---

[1]The assignment of the uninformative prior probability density requires invariance properties of the density in phase space. This is one of the few occasions on which details of the microscopic problem are important for the MaxEnt formalism.

phase-space points to the hypersphere of fixed energy. For the pdf in that part of phase space there is only a single constraint: the normalization. Maximising the entropy yields a constant probability density on the hypersurface of constant energy. The restriction in phase space on the hyper surface can be described mathematically by the delta-distribution, resulting in:

$$p(\pi|E, V, N, d, \mathbf{mkG}) = \frac{\delta(H(\pi) - E)}{Z(E, N, V, d)}$$

$$Normalisation \Rightarrow \quad Z(E, N, V, d) = \int \delta(H(\pi) - E)\, \mathcal{D}_\pi^\mathcal{N}\,.$$

This result is the only consistant one we can get with the information we have.[2] It is consistent with what we discussed in Section (2.2) [Page 43]. The value of the Gibbs entropy at the point of the MaxEnt solution for $p(\pi)$ then yields

$$S^* = -k_B \int p(\pi|E, V, N, d, \mathbf{mkG}) \ln\left[p(\pi|\mathrm{E, V, N, d}, \mathbf{mkG})\right] \mathcal{D}_\pi^\mathcal{N}$$

$$= -k_B \int_{H(\pi)=E} \frac{1}{Z} \ln\left[1/Z\right] \mathcal{D}_\pi^\mathcal{N} = k_B ln(Z) \underbrace{\int_{H(\pi)=E} \frac{1}{Z}\, \mathcal{D}_\pi^\mathcal{N}}_{=1}$$

$$= k_B \ln\left[\mathrm{Z}\right] = S^B\,.$$

The Gibbs entropy at the MaxEnt solution therefore corresponds to the Boltzmann entropy. In this respect the Gibbs entropy, therefore, is a more general construct, which makes it possible to determine the probability density of an individual statistical population by means of maximising. When one plugs in the physical probability density, one gets the Boltzmann entropy, from which in turn thermodynamic relations (among others potentials) can be calculated.

In order to avoid overencumbering the notation, we omit the upper index for the entropy, as its meaning is defined by the arguments of the entropy. This means that if the probability density is an argument, we are dealing with the Gibbs entropy. Otherwise we are dealing with the maximum of the Gibbs entropy or the Boltzmann entropy. Additionally we shall neither state the dimension d explicitly as an argument, as it does not change during the calculation.

---

[2]See script for *'Probability theory, Statistics and Data analysis'*.

3.2.1 Extremum condition

In the case of the microcanonical ensemble, the extremum condition is trivial. As the name **MaxEnt** suggests, for all normed probability densities, the equilibrium is described by the one, which is maximises the entropy S.

<div style="border:1px solid">

EXTREMAL CONDITION FOR THE MICROCANONICAL ENSEMBLE

$$\text{Entropy is maximal for fixed } E,\, N, V. \tag{3.1}$$

</div>

3.3 Canonical ensemble

In the case of the canonical ensemble instead of the energy, the temperature is fixed. That does not restrict the allowed regions in phase space, but the entire phase space is available. Temperature, however, defines the mean kinetic energy, which results in an additional constraint.

$$\langle H \rangle = \int H(\pi)\, p(\pi|T,N,V,\mathrm{kG})\, \mathcal{D}_\pi^{\mathcal{N}} := \overline{E}\ .$$

Plugging this constraint into the MaxEnt procedure via Lagrange parameters, yields

$$0 = -k_B - k_B \ln\left[\mathrm{p}(\pi)\right] - \lambda_0 - \lambda_1 H(\pi)$$

$$\text{resp.}\quad p(\pi) = \frac{1}{Z} e^{-\lambda_1 H(\pi)}\ ,$$

with Z defining the norming factor as

$$Z(T,N,V) = \int e^{-\lambda_1 H(\pi)}\, \mathcal{D}_\pi^{\mathcal{N}}\ .$$

Then the entropy at the position of the MaxEnt solution (Boltzmann en-

tropy) is

$$
\begin{aligned}
S^* &= -k_B \int p(\pi)\ln\left[p(\pi)\right] \mathcal{D}_\pi^{\mathcal{N}} \\
&= -k_B \int p(\pi)\ln\left[\frac{e^{-\lambda_1 H(\pi)}}{Z}\right] \mathcal{D}_\pi^{\mathcal{N}} \\
&= k_B \int p(\pi)\lambda_1 H(\pi)\, \mathcal{D}_\pi^{\mathcal{N}} + k_B\ln\left[Z\right] \int p(\pi)\, \mathcal{D}_\pi^{\mathcal{N}} \\
&= k_B\lambda_1 \underbrace{\langle H\rangle}_{:=\overline{E}} + k_B\, \ln\left[Z\right] .
\end{aligned}
$$

The temperature condition yields

$$
\begin{aligned}
\frac{1}{T} &= \frac{\partial S^*}{\partial \overline{E}} = k_B\lambda_1 \\
\Rightarrow \quad \lambda_1 &= \beta .
\end{aligned}
$$

The temperature constraint no follows from the comparison with the previous considerations, where the pdf had the same structure. So we have

$$
T\,S(T,N,V) = \overline{E} + \underbrace{k_B T\ln\left[Z(T,N,V)\right]}_{=-F(T,N,V)}
$$

$$
U(T,N,V) = S\,T + F . \tag{3.2}
$$

Here we used the notion for the internal energy instead of the one for the average energy. We see, that the MaxEnt approach also yields the relations between free energy, entropy and internal energy, which we previously had to adopt from thermodynamics, easily. These results are all identical to the ones from Section (2.4) [Page 58]. The Gibbs/Bayes approach is therefore more powerful than the Boltzmann approach.

3.3.1 Extremal conditions

In the canonical case we have maximised the functional

$$
\Phi := S - \lambda_1\langle H\rangle
$$

w.r.t. the pdf and under the the additional constraint of the normalisation. This maximisation is valid for all values of λ_1 and therefore especially for $\lambda_1 = 1/T$. Then along with equation (3.2) [Page 83] we have

$$
\frac{ST - \langle H\rangle}{T} = -\frac{F}{T}
$$

and this quantitiy becomes maximal for fixed T, meaning that among all normalised probability densities the one that minimises the free energy corresponds to the equilibrium.

EXTREMAL CONDITIONS FOR THE CANONICAL ENSEMBLE

$$\text{The free energy is minimal for fixed } T, N, V. \qquad (3.3)$$

3.4   Grand canonical ensemble

If the particle number is also variable and μ fixes the mean particle number, then the entropy must be expanded accordingly.

$$S := k_B \sum_{N=0}^{\infty} \int p(\pi^N) \ln \left(p(\pi^N) \right) \mathcal{D}_\pi^{\mathcal{N}} .$$

The constraints now are

$$\sum_N \int p(\pi^N) \, \mathcal{D}_\pi^{\mathcal{N}} = 1$$

$$\sum_N \int H(\pi^N) \, p(\pi^N) \, \mathcal{D}_\pi^{\mathcal{N}} = \overline{E}$$

$$\sum_N N \int p(\pi^N) \, \mathcal{D}_\pi^{\mathcal{N}} = \langle N \rangle .$$

Maximising yields

$$0 = -k_B - k_B \ln \left[p(\pi^{\mathrm{N}}) \right] - \lambda_0 - \lambda_1 H(\pi^N) - \lambda_2 N$$

bzw. $\qquad p(\pi^N) = \dfrac{1}{Z} \, e^{-\lambda_1 H(\pi^N) - \lambda_2 N} .$

The maximal entropy then is

$$S^* = k_B \lambda_1 \langle H \rangle + k_B \lambda_2 \langle N \rangle + k_B \ln \left[Z \right] .$$

As before, from the definition of temperature follows $\lambda_1 = \beta$. The definition of the chemical potential yields

$$\frac{\partial S}{\partial \langle N \rangle} = -\frac{\mu}{T} = k_B \lambda_2$$

$$\lambda_2 = -\beta \mu .$$

Therefore we have the same result as in Section (2.5) [Page 71].

$$p(\pi|T, \mu, V, \mathrm{dkG}) = \frac{1}{Z(T, \mu, V)} e^{-\beta H + \beta \mu N}$$

$$S(T, \mu, V) = \frac{U}{T} - \frac{\mu\langle N\rangle}{T} + \frac{k_B T \ln[Z]}{T}$$

$$ST = U - \mu\langle N\rangle + \Omega \ .$$

3.4.1 Extremal condition

Analogous to the discussion in the case of the canonical ensemble the functional

$$\Phi := S - \lambda_1\langle H\rangle - \lambda_2\langle N\rangle$$

was maximised with regard to the possible probability density while considering normalisation. In paricular, Φ is maximal for fixed values $\lambda_1 = 1/T$ and $\lambda_2 = \mu/T$. This leads to

$$\frac{ST - \langle H\rangle + \mu\langle N\rangle}{T} = -\frac{\Omega}{T}$$

becoming maximal for fixed T and μ, meaning that among all normalised probability densities, the one minimising the grand canonical potential corresponds to the equilibrium.

EXTREMAL CONDITION OF THE GRAND CANONICAL POTENTIAL

The grand canonical potential is minimal for fixed V.   (3.4)

3.5 Basic relation

The extremal conditions are equivalent to the basic relation of thermodynamics

$$0 \geq dU - TdS - pdV - \mu dN \ .$$

- E, N, V fixed $\Rightarrow 0 \geq -dS$, thus S maximum.

- N, V fixed $\Rightarrow dU - TdS = dF \geq 0$, thus F minimum.

- V fixed $\Rightarrow dU - TdS - \mu dN = d\Omega \geq 0$, thus Ω minimum.

Important equilibrium properties of thermodynamic systems therefore are closely related to the extremal properties of the thermodynamic potentials. For all (irreversible) processes, which are possible for certain boundary conditions, the potential with the corresponding natural variable increases or decreases.

3.6 Boltzmann H-function (supplementary)

BOLTZMANN H-FUNCTION

$$H := -k_B \int p_g(\pi) \ln \left[\frac{\mathrm{p_g}(\pi)}{\mathrm{p}(\pi)} \right] \mathcal{D}_\pi^{\mathcal{N}}$$
$$= \left\langle \ln \left[\frac{\mathrm{p_g}(\pi)}{\mathrm{p}(\pi)} \right] \right\rangle_g .$$

It can be easily shown that $H \leq 0$ for arbitrary probability densities p_g and p. First we prove that

$$\ln(x) \leq x - 1 ; \qquad \forall x \geq 0 . \tag{3.5}$$

For this we define $f(x) = \ln(x) - x + 1$. The second derivative

$$f''(x) = -\frac{1}{x^2} \leq 0 \qquad \forall x \geq 0$$

is negative, which means that $f(x)$ is convex and therfore has a definitive maximum. The derivative

$$f'(x) = \frac{1}{x} - 1$$

vanishes at the position $x = 1$. The maximum therefore is at $x = 1$ and has a value of

$$f^{max} = f(1) = 0 .$$

Therefore, $f(x) \leq 0$ applies to all $x \geq 0$ and with that, equation (3.5) [Page 86] is proven.

Now we shall use this in the equation for the H-function

$$H = k_B \int p_g(\pi)\ln\left[\frac{p(\pi)}{p_g(\pi)}\right] \mathcal{D}_\pi^\mathcal{N} \leq k_B \int p_g(\pi)\left(\frac{p(\pi)}{p_g(\pi)} - 1\right) \mathcal{D}_\pi^\mathcal{N}$$

$$H \leq k_B \int \left(p(\pi) - p_g(\pi)\right) \mathcal{D}_\pi^\mathcal{N} = k_B \left(\int p(\pi)\, \mathcal{D}_\pi^\mathcal{N} - \int p_g(\pi)\, \mathcal{D}_\pi^\mathcal{N}\right)$$

$$H \leq 0 \,.$$

This means, that the H-function is smaller than or equal to zero. H vanishes when both probability densities are equal and its absolut value increases with the difference between the two densities. Therefore, the negative H-function is also used as a measure of distance for probability densities.

We shall exemplarily consider two Gaussians with equal variance but different mean value

$$p_g(\pi) = \frac{1}{Z}e^{-\frac{1}{2\sigma^2}(\pi-\pi_{g,0})^2}$$

$$p(\pi) = \frac{1}{Z}e^{-\frac{1}{2\sigma^2}(\pi-\pi_0)^2} \,,$$

Here the H-function is

$$H = \underbrace{\left\langle(\pi - \pi_{g,0})^2\right\rangle_g}_{\sigma^2} - \left\langle(\pi - \pi_0)^2\right\rangle_g$$

$$= \sigma^2 - \left\langle((\pi - \pi_{g,0}) + (\pi_{g,0} - \pi_0))^2\right\rangle_g$$

$$= \sigma^2 - \underbrace{\left\langle(\pi - \pi_{g,0})^2\right\rangle_g}_{\sigma^2} - 2\underbrace{\left\langle(\pi - \pi_{g,0})\right\rangle_g}_{=0}(\pi_{g,0} - \pi_0) - (\pi_{g,0} - \pi_0)^2$$

$$= -(\pi_{g,0} - \pi_0)^2 \,.$$

The extremal conditions can be derived from the inequation $H \leq 0$. For further consideration consult books such as the one of W. Nolting.

3.7 Gibbs ensemble (supplementary)

It is easy to deduce what happens when energy and volume are variable and only temperature and pressure, and hence the average energy and volume, are fixed. In comparison to the previous derivation (grand canonical potential) one only has to formally replace the upper index N for the particle number by V in the MaxEnt formalism. Instead of summating over N, one has to integrate over V, and the third constraint is the following:

$$\int dV\, V\, \underbrace{\left(\int p(\pi^V)\, \mathcal{D}_\pi^\mathcal{N}\right)}_{\text{here } V \text{ is fixed}} = \langle V\rangle \,.$$

The MaxEnt condition yields

$$-k_B - k_B \ln\left[\mathrm{p}(\pi^{\mathrm{N}})\right] - \lambda_0 - \lambda_1 H(\pi|V) - \lambda_2 V = 0 \;,$$

or respectively

$$p(\pi|T,N,p) = \frac{1}{\tilde{Z}}\, e^{-\lambda_1 H(\pi) - \lambda_2 V} \;.$$

In this case the entropy at the maximum (Boltzmann entropy) is

$$S^* = k_B \lambda_1 \langle H \rangle + k_B \lambda_2 \langle V \rangle + k_B \ln\left[Z\right]$$

$$\text{bzw.}\quad TS^* = k_B T \lambda_1\, U + k_B T \lambda_2\, \langle V \rangle + k_B T \ln\left[Z\right]$$

$$-k_B T \ln\left[Z\right] = k_B T \lambda_1\, U + k_B T \lambda_2\, \langle V \rangle - TS^* \;.$$

As we fixed temperature and pressure, the Lagrange parameter, as well as S^* and Z are functions of T, N, p. From phenomenologic thermodynamics we adopt the definition of the **free Gibbs energy**

$$G(T,N,p) := U + p\langle V \rangle - TS \;.$$

Comparison shows that

$$\lambda_1 = \beta$$
$$\lambda_2 = \beta p$$

Additionally, we get the connection between the free enthalpy and the microscopic quantities

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<div style="text-align:center">FREE GIBBS ENTHALPY</div>

$$G(T,N,p) = -k_B T \ln\left[Z\right]$$
$$Z(T,N,p) = e^{-\beta G}$$
$$p(\pi|T,N,p) = \frac{1}{Z(T,N,p)}\, e^{-\beta(H(\pi)+pV)}$$
$$Z(T,N,p) := \int e^{-\beta(H(\pi)+pV)}\, \mathcal{D}_\pi^{\mathcal{N}} \;.$$

From this it can be easily derived that

$$\left(\frac{\partial \ln\left[Z(T,N,p)\right]}{\partial T}\right)\bigg|_{N,p} = -\beta\langle H\rangle$$

$$\left(\frac{\partial \ln\left[Z(T,N,p)\right]}{\partial p}\right)\bigg|_{T,N} = -\beta\langle V\rangle$$

and therefore because of $G = -k_B T\ln\left[Z\right]$ the following applies:

$$\left(\frac{\partial G(Z(T,N,p))}{\partial p}\right)\bigg|_{T,N} = k_B T\beta\langle V\rangle = \langle V\rangle\ .$$

Having performed a Legendre transformation from $F(T,N,V)$ to $G(T,N,p)$, in the process of which we switched V with p, the following applies:

$$G(T,N,p) = F(T,N,V) + pV\ .$$

Together with equation (2.15) [Page 62] the total differential yields

$$\begin{aligned}
dG &= dF + pdV + V\,dp \\
&= -SdT + \mu dN - pdV + pdV + V\,dp \\
&= -SdT + \mu dN + V\,dp\ .
\end{aligned}$$

In addition we can use the homogenity of the only extensive quantitiy N

$$G(T,\lambda N,p) = \lambda G(T,N,p)$$

This yields

$$G = \underbrace{\left(\frac{\partial G}{\partial N}\right)\bigg|_{N,p}}_{\mu} N = \mu\,N$$

Therefore, for a gas of a single species for the free Gibbs energy we get

$$G = \mu\,N$$
$$\text{applies as well as}\quad G = F + pV = U - TS + pV\ .$$

Chapter 4

Applications

4.1 Ideal Gas of classical particles

Here we shall consider the case of noninteracting free (constant potential) particles. The N particles are located in a cuboid with the edges (L_x, L_y, L_z).

4.1.1 Microcanonical ensemble

Number of microstates

In classical problems, the number $Z(E, N, V)$ of microstates for the energy E corresponds to the associated volume of the hypersurface in phase space. It is, however easier to to calculate $\Gamma_N^{kl}(E)$ first

$$
\Gamma_N^{\mathrm{kl}}(E) := \int \theta(E - H(\pi)) \, \mathcal{D}_\pi^{\mathcal{N}}
$$

$$
= \frac{1}{h^{\mathcal{N}} N!} \int \theta(E - \frac{p_{ges}^2}{2m}) d^{\mathcal{N}} x \, d^{\mathcal{N}} p
$$

$$
= \frac{V_{\mathcal{N}}}{h^{\mathcal{N}} N!} \, V^N \, (\sqrt{2mE}) \, .
$$

With the volume of the $\mathcal{N} = 3N$-dimensional hypersphere of radius $\sqrt{2mE}$ from equation (C.2) [Page 211] we eventually obtain

$$
\Gamma_N^{\mathrm{kl}}(E) = \frac{V^N}{h^{\mathcal{N}} N!} \, (2mE)^{\frac{\mathcal{N}}{2}} \, \frac{\pi^{\frac{\mathcal{N}}{2}}}{\Gamma(\frac{\mathcal{N}}{2} + 1)} \tag{4.1}
$$

$$
= \frac{V^N}{N!} \left(\frac{2\pi mE}{h^2} \right)^{\mathcal{N}/2} \frac{1}{\Gamma(\frac{\mathcal{N}}{2} + 1)} \, . \tag{4.2}
$$

Entropy

Now we calculate the entropy, which is actually defined by the volume $Z(E, N, V)$ of the hypersurface for the energy E and not by the enclosed volume $\Gamma_N(E)$ However, at first we are going to calculate the entropy by means of the latter and only after that calculate it while using the correct quantity $Z(E, N, V)$.

$$S = k_B \ln(\Gamma_N^{\text{kl}}(E))$$
$$= k_B \left\{ N\ln \left[V \left(\frac{2\pi\text{mE}}{\text{h}^2} \right)^{\frac{d}{2}} \right] - \ln(N!) - \ln \left[\Gamma(\frac{\mathcal{N}}{2} + 1) \right] \right\}$$

$$\ln(N!) + \ln \left[\Gamma(\frac{\mathcal{N}}{2} + 1) \right] = N\ln(N) - N + \frac{\mathcal{N}}{2} \ln(\frac{\mathcal{N}}{2}) - \frac{dN}{2}$$
$$= N \left\{ \ln(N) + \ln \left[(\frac{\mathcal{N}}{2})^{\frac{d}{2}} \right] - \frac{d+2}{2} \right\} .$$

For the entropy we find

$$S = k_B N \left\{ \ln \left[V \left(\frac{2\pi mE}{h^2} \right)^{\frac{d}{2}} \right] - \ln(N) - \ln \left[(\frac{\mathcal{N}}{2})^{\frac{d}{2}} \right] + \frac{d+2}{2} \right\}$$
$$= k_B N \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi mE}{\mathcal{N}h^2} \right)^{\frac{d}{2}} \right] + \frac{d+2}{2} \right\} .$$

ENTROPY OF THE CLASSICAL IDEAL GAS
(microcanonical ensemble, classical)
[Sackur-Tetrode equation]

$$S(E, V, N) = k_B N \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi mE}{dh^2 N} \right)^{\frac{d}{2}} \right] + \frac{d+2}{2} \right\} \qquad (4.3a)$$
$$= k_B N \left\{ \ln \left[\frac{1}{n} \left(\frac{4\pi m\tilde{E}}{dh^2} \right)^{\frac{d}{2}} \right] + \frac{d+2}{2} \right\} . \qquad (4.3b)$$

In the second equation we introduced the particle density $n := N/V$ and the energy per particle $\tilde{E} := E/N$. The extensivity of entropy can now be seen explicitly. It is equally easy to see that entropy is a homogenous function in the extensive quantities. **This would not be the case without the quantum mechanical correction.**

Actually, the entropy should be calculated with $Z(E,N,V) = \frac{\partial \Gamma_N(E)}{\partial E}$. We shall temporarily call the *real* entropy $\tilde{S}$. According to equation (4.1) [Page 90] $\Gamma = cE^{\frac{N}{2}}$ we obtain

$$\tilde{S} = k_B \ln\left[Z(E, N, V)\right] = k_B \ln\left[\frac{\partial \Gamma_N(E)}{\partial E}\right]$$

$$= k_B \ln\left[\Gamma \frac{\mathcal{N}}{2E}\right]$$

$$= S + k_B \ln\left[\frac{\mathcal{N}}{2E}\right]$$

$$\tilde{S} = S + O(1) .$$

As the entropy S is extensive (proportional to N) the relative difference between $\tilde{S}$ and S is of the order $1/N$ and therefore negligible in the thermodynamic limit. This is universally valid, meaning that for high dimensions, the entire volume is enclosed within an infinitesimal shell at the hypersurface of constant energy.

4.1.2   Temperature

In equation (2.3) [Page 48] temperature is defined as:

$$\frac{1}{T} = \left(\frac{\partial S(E, V, N)}{\partial E}\right)\Bigg|_{V,N} .$$

We just calculated the derivation that appears here, and therefore we get

$$\frac{1}{T} = \frac{d\, k_B N}{2E}$$

$$T = \frac{2E}{d\, k_B N}$$

or rather $\qquad E = \mathcal{N}\frac{k_B T}{2}$ \hfill (4.4)

I.e. The energy is $k_B T/2$ per degree of freedom.

Internal energy

Now we shall solve equation (4.3a) [Page 91] according to the energy

$$\frac{S}{k_B N} = \ln(\frac{V}{N}) + \frac{d}{2} \ln\left(\frac{4\pi m}{dh^2}\right) + \frac{d}{2} \ln\left(\frac{E}{N}\right) + \frac{d+2}{2}$$

$$\ln\left(\frac{E}{N}\right) = \frac{2S}{dk_B N} - \frac{d+2}{d} - \frac{2}{d}\ln(\frac{V}{N}) - \ln\left(\frac{4\pi m}{dh^2}\right)$$

and this defines the internal energy as a function of entropy S

$$U(S,V,N) := E = N \; e^{\frac{2S}{dk_B N} - \frac{d+2}{d}} \left(\frac{N}{V}\right)^{\frac{2}{d}} \left(\frac{dh^2}{4\pi m}\right) .$$

Pressure

The pressure is calculated from the internal energy. At first we shall isolate the volume-dependence of the internal energy

$$U = cV^{-\frac{2}{d}} .$$

From this we calculate the pressure

$$p = -\left(\frac{\partial U}{\partial V}\right)\bigg|_{S,N} = -c(-\frac{2}{d}) \; V^{-\frac{2}{3}-1} = U\left(\frac{2}{dV}\right) .$$

And we obtain

PRESSURE OF THE IDEAL GAS
(microcanonical ensemble, classical)
[Caloric state equation]

$$pV = \frac{2}{d} \, U . \tag{4.5}$$

Equation of state (ideal gas law)

Alternatively, via equation (2.4) [Page 50] together with equation (4.3a) [Page 91] we obtain

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)\bigg|_{E,N} = \frac{k_B N}{V}$$

which leads to

THEMAL EQUATION OF STATE OF THE IDEAL GAS (IDEAL GAS LAW)
(*microcanonical ensemble, classical*)

$$pV = Nk_BT .$$ (4.6)

Interestingly, the ideal gas law is independent of the spatial dimension d.

Internal energy

equation (4.6) [Page 94] together with equation (4.5) [Page 93] yields

---

INTERNAL ENERGY
(*microcanonical ensemble, classical*)

$$U = \frac{d}{2} Nk_BT .$$ (4.7)

---

a result we have obtained already earlier by a different derivation.

4.1.3   Gibbs paradox

We shall consider the following situation: Initially, we have two separate chambers with volumes V_i and numbers of particles N_i. The particles are supposed to be ideal and indistinguishable. The two chambers are separated by a mobile wall, which ensures equal pressure in both chambers. Additionally, the chambers are in thermal contact to ensure equal temperature, as well. Now we remove the separating wall. Because of the particular preparation neither temperature, nor pressure changes when the wall is removed. From the ideal gas law, equation (4.6) [Page 94], we can derive that the particle densities are the same in both chambers

$$n_i := \frac{N_i}{V_i} = \frac{p}{kT} = n$$

and they do not change when the wall is removed. Because of equation (4.7) [Page 94] the same is true for the energy per particle $\tilde{E} := E/N$.

Now we shall calculate the entropy before the removal of the separating wall. According to equation (4.3b) [Page 91] in chamber i the entropy is

$$S(E_i, V_i, N_i) = k_B N_i \left(\ln \left[\frac{1}{n} \left(\frac{4\pi m \tilde{E}}{dh^2} \right)^{d/2} \right] + \frac{d+2}{2} \right) .$$

The total entropy is the sum of the partial entropies. Therefore it is

$$S^{\text{before}} = \sum_{i=1}^{2} S(E_i, V_i, N_i) = k_B N \left(\ln \left[\frac{1}{n} \left(\frac{4\pi m \tilde{E}}{dh^2} \right)^{d/2} \right] + \frac{d+2}{2} \right) . \quad (4.8)$$

The total number of particles is of course $N = N_1 + N_2$. After the coupling equation (4.3b) [Page 91] still applies, however, now with the total number of particles. So we find

$$S^{\text{before}} = S^{\text{after}}, \quad (4.9)$$

as it should be for identical particles. Without the quantum correction factor $1/N!$ we would have found

$$S^{\text{before}} \neq S^{\text{after}}, \quad (4.10)$$

Before it was realised, that identical quantum particles ares strictly indistinguishable the correction term had not been used, resulting in different entropies. This is called the Gibbs paradox.

Mixing entropy However, it is a completely different situation if the particles are distinguishable. Suppose before the removal of the separating wall, the particles in chamber one were colored red and those in chamber two were colored blue. The the new (color) state is of course different before and after the mixing. The same applies to the entropy, which is the logarithm of the number of microstates.

Of course, the particles in the two chambers are initially indistinguishable because they all have the same color and with

$$n_i = \frac{N_i}{V_i} = n , \qquad \text{and } \tilde{E}_i = \tilde{E}$$

we obtain the previous result

$$S^{\text{before}} = \sum_{i=1}^{2} S(E_i, V_i, N_i) = \sum_i k_B N_i \left(\ln \left[\frac{V_i}{N_i} \left(\frac{4\pi m \tilde{E}_i}{dh^2} \right)^{d/2} \right] + \frac{d+2}{2} \right)$$

$$= k_B N \left(\ln \left[V \left(\frac{4\pi m \tilde{E}}{dh^2} \right)^{d/2} \right] + \frac{d+2}{2} \right) .$$

After the mixing we can still consider the two species (colors) separately and the corresponding entropies are still additive. However, the two species now spread over the entire volume V and thus also the densities change. However, the energy per particle remains the same since we are still dealing with non-interacting particles. So we have:

$$
\begin{aligned}
S^{\text{after}} = \sum_{i=1}^{2} S(E_i = N_i, \tilde{E}, V, N_i) &= k_B \sum_{i=1}^{2} N_i \left(\ln \left[\frac{V}{N_i} \left(\frac{4\pi m \tilde{E}}{dh^2} \right)^{\frac{d}{2}} \right] + \frac{d+2}{2} \right) \\
&= k_B \sum_{i=1}^{2} N_i \left(\ln \left[\frac{V}{N} \left(\frac{4\pi m \tilde{E}}{dh^2} \right)^{\frac{d}{2}} \right] + \frac{d+2}{2} - \ln \left(\frac{N}{N_i} \right) \right) \\
&= k_B \underbrace{\sum_{i=1}^{2} N_i}_{=N} \left(\ln \left[V \left(\frac{4\pi m \tilde{E}}{dh^2} \right)^{\frac{d}{2}} \right] + \frac{d+2}{2} \right) \\
\ldots &- k_B \underbrace{\sum_{i} N_i \ln N}_{=N} + k_B \sum_{i} N_i \ln N_i \qquad (4.11)
\end{aligned}
$$

So the difference in entropy is now

$$
\Delta S^{\text{mixing}} := S^{\text{after}} - S^{\text{before}} = -k_B N \ln(N) + k_B \sum_{i=1}^{2} N_i \ln(N_i))
$$

$$
\overset{\text{Stirling}}{=} -k_B \ln \left(\frac{N!}{N_1! N_2!} \right) = -k_B \ln \binom{N}{N_1}
$$

This difference in entropy is called *mixing entropy*. It is due to the colors of the particles and the argument of the logarithm is the number of microstates (color arrangements).
So the entropy is the sum of the entropy resulting from the spatial arrangement plus the entropy due to the color arrangements.

4.1.4   Canonical ensemble

Partition function

Now we will consider the ideal gas in the canonical ensemble.

$$
\begin{aligned}
Z(T, V, N) &= \frac{V^N}{h^{\mathcal{N}} N!} \int e^{-\beta E(p)} d^{\mathcal{N}} p \\
&= \frac{V^N}{h^{\mathcal{N}} N!} \, \Omega_{\mathcal{N}} \int_0^{\infty} e^{-\frac{\beta}{2m} p^2} p^{\mathcal{N}} \, \frac{dp}{p} \, ,
\end{aligned}
$$

with the substitution $p = \sqrt{2m/\beta}\sqrt{x}$ we get

$$
\begin{aligned}
Z(T,V,N) &= \frac{V^N}{h^{\mathcal{N}} N!} \, \Omega_{\mathcal{N}} \left(\frac{2m}{\beta}\right)^{\mathcal{N}/2} \frac{1}{2} \int_0^\infty e^{-x} x^{\mathcal{N}/2} \, \frac{dx}{x} \\
&= \frac{V^N}{h^{\mathcal{N}} N!} \, \frac{2\pi^{\mathcal{N}/2}}{\Gamma(\mathcal{N}/2)} \left(\frac{2m}{\beta}\right)^{\mathcal{N}/2} \frac{1}{2} \Gamma(\mathcal{N}/2) \\
&= \frac{V^N}{N!} \left(\frac{2\pi m}{h^2 \beta}\right)^{\mathcal{N}/2} = \frac{V^N}{N!} \, \lambda_T^{-dN} \, .
\end{aligned}
$$

Thus, we have already calculated the key quantity, the partition function.

CANONICAL PARTITION FUNCTION OF THE IDEAL GAS
(*classical*)

$$
Z(T,N,V) = \frac{V^N}{N!} \, \lambda_T^{-dN} \tag{4.12}
$$

$$
\lambda_T := \frac{h}{\sqrt{2\pi m k_B T}} \quad \text{(thermal de Broglie wavelength)} . \tag{4.13}
$$

Here we introduced the definition of the thermal de Broglie wavelength, which will be, among other things, relevant for Bose-condensation.

Free energy

Next we calculate the free energy

$$
F(T,N,V) = -k_B T \ln(Z) = -k_B T \left[N \ln \left(V \lambda_T^{-d} \right) - N \ln(N) + N \right] \, .
$$

So we have

FREE ENERGY OF AN IDEAL GAS
(*classical*)

$$
F(T,N,V) = -N \, k_B T \left[\ln \left(\frac{V}{N} \lambda_T^{-d} \right) + 1 \right] \, .
$$

The free energy is extensive and has the correct homogeneity (scaling when increasing extensive quantities by a factor λ)

Entropy

The entropy derived from the free energy yields

$$
\begin{aligned}
S &= - \left(\frac{\partial F(T,N,V)}{\partial T} \right) \Big|_{N,V} \\
&= N \ k_B \left[\ln \left(\frac{V}{N} \lambda^{-d} \right) + 1 \right] + N \ k_B T \ \frac{d}{dT} \ln(T^{d/2}) \\
&= N \ k_B \left[\ln \left(\frac{V}{N} \lambda^{-d} \right) + 1 \right] + \frac{d}{2} N \ k_B \frac{T}{T} \ .
\end{aligned}
$$

ENTROPY OF AN IDEAL GAS
(*canonical ensemble, classical*)

$$
S(T,N,V) = N \ k_B \left[\ln \left(\frac{V}{N} \lambda_T^{-d} \right) + \frac{d+2}{2} \right] \ . \qquad (4.14)
$$

This corresponds to the result, which we got for the microcanonical ensemble in equation (4.3a) [Page 91] when one considers that there, because of equation (4.4) [Page 92], $\tilde{E}$ has to be replaced by $\frac{d}{2} k_B T$.

Chemical potential

Next we will calculate the chemical potential for the canonical ensemble via equation (2.15) [Page 62]

$$
\mu = \left(\frac{\partial F(T, N, V)}{\partial N} \right) \bigg|_{T,V}
$$

$$
= -k_B T \left(\frac{\partial}{\partial N} \right) \bigg|_{T,V} \left(N \left[\ln \left(\frac{V}{N} \lambda_T^{-d} \right) + 1 \right] \right)
$$

$$
= -k_B T \left\{ \ln \left(\frac{V}{N} \lambda_T^{-d} \right) + 1 + N \underbrace{\left(\frac{\partial}{\partial N} \right) \bigg|_{T,V} \ln \left(\frac{V}{N} \lambda_T^{-d} \right)}_{=-1/N} \right\}
$$

$$
= -k_B T \left\{ \ln \left(\frac{V}{N} \lambda_T^{-d} \right) \right\}
$$

CHEMICAL POTENTIAL OF THE IDEAL GAS
(kanonical ensemble, classical)

$$
\mu = -k_B T \, \ln \left(\frac{V}{N} \lambda_T^{-d} \right)
$$

$$
= \frac{F}{N} + k_B T \, .
$$

By the way, the same result would be obtained in the frame of the micro-canonical ensemble. (exercise for you)

Internal energy

Now we shall calculate the internal energy

$$
U = F(T, V, N) + TS(T, V, N)
$$

$$
= -N \, k_B T \left[\ln \left(\frac{V}{N} \lambda_T^{-d} \right) + 1 \right] + N \, k_B T \left[\ln \left(\frac{V}{N} \lambda_T^{-d} \right) + \frac{d+2}{2} \right]
$$

$$
= \frac{3}{2} N k_B T \, .
$$

INTERNAL ENERGY OF AN IDEAL GAS
(*canonical ensemble, classical*)

$$U(T, N, V) = \frac{d}{2} N k_B T \ .$$

This is exactly the same result as for the microcanonical ensemble in equation (4.7) [Page 94]. We can use this result and insert it for the energy in the expression for the entropy and we get the Sackur-Tetrode result from equation (4.3a) [Page 91]. This confirms, that in the thermodynamic limit it does not matter which ensemble is chosen.

Energy uncertainty in the canonical ensemble

For the canonical ensemble the temperature and not the energy is fixed. We just calculated the average energy (internal energy). Now we want to calculate the variance of the energy in the canonical ensemble. For this we can use the derivative of the internal energy with respect to β.

$$-\frac{\partial}{\partial \beta} \frac{\operatorname{tr}\left\{\mathrm{H}e^{-\beta \mathrm{H}}\right\}}{\operatorname{tr}\left\{e^{-\beta \mathrm{H}}\right\}} = \frac{\operatorname{tr}\left\{\mathrm{H}^2 e^{-\beta \mathrm{H}}\right\}}{\operatorname{tr}\left\{e^{-\beta \mathrm{H}}\right\}} + \frac{\operatorname{tr}\left\{\mathrm{H}e^{-\beta \mathrm{H}}\right\}}{(\operatorname{tr}\left\{e^{-\beta \mathrm{H}}\right\})^2}\left(\frac{\partial}{\partial \beta}\operatorname{tr}\left\{e^{-\beta \mathrm{H}}\right\}\right)$$

$$= \langle H^2 \rangle - \langle H \rangle^2$$

$$\Rightarrow \qquad \sigma_E^2 := \langle (\Delta H)^2 \rangle = -\left(\frac{\partial U(T, N, V)}{\partial \beta}\right)\bigg|_{N,V}$$

The variance of the energy of an ideal classical gas yields

$$\sigma_E^2 = -\frac{\partial}{\partial \beta}\frac{dN}{2\beta} = \frac{dN}{2\beta^2}$$

$$\sigma_E = \sqrt{\frac{dN}{2}} k_B T$$

$$\Rightarrow \qquad \frac{\sigma_E}{\langle E \rangle} = \frac{\sqrt{\frac{dN}{2}} k_B T}{\frac{dN k_B T}{2}} = \sqrt{\frac{2}{dN}} \ .$$

As was shown universally, the relative uncertainty vanishes for an increasing number of particles proportional to $1/\sqrt{N}$.

4.1.5 Grand canonical ensemble

Partition function

The partition function of the grand canonical ensemble is aquried from the canonical partition function by summing over the number of particles with the weight z^N.

$$Z(T, \mu, V) = \sum_{N=0}^{\infty} z^N \, Z(T, N, V) \tag{4.15}$$

$$= \sum_N z^N \, \frac{(V\lambda_T^{-d})^N}{N!} \, . \tag{4.16}$$

PARTITION FUNCTION OF THE IDEAL GAS
(*grand canonical ensemble, classical*)

$$Z(T, \mu, V) = \exp\left(V z \lambda_T^{-d}\right) \, .$$

Grand canonical potential

From this follows

GRAND CANONICAL POTENTIAL OF THE IDEAL GAS
(*classical*)

$$\Omega(T, \mu, V) = -k_B T \ln(Z) = -k_B T z V \, \lambda_T^{-d} \, .$$

The average number of particles is

$$\langle N \rangle = -\left(\frac{\partial \Omega(T, \mu, V)}{\partial \mu}\right)\bigg|_{T,V}$$

$$= k_B T V \lambda_T^{-d} \, \underbrace{\frac{\partial z}{\partial \mu}}_{z\beta} = V z \lambda_T^{-d} \, .$$

Or rather the average density

$$\left\langle \frac{N}{V} \right\rangle = (\frac{2\pi m k_B}{h^2})^{\frac{d}{2}} \, e^{\beta \mu} \, T^{\frac{d}{2}}$$

Do the dependences on μ and T make sense?

Pressure

From the universally valid formula $\Omega = -pV$ we conveniently get the pressure

---

PRESSURE OF THE IDEAL GAS
(*grand canonical ensemble, classical*)

$$p = k_B T z \, \lambda_T^{-d} \, . \tag{4.17}$$

Thus, the average number of particles can also be expressed by

$$\langle N \rangle = V p \beta$$

This in turn corresponds to the ideal gas law, we derived in the frame of the microcanonical ensemble in equation (4.5) [Page 93]. This proves that the average number of particles of the large canonical ensemble is equal to the fixed number of particles of the microcanonical ensemble, if the other variabels are the same.

Distribution of the numbers of particles

We now want to determine the distribution P_N of the numbers of particles for the grand canonical ensemble. For this we once more consider the expression for the average of the number of particles, but this time in a slightly different

form.

$$
\begin{aligned}
\langle N \rangle &= - \left(\frac{\partial \Omega}{\partial \mu} \right) \bigg|_{T,V} \\
&= k_B T \frac{1}{Z(T,\mu,V)} \left(\frac{\partial Z(T,\mu,V)}{\partial \mu} \right) \bigg|_{T,V} \\
&= k_B T \frac{1}{Z(T,\mu,V)} \sum_{N=0}^{\infty} Z(T,N,V) \frac{\partial}{\partial \mu} z^N \\
&= k_B T \frac{1}{Z(T,\mu,V)} \sum_{N=0}^{\infty} Z(T,N,V) \, N z^N \beta \\
&= \sum_{N=0}^{\infty} N \underbrace{\frac{Z(T,N,V)}{Z(T,\mu,V)} \, z^N}_{=P_N}
\end{aligned}
$$

$$
P_N \overset{(4.12)}{=} \frac{1}{Z(T,\mu,V)} \frac{\left(V \lambda_T^{-d} z \right)^N}{N!} \ .
$$

Together with equation (4.15) [Page 101] we get the Poisson distribution

---

DISTRIBUTION OF NUMBERS OF PARTICLES IN THE IDEAL GAS
(*grand canonical ensemble, classical*)

$$
P_N = e^{-\eta} \frac{\eta^N}{N!}
$$
$$
\eta := \langle N \rangle = V \lambda_T^{-d} z \ .
$$

This also confirms that the relative uncertainty of the particle number is proportional to $1/\sqrt{N}$.

Determination of the chemical potential

Finally, we want to determine the chemical potential

$$
\langle N \rangle \overset{(4.17)}{=} z V \lambda_T^{-d} \ ,
$$
$$
\Rightarrow \quad e^{\beta \mu} = z = \frac{\langle N \rangle}{V} \lambda_T^d \ .
$$

4.1.6   Velocity distribution

We will calculate the velocity distribution of an ideal classical gas for three dimensions. They are confined to a cuboid with a constant potential. We shall use the canonical ensemble. Then the probability density in phase space can be split into the contributions of the individual particles and is also independent from the spatial coordinates.

$$p(\pi|N,V,T) = \frac{1}{Z}\,e^{-\beta H(\pi)} = \prod_{i=1}^{N} p_0(\vec{p}_i^{\,2})\ ,$$

$$p_0(\vec{p}) := \left(\frac{1}{2\pi m k_B T}\right)^{3/2} e^{-\frac{\vec{p}_i^{\,2}}{2mk_B T}}\ .$$

We now pick a particle at random and determine the probability density of its momentum $p(\vec{p})$. We marginalize over phasespace of all other particles and and over the spatial coordinates of the chosen particle and obtain

$$p(\vec{p}) = p_0(\vec{p})\ .$$

By considering the relation $\vec{p} = m\vec{v}$ and also transforming to spherical coordinates we get

$$p(\vec{v})d^3v = p_0(m\vec{v})d^3p = p_0(m\vec{v})m^3 d^3v$$

$$= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\frac{m\,\vec{v}^2}{2k_B T}}\ d^3v$$

$$= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\frac{m\,v^2}{2k_B T}}\ v^2\ \sin(\theta)\ dv d\theta d\phi\ .$$

So we have

MAXWELL VELOCITY DISTRIBUTION IN SPHERICAL COORDINATES

$$p(v,\theta,\phi) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2\, e^{-\frac{m}{2k_B T}\,v^2}\ \sin(\theta)\ . \qquad (4.18)$$

If we are only interested in the absolute value of the velocity, we can marginalise

the angular parts as well

$$p(v) = \int p(v, \theta, \phi) d\theta d\phi$$
$$= \frac{1}{z'} \, v^2 \, e^{-\frac{m}{2k_B T} v^2}$$

We calculate the norming constant z':

$$z' = \int_0^\infty e^{-\frac{m}{2k_B T} v^2} \, v^3 \frac{dv}{v} \; .$$

With the substitution $v = \sqrt{x 2 k_B T / m}$ we get

$$z' = \left(\frac{2k_B T}{m} \right)^{3/2} \frac{1}{2} \int_0^\infty e^{-x} x^{3/2} \frac{dx}{x}$$
$$= \left(\frac{2k_B T}{m} \right)^{3/2} \frac{1}{2} \Gamma(3/2)$$
$$= \left(\frac{2k_B T}{m} \right)^{3/2} \frac{\sqrt{\pi}}{4} = \left(\frac{2k_B T \pi}{m} \right)^{3/2} \frac{1}{4\pi} \; .$$

So we end up with

MAXWELL VELOCITY DISTRIBUTION

$$p(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 \, e^{-\frac{m}{2k_B T} v^2} \; . \tag{4.19}$$

In addition we calculate the moments of this distibution

$$\langle v^n \rangle = \frac{\int_0^\infty v^{2+n} e^{-\alpha v^2} dv}{\int_0^\infty v^2 e^{-\alpha v^2} dv}$$
$$\alpha := \frac{m}{2k_B T} \; .$$

At first we want to calculate integrals of the type

$$I_m := \int_0^\infty v^m e^{-\alpha v^2} \frac{dv}{v}$$

With the substitution $v = \sqrt{x/\alpha}$ we get

$$I_m = \frac{1}{2}\alpha^{-\frac{m}{2}} \int_0^\infty x^{\frac{m}{2}} e^{-x} \frac{dx}{x} = \frac{1}{2}\alpha^{-\frac{m}{2}} \, \Gamma(\frac{m}{2})$$

$$\int_0^\infty v^{3+n} e^{-\alpha v^2} \frac{dv}{v} = \frac{1}{2} \, (\alpha)^{-\frac{n+3}{2}} \int_0^\infty x^{\frac{n+3}{2}} e^{-x} \frac{dx}{x}$$

$$= \frac{1}{2} \, \alpha^{-\frac{n+3}{2}} \, \Gamma(\frac{n+3}{2})$$

$$\int_0^\infty v^{3+m} e^{-\alpha v^2} \frac{dv}{v} = \frac{1}{2} \, \alpha^{-\frac{m+3}{2}} \, \Gamma(\frac{m+3}{2}) \qquad\qquad (4.20)$$

Thus we have

$$\langle v^n \rangle = \frac{\alpha^{-\frac{n+3}{2}} \Gamma(\frac{n+3}{2})}{\alpha^{-\frac{3}{2}} \Gamma(\frac{3}{2})} = \alpha^{-\frac{n}{2}} \, \frac{\Gamma(\frac{n+1}{2} + 1)}{\frac{1}{2}\sqrt{\pi}} = \left(\frac{2k_B T}{m}\right)^{\frac{n}{2}} \frac{n+1}{\sqrt{\pi}} \, \Gamma(\frac{n+1}{2})$$

and in particular

$$\text{\textsc{Moments of the Maxwell distribution}}$$

$$\langle v \rangle = \left(\frac{2k_B T}{m}\right)^{\frac{1}{2}} \frac{2}{\sqrt{\pi}} \, \Gamma(1) = 4\left(\frac{k_B T}{2\pi m}\right)^{\frac{1}{2}} \qquad (4.21a)$$

$$\langle v^2 \rangle = \frac{2k_B T}{m} \frac{3}{\sqrt{\pi}} \, \Gamma(\frac{3}{2}) = \frac{3k_B T}{m} \, . \qquad\qquad (4.21b)$$

From the last equation follows

$$\frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}k_B T \, ,$$

which corresponds to the previous results.

4.1.7 Effusion

We now want to consider what happens, if there is an infinitesimally small hole in one wall of the box.
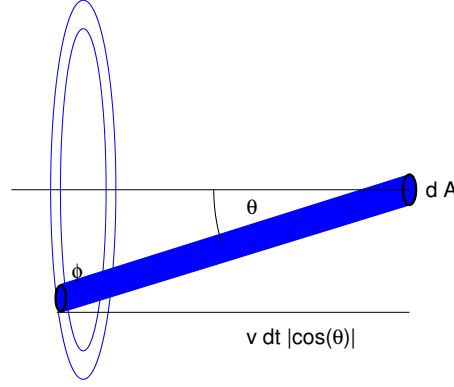
Figure 4.1: All particles within the blue cylinder, whose velocity vector is infinitesimally close to (v, θ, ϕ) will reach the infinitesimal opening dA within the time dt.

We consider the geometry depicgted in the figure. We calculate the number of particles that move through the opening within the time interval dt with an angle of θ, ϕ. For a particle to move through the hole with a velocity of (v, θ, ϕ) in $(dv, d\theta, d\phi)$ in the time dt, it has to have been in the cylindrical volume, depicted in the figure, just before that time. The cylinder has a volume of

$$dV = dA \, v \, dt \, |\cos(\theta)| \, .$$

Particles that are not within dV either are too late or they hit the wall in the wrong place. Assuming a homogenous density ρ, the total number of particles within dV is

$$dN(v, \theta, \phi) = \rho \cdot dV = \rho \cdot dA \, v \, dt \, |\cos(\theta)| \, .$$

Of all particles within the defined volume, only the ones whose velocity is within the interval $(v, v + dv), (\theta, \theta + d\theta, (\phi, \phi + d\phi)$ come through the hole. The probability density to find particles with a velocity in this infinitesimal interval is $p(v, \theta, \phi)$. Thus the number of particles whose angle and absolute value of velocity are within the given infinitesimal intervals that are hitting the wall per unit of time and area, is given by

$$
\begin{aligned}
dN(v, \theta, \phi) &= dN(v, \theta, \phi) \cdot p(v, \theta, \phi) \cdot dv d\theta d\phi \\
&= \rho \, dA \, dt \, v \, |\cos(\theta)| \cdot p(v, \theta, \phi) \cdot dv d\theta d\phi
\end{aligned}
$$

Comparison of equation (4.19) [Page 105] and equation (4.18) [Page 104] yields the following relation:

$$p(v, \theta, \phi) = p(v) \, \frac{\sin(\theta)}{4\pi} \; .$$

Therefore we get

$$\frac{d^2 N(v, \theta, \phi)}{dt dA} = \rho \, v \cdot |\cos(\theta)| \cdot p(v) \cdot \frac{\sin(\theta)}{4\pi} \cdot dv d\theta d\phi \; .$$

Within the volume now there are only particles with the stated properties. However, it is not yet defined whether the particles move towards the hole or away from it. We define the number of particles to be positive for a particle moving towards the hole and negative for the opposite case. For the so defined number of particles, which we call $\tilde{N}$, we get

$$\frac{d^2 \tilde{N}(v, \theta, \phi)}{dt dA} = \rho \, v \cos(\theta) p(v) dv \frac{d\cos(\theta) \, d\phi}{4\pi} \tag{4.22}$$

after multiplication with $\text{sign}(\cos(\theta))$. Therefore, if we position the hole as a virtual hole within the volume and integrate over all angles, we get zero. This is because the number of particles moving through the opening from one side is equal to the number of those moving in the other direction. This is different if the hole is located in the wall. Then we may integrate only over $\theta \in (0, \pi/2)$. Next we shall integrate over both angles. This yields

$$\int_0^{2\pi} d\phi \int_0^{\pi/2} \cos(\theta) d\cos(\theta) = \pi \; .$$

With this the number of particles hitting the opening per unit time and area that have the velocity $(v, d + dv)$ is given by

$$\frac{d^2 \tilde{N}(v|B)}{dt dA} = \frac{1}{4} \, \rho \, v \, p(v) dv \; . \tag{4.23}$$

Hence we can define the denstiy of the effusion rate

DENSITY OF THE EFFUSION RATE

$$\frac{d^3 \tilde{N}(v|B)}{dt \, dA \, dv} = \frac{1}{4} \, \rho \, v \, p(v) \; . \tag{4.24}$$

At the same time this is also the velocity distribution of the particles that move through the hole, respectively those that are observed directly behind the hole. Because of the additional factor v the corresponding probability density is

$$p_{\text{effusion}}(v) = \frac{1}{z} \, v^3 e^{-\frac{m}{2kT}v^2}$$

$$z = \int_0^\infty v^3 e^{-\alpha v^2} dv = \frac{1}{2} \int_0^\infty v^2 e^{-\alpha v^2} d(v^2)$$

$$= \frac{1}{2} \int_0^\infty x e^{-\alpha x} dx$$

$$= \frac{1}{2} \left(-\frac{\partial}{\partial \alpha} \right) \int_0^\infty e^{-\alpha x} dx = \frac{1}{2} \left(-\frac{\partial}{\partial \alpha} \right) \frac{1}{\alpha} = \frac{1}{2\alpha^2}$$

$$z = \frac{1}{2\alpha^2} = \frac{1}{2} \left(\frac{2kT}{m} \right)^2 .$$

$$\text{\scshape Velocity distribution for effusion}$$

$$p_{\text{effusion}}(v) = \frac{m^2}{2(kT)^2} \, v^3 e^{-\frac{m}{2kT}v^2}$$

Outflow velocity

This results in the average outflow velocity

$$\langle v \rangle_{\text{effusion}} = \frac{\int_0^\infty v^4 e^{-\alpha v^2} dv}{\int_0^\infty v^3 e^{-\alpha v^2} dv}$$

$$\overset{(4.20)}{=} \frac{\alpha^{-\frac{5}{2}} \Gamma(\frac{5}{2})}{\alpha^{-\frac{4}{2}} \Gamma(\frac{4}{2})} = \alpha^{-\frac{1}{2}} \frac{3\sqrt{\pi}}{4}$$

$$= \frac{3\sqrt{\pi}}{4} \left(\frac{2k_B T}{m} \right)^{\frac{1}{2}} .$$

$$\langle v \rangle = 4 \left(\frac{k_B T}{2\pi m} \right)^{\frac{1}{2}} :$$

Only the numeric prefactor differs. Interestingly, this is dependent on $1/\sqrt{m}$.
This dependence is called *Graham's law*. It is used technically, for example
for uranium enrichment.

We compare that result to the mean velocity inside the box (discussed above)

Rate of effusion

Finally we will calculate the rate of effusion, i.e. calculate the number of
particles leaving the volume per unit of time and area (not regarding veloc-
ity). For this we only need to integrate the density of the rate of effusion in
equation (4.24) [Page 108] over all velocities, which yields

$$\frac{d^2\tilde{N}(A)}{dAdt} = \frac{1}{4}\,\rho\,\langle v \rangle$$

Where $\langle v \rangle$ is the average of the absolute value of the velocity of the fluid
as it flows out. In retrospect, the structure of the result is trivial, because
on the left side is the number of particles per unit time and area, and thus
the current density. The product of velocity and particle density is a current
density too.

As was already mentioned, $\langle v \rangle$ is the average of the Maxwell distribution
from equation (4.19) [Page 105]. This was stated in equation (4.21) [Page
106]. Hence the average number of particles leaving the box per unit of time
and area is

RATE OF EFFUSION

$$\frac{d^2\tilde{N}(A)}{dAdt} = \rho\left(\frac{k_B T}{2\pi m}\right)^{\frac{1}{2}}. \qquad (4.25)$$

This law was also discovered by Thomas Graham.

Pressure

On a microscopic level, pressure is generated by the collisions of the particles
with the walls. When a particle is reflected at a wall that is perpendicular to
the x-direction, then its x-component changes from p_x to $-p_x$. This yields a
change in momentum of

$$\Delta\vec{p} = -2p_x\vec{e}_x . \qquad (*)$$

Per collision of a particle with an absolute value of velocity of $(v, v + dv)$ hitting at an angle of $(\theta, \theta + d\theta)$ the momentum transfer to the wall is

$$\Delta p_x(v, \theta) = 2mv \cos(\theta) .$$

This momentum transfer is independent of the angle ϕ. In equation (4.22) [Page 108] we stated the number of particles that hit the area dA per unit of time and area with a velocity that is contained within the infinitesimal volume $dv d\theta d\phi$ at (v, θ, ϕ):

$$\frac{d^2 \tilde{N}(v, \theta, \phi)}{dt dA} = \rho \, v \cos(\theta) p(v) dv \frac{d \cos(\theta) \, d\phi}{4\pi} .$$

Each of those particles transfers the momentum (*). Therefore the total momentum transfer per unit of time and area of all particles that hit the area dA within the time dt is

$$
\begin{aligned}
\frac{d^2 \Delta p_x}{dA dt} &= \int_0^\infty dv \int_0^{\pi/2} d\theta \int_0^{2\pi} d\phi \left[2mv \cos(\theta) \right] \rho \, v \cos(\theta) p(v) dv \frac{d \cos(\theta) \, d\phi}{4\pi} \\
&= \frac{2m \, 2\pi \, \rho}{4\pi} \int_0^\infty dv \, v^2 \, p(v) \underbrace{\int_0^{\pi/2} d\phi \, \cos(\theta)^2 \, d \cos(\theta)}_{= \int_0^1 \xi^2 d\xi = 1/3} \\
&= \frac{m\rho}{3} \int_0^\infty dv \, v^2 \, p(v) = \frac{m\rho}{3} \langle v^2 \rangle .
\end{aligned}
$$

According to the second and third Newtonian axiom the change of momentum per unit of time corresponds to the force that the particles exert on the wall when they collide with it. In turn this is correlated with the pressure p via $p = dF/dA$. We therefore have

$$p = \frac{dF}{dA} = \frac{d^2 \Delta p_x}{dA \, dt} = \frac{m\rho}{3} \langle v^2 \rangle .$$

We have already calculated the average $\langle v^2 \rangle$ in equation (4.21) [Page 106], getting $\langle v^2 \rangle = \frac{3}{m} k_B T$ as the result. So we finally have again the ideal gas law

$$p = \rho k_B T = \frac{N}{V} k_B T$$
$$pV = N k_B T .$$

4.2   Bohr Van-Leeuwen theorem

We will now discuss non-interacting charged particles in a static electro-magnetic magnetic field. The Hamilton function is

$$H = \sum_{i=1}^{N} \frac{1}{2m}\left(\vec{p}_i - \frac{q_i}{c}\vec{A}(\vec{x}_i)\right)^2 + V(\mathbf{x}) \,,$$

with $V(x)$ as the scalar potential, which dependson the locations of the particles. The dependence on the magnetic field originates from the vector potential $\vec{A}$. The canonical partition function is

$$Z(T,N,V,B) = \frac{1}{h^{\mathcal{N}}N!}\int d^{\mathcal{N}}x \; e^{-\beta V(\mathbf{x})} \underbrace{\int d^{\mathcal{N}}p \; e^{-\beta\sum_{i=1}^{N}\frac{1}{2m}\left(\vec{p}_i - \frac{q_i}{c}\vec{A}(\vec{x}_i)\right)^2}}_{:=I_p}.$$

With the substitution

$$\vec{p}_i - \frac{q_i}{c}\vec{A}(\vec{x}_i) := \vec{z}_i$$

the integral over the momenta

$$I_p = \int d^{\mathcal{N}}z \; e^{-\beta\sum_{i=1}^{N}\frac{1}{2m}\vec{z}_i^{\,2}}$$

becomes a quantity that is independent of the magnetic field. From the partition function we get the magnetisation via

$$\langle M \rangle = k_B T \nabla_B \ln(Z) = 0 \,.$$

This yields the astonishing result that, with no dependence on the applied magnetic field, the magnetisation is always zero.

For purely classical considerations the magnetisation is zero, without any dependence on the magnetic field.
Magnetism is a quantum mechanical effect.
This is the Bohr van-Leeuwen theorem.
An additional important contribution to magnetism is the electronic spin, which obviously is an quantum effect as well

4.3   Solid spheres (Derivation supplementary)

Until now we did not consider the interactions between the particles. We will now change that. A simple classical model for this is the free gas of

spherical particles. Here the particles are able to interact with each other and the walls of the container via collision. This model played an important role in the developement of statistical physics.

The container is of volume V and the particles have their *own volume* of V_K. Additionally we also define $v := V/V_K \gg 1$. There shall be N spherical particles of the radius σ. The Hamilton function consists of the cinetic energy $T(\vec{p})$ and the potential energy $V(\vec{x})$.

$$T(\vec{p}) = \frac{1}{2m}\vec{p}^2$$

$$V(\vec{x}) = \begin{cases} 0 & \text{in case all distances between couples are greater than } 2\sigma \\ \infty & \text{otherwise} \end{cases}$$

The canonical partition function then is

$$Z = \int e^{-\beta T(\vec{p}) - \beta V(\vec{x})} \, \mathcal{D}_\pi^\mathcal{N} = \underbrace{\frac{1}{h^\mathcal{N} N!} \left(\int e^{-\beta T(\vec{p})} d^\mathcal{N}p \right)}_{Z_p} \underbrace{\left(\int e^{-\beta V(\vec{x})} d^\mathcal{N}x \right)}_{Z_x} .$$

The first contribution is already known from equation (4.12) .

$$Z_p(T, N, V) = \frac{1}{N!} \, \lambda_T^{-\mathcal{N}} .$$

We then proceed to calculate the contribution of the spatial integration, which yielded V^N for dot-like particles. At first we only need one dimension for this. In any case, the center of each particle is constrained to an interval $(\sigma, L - \sigma)$. We then define two auxiliary functions

$$\Theta(x) = \begin{cases} 1 & \text{if:} \quad |x_i - x_j| \geq 2\sigma \qquad \forall i, j \\ 0 & \text{else} \end{cases}$$

$$O(x) = \begin{cases} 1 & \text{if:} \quad x_1 \leq x_2 \ldots \leq x_N \\ 0 & \text{else} \end{cases} .$$

The contribution of the spatial integration to the partition function is

$$Z_x = \int e^{-\beta V(\vec{x})} d^N x = \int_\sigma^{L-\sigma} \ldots \int_\sigma^{L-\sigma} \Theta(x) d^N x$$

$$= \int_\sigma^{L-\sigma} \ldots \int_\sigma^{L-\sigma} \Theta(x) \underbrace{\left(\sum_P O(Px) \right)}_{=1} d^N x ,$$

summing over all permutations. However, to each configuration x only the permutation P with $O(Px) = 1$ contributes.

$$Z_x = \sum_P \int_\sigma^{L-\sigma} \cdots \int_\sigma^{L-\sigma} \Theta(x)O(Px)d^N x$$

$$\overset{y=Px}{=} \sum_P \int_\sigma^{L-\sigma} \cdots \int_\sigma^{L-\sigma} \Theta(P^{-1}y)O(y)d^N P^{-1}y$$

$d^N x$ as well as $\Theta(x)$ are invariant to renumbering of the variables of integration, i.e. $d^N P^{-1}y = d^N y$ and $\Theta(P^{-1}y) = \Theta(y)$. Therefore the following applies:

$$Z_x = \sum_P \int_\sigma^{L-\sigma} \cdots \int_\sigma^{L-\sigma} \Theta(y)O(y)d^N y$$

$$= N! \int_\sigma^{L-\sigma} dy_1 \int_{y_1+2\sigma}^{L-\sigma} dy_2 \cdots \int_{y_{N-1}+2\sigma}^{L-\sigma} dy_N .$$

The functions Θ and O have been considered for the integration borders. On the right side of the particle k there is are $N - k$ particles, occupying a volume of $2\sigma(N - k)$ (figure). Considering the radius of the kth sphere we
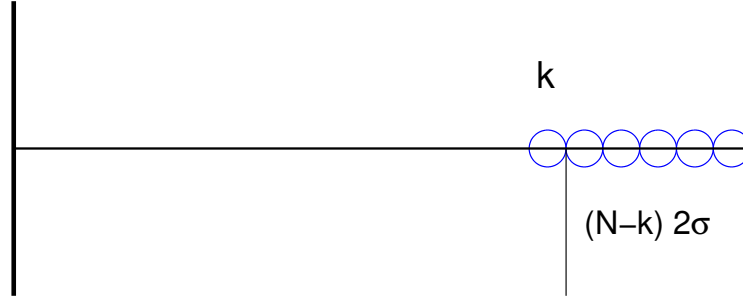
Figure 4.2: On the right side of the sphere k there are $N - k$ spheres that when lined up have a length of $(N - k)2\sigma$.

get

$$x_k \leq L - (2\sigma(N - k) + \sigma) = L - 2N\sigma + \sigma(2k - 1) .$$

Therefore we can further simplify Z_x to

$$Z_x = N! \int_\sigma^{L-2\sigma N+\sigma(2-1)} dy_1 \cdots \int_{y_{k-1}+2\sigma}^{L-2\sigma N+\sigma(2k-1)} dy_k \cdots \int_{y_{N-1}+2\sigma}^{L-2\sigma N+\sigma(2N-1)} dy_N .$$

Finally we substitute $y_k = x_k + (2k-1)\sigma$. This means that the integration borders for y_k transition from

$$y_k \in \left(y_{k-1} + 2\sigma, L - 2N\sigma + (2k-1)\sigma \right)$$

to

$$x_k \in \left(y_{k-1} + 2\sigma - (2k-1)\sigma, L - 2N\sigma + (2k-1)\sigma - (2k-1)\sigma \right)$$

$$\in \left(\underbrace{y_{k-1} - (2(k-1)-1)\sigma}_{x_{k-1}}, L - 2N\sigma \right) .$$

With this the integrals can be simplified even further.

$$Z_x = N! \int_0^{L-2\sigma N} dx_1 \ldots \int_{x_{k-1}}^{L-2\sigma N} dx_k \ldots \int_{x_{N-1}}^{L-2\sigma N} dx_N .$$

For the new variables of integration the following applies: $0 \le x_1 \le x_2 \le \ldots \le L - 2\sigma N$. We can choose the same integration interval $(0, L - 2\sigma N)$ for all integrals, if we introduce the $O(x)$ to enforce the correct order. This yields

$$Z_x = N! \int_0^{L-2\sigma N} \ldots \int_0^{L-2\sigma N} O(x) \, d^N x .$$

In addition we introduce the sum over the permutations

$$Z_x = \sum_P \int_0^{L-2\sigma N} \ldots \int_0^{L-2\sigma N} O(Px) \, d^N Px$$

$$= \int_0^{L-2\sigma N} \ldots \int_0^{L-2\sigma N} \underbrace{\left(\sum_P \Theta(Px) \right)}_{=1} d^N x$$

$$= \int_0^{L-2\sigma N} \ldots \int_0^{L-2\sigma N} d^N x = (L - \underbrace{2\sigma}_{:=L_0} N)^N$$

SPATIAL COMPONENT OF THE PARTITION FUNCTION

$$Z_x = (L - N L_0)^N := V_{\text{eff}}^N .$$

This means, that in one dimension the own volume of the particles is reduced to the volume $V \to V_{\text{eff}} = V - V_0$ that is available for the partition function. The partition function therefore reads as follows:

PARTITION FUNCTION

$$Z(T, N, V) = \frac{V_{\text{eff}}^N}{N!} \lambda_T^{-N} .$$

When generalising the result to arbitrary numbers of dimensions, we formally have the same result as for dot-like particles. Therefore the free energy is, as always,

$$F = -N k_B T \left[\ln \left[\frac{V_{\text{eff}}}{N} \lambda_T^{-3} \right] + 1 \right] .$$

From this the pressure is calculated as follows:

$$p = - \left(\frac{\partial F(T, N, V)}{\partial V} \right) \Bigg|_{T,N}$$

$$= N k_B T \left(\frac{\partial \ln(V_{\text{eff}})}{\partial V} \right) \Bigg|_{T,N} = N k_B T \frac{1}{V_{\text{eff}}} \frac{\partial V_{\text{eff}}}{\partial V}$$

$$= \frac{N k_B T}{V_{\text{eff}}} ,$$

$$p V_{\text{eff}} = N K_B T .$$

Concerning the effective volume, this corresponds to the van-der-Waals function fo state, which actually reads as follows:

VAN-DER-WAALS FUNCTION OF STATE

$$p_{\text{eff}} V_{\text{eff}} = N k_B T . \tag{4.26}$$

The effective pressure is one that is increased by the interaction between particles. However, the simple model, which we discussed here does not consider this interaction.
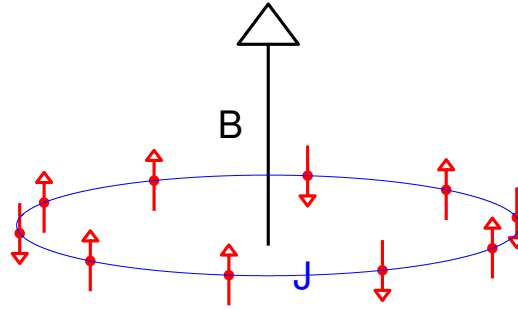
Figure 4.3: *Arrangement of the Ising spins as a chain with periodical boundary conditions*

4.4 The Ising model

We will now discuss collective magnetism. The simplest model for this is the Ising model, which is defined by the following Hamilton:

$$H = -J \sum_{\langle i,j \rangle} s_i s_j - \mu B \sum_i s_i \ ,$$

Here the spins s_i can only assume the values $s_i = \pm 1$. J is the exchange interaction and the sum is constrained to those indices, for which $\vec{x}_i$ and $\vec{x}_j$ are directly neighbouring lattice points. Here μ is the magnetic moment, not the chemical potential and B is the magnetic flux density. This model is also used to describe binary alloys. For that, however, the parameters have a different meaning. Only in 1d and 2d the Ising model can be solved exactly. In $2d$ it even yields a phase transition. However, the solution of the 2d problem cannot be discussed within the time frame of this lecture. Therefore we will only discuss the 1d case. For periodic boundary conditions[1] the Hamilton function is

$$H = -J \sum_{i=1}^{N} s_i s_{i+1} - \frac{\mu B}{2} \sum_i (s_i + s_{i+1})$$

(pbc): $\qquad s_{i+N} = s_i \ .$

---

[1]As a general rule, in the thermodynamic limit the boundary conditions are irrelevant.

Canonical partition function

For the canonical ensemble the evaluation is especially easy. In that case the partition function is

$$Z(T, N, B) = \sum_{\{s_i\}=\pm 1} e^{\beta J \sum_i s_i s_{i+1} + \frac{\mu \beta B}{2} \sum_i (s_i + s_{i+1})}$$

$$= \sum_{\{s_i\}=\pm 1} \prod_{i=1}^{N} e^{j s_i s_{i+1} + \frac{b}{2}(s_i + s_{i+1})} .$$

Here the abbreviations $j = \beta J$ and $b = \mu \beta B$ were introduced. With the definition of the **transfer matrix**

$$M_{s,s'} := e^{j\,ss' + \frac{b}{2}(s+s')}$$

with the matrix elements $\quad M_{s,s'} = $

$s \backslash s'$	$+1$	-1
$+1$	e^{j+b}	e^{-j}
-1	e^{-j}	e^{j-b}

we have: $\quad Z(T, N, B) = \sum_{\{s_i\}=\pm 1} \prod_{i=1}^{N} M_{s_i, s_{i+1}} .$

Let us first consider the case of $N = 2$, for which the partition function is

$$Z(T, N = 2, B) = \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} M_{s_1,s_2} \, M_{s_2,s_1} = \sum_{s_1} \left(M^2 \right)_{s_1,s_1} = \text{tr} \left\{ M^2 \right\}$$

The generalization should now be obvious

$$Z(T, N, B) = \text{tr} \left\{ M^N \right\} .$$

The transfer matrix is real and symmetric. It can be expressed in spectral representation as

$$M = U D U^\dagger ,$$

with U being the unitary matrix of the eigenvectors and D being the diagonal matrix of the eigenvalues d_1, d_2. Then we get

$$Z(T, N, B) = \text{tr} \left\{ M^N \right\} = \text{tr} \left\{ (U D U^\dagger)^N \right\} = \text{tr} \left\{ U D^N U^\dagger \right\} = \text{tr} \left\{ D^N \right\}$$
$$= d_1^N + d_2^N .$$

The eigenvalues of the transfer matrix are

$$d_{1/2} = \frac{e^{j+b} + e^{j-b}}{2} \pm \sqrt{\left(\frac{e^{j+b} - e^{j-b}}{2} \right)^2 + e^{-2j}}$$

$$= e^j \left(\cosh(b) \pm \sqrt{\sinh^2(b) + e^{-4j}} \right)$$

Using $d_1 > d_2$ in the calculation of the partition function, in the thermodynamic limit we get

$$Z(T, N, B) = d_1^N \left[1 + \left(\frac{d_2}{d_1} \right)^N \right] .$$

Free energy

The free energy then is

$$F(T, N, B) = -k_B T \ln\left[Z(T, V) \right] = -k_B T N \ln(d_1) - k_B T \ln \left[1 + \underbrace{\left(\frac{d_2}{d_1} \right)^N}_{\to 0} \right]$$

$$= -N k_B T \ln(d_1) .$$

Magnetisation

The magnetisation is defined as

$$M = \mu \left\langle \sum_i s_i \right\rangle .$$

Comparison with the partition sum immediately shows the following:

$$M = \frac{1}{\beta} \left(\frac{\partial \ln(Z)}{\partial B} \right) \bigg|_{T,N} = - \left(\frac{\partial F}{\partial B} \right) \bigg|_{T,N}$$

$$= -\mu\beta \left(\frac{\partial F}{\partial b} \right) \bigg|_{T,N}$$

$$= -\mu\beta(-k_B T N) \left(\frac{\partial \ln(d_1)}{\partial b} \right) \bigg|_{T,N}$$

$$= N\mu \frac{\frac{\partial d_1}{\partial b}}{d_1} = N\mu \frac{\sinh(b) + \frac{\sinh(b)\cosh(b)}{\sqrt{\sinh^2(b) + e^{-4j}}}}{\cosh(b) + \sqrt{\sinh^2(b) + e^{-4j}}}$$

$$= N\mu \sinh(b) \frac{1 + \frac{\cosh(b)}{\sqrt{\sinh^2(b) + e^{-4j}}}}{\cosh(b) + \sqrt{\sinh^2(b) + e^{-4j}}}$$

$$= N\mu \frac{\sinh(b)}{\sqrt{\sinh^2(b) + e^{-4j}}} \frac{\sqrt{\sinh^2(b) + e^{-4j}} + \cosh(b)}{\cosh(b) + \sqrt{\sinh^2(b) + e^{-4j}}} .$$

<div style="text-align: center">

MAGNETISATION OF THE 1D ISING MODEL

$$M(T, N, B) = N\mu \frac{\sinh(\mu\beta B)}{\sqrt{\sinh^2(\mu\beta B) + e^{-4J\beta}}} \ .$$

</div>

Paramagnet

Without interaction of the magnetic moments – $J = 0$ – we get

$$M(T, N, B) = N\mu \frac{\sinh(\mu\beta B)}{\sqrt{\sinh^2(\mu\beta B) + 1}} = N\mu \tanh(\mu\beta B) \ ,$$

which is the well known result for a paramagnet.

Order of the limits

There is a dependence on the order in which we take the limits. If we at first choose $B \to 0$ (and then $T \to 0$),we get a vanishing magnetisation:

$$M(T, N, B = 0) = 0$$

On the other hand, if we choose $B > 0$ and let T go to zero, i.e. $\beta \to \infty$, we get

$$M(T, B \neq 0) = N\mu \frac{\sinh(\mu\beta B)}{\sqrt{\underbrace{\sinh^2(\mu\beta B)}_{\gg 1} + \underbrace{e^{-4J\beta}}_{\ll 1}}}$$

$$\xrightarrow[T \to 0]{} N\mu \operatorname{sign}(B) \ .$$

In this limit we get perfect alignment of all spins, even for B going to zero. The 1d Ising model has a kind of phase transition at $T = 0$.

Magnetisation curve

We choose the interaction coupling J as the unit of energy. Then only $k_B T$ and $\tilde{B} := \mu B$ remain as independent paramaters. We now plot the magnetisation as a function of $\tilde{B}$.
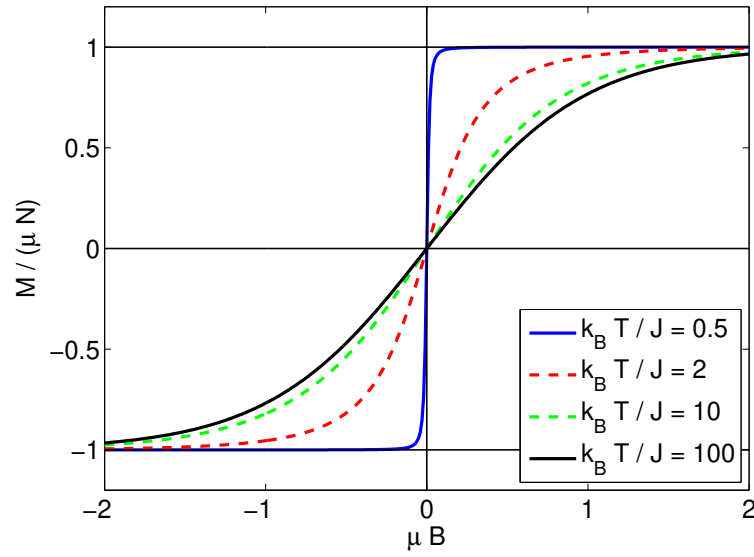
Figure 4.4: Magnetisation curve of the 1d Ising model.

On the basis of the comparison with the result for the paramgnet we see that the influence of the interaction increases the absolute value of the magnetisation everywhere. For low temperatures the magnetisation abruptly changes into the totally polarised state.

Chapter 5

Quantum statistics

5.1   Introduction

In quantum statistics now also the characteristics of quantum mechanics have
to be taken into account. There are dynamical variables of an object, which
are incompatible with each other (as for example location and momentum or
L_x and L_y) and for which the object cannot have assigned values at the same
time. This may be because the **object itself** is not a particle with location
and momentum in the classicle sense anymore, or because location and mo-
mentum are altogether senseless in the quantum mechanical dimension, or
that it is impossible to measure these quantities without disturbing the sys-
tem. This, of course, makes the concept of phase space obsolete. However,
even with constraining to one dynamic variable, e.g. to the spatial coordi-
nate of the particles, on a quantum level one has to give up determinism.
Normally one cannot predict the outcome of an experiment with absolute
certainty, but one can only describe the state by means of probability ampli-
tudes for which however the time behaviour can be calculated. It still goes
on: The many particle state cannot be described by the spatial coordinates
of the single particles anymore. Interacting particles lose their identity and
usually form a collective probability density that does not factorise.
At best we can specify the state vector $|\Psi\rangle$ of a system after a measurement.
From this vector we can calculate the probability that in a future measure-
ment of an observable one of the possible eigenvalues will be measured. This
pure state can be described by the density operator

$$\hat{\rho} = |\Psi\rangle\langle\Psi|$$

Although we are already only dealing with probabilities here, we assume that
we can determine the initial vector of the many-particle system and are able
to make unambiguous predictions for the state vector at a later time. This is

possible when there are only a few particles to consider. This corresponds to the situation in analytical mechanics, where we can make exact statements about the initial conditions. As in classical statistical mechanics, also in quantum statistics the situation changes drastically if a macroscopic number of particles is involved. In classical statistical mechanics we introduced the probability density $p(\pi)$ for the system to be at the phase space point π. The quantum mechanical equivalent to a phase space points is the pure state. The generalization that also includes probabilities for the pure states is the density operator $\hat{\rho}$ with the following characteristics

- $\hat{\rho}$ it is Hermitian:

  - $\hat{\rho}^\dagger = \hat{\rho} \Rightarrow$

  - real eigenvalues p_i

  - complete set of orthonormal eigenvectors

- Eigenvalues are probabilities:

  - $0 \leq p_i \leq 1$

  - $\sum_i p_i = 1$

  - $\Rightarrow \operatorname{tr}\{\hat{\rho}\} = 1$

- pure (coherent) states $\hat{\rho} = |\psi\rangle\langle\psi|$

- mixed (incoherent) states $\hat{\rho} = \sum_i p_i |\psi_i\rangle\langle\psi_i|$

  - $|\psi_i\rangle$ shall be orthonormal vectors

  - then they also are the eigenvectors of $\hat{\rho}$ with an eigenvalue p_i.

QUANTUM STATISTICAL DENSITY OPERATOR

$$\hat{\rho} = \sum p_i |\psi_i\rangle\langle\psi_i| \ .$$

THERMODYNAMIC EXPECTATION VALUES
(of an observable O)

$$\langle O \rangle = \text{tr} \left\{ \hat{\rho} \, \hat{O} \right\} .$$

So far, everything only concerns the description of a quantum state at a fixed point in time, e.g. preparation. At a later time, the density operator is a consequence of the Schrödinger equation

TIME EVOLUTION OF THE DENSITY OPERATOR

$$i\hbar \frac{\partial \hat{\rho}(t)}{\partial t} = [\hat{H}, \hat{\rho}(t)] ,$$

with $\hat{H}$ being the Hamiltonian of the system.

Baes on the probabilities p_i we define the Gibbs entropy

$$S := -k_B \sum_i p_i \, \ln(p_i) . \tag{5.1}$$

As p_i are the eigenvalues of $\hat{\rho}$ the quantum entropy can be expressed as follows:

QUANTUM ENTROPY

$$S := -k_B \text{tr} \left\{ \hat{\rho} \ln(\hat{\rho}) \right\} .$$

5.2   Ensembles

The Correspondence-Principle then yields the density matrix for the previously discussed ensembles

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DENSITY OPERATOR FOR THE MICROCANONICAL ENSEMBLE

$$\hat{\rho}_E^{mkG} = \frac{1}{Z(E,N,V)} \begin{cases} \delta_{E,\hat{H}} \; ; & \text{discrete spectrum} \\ \delta(E - \hat{H}) \; ; & \text{continuous spectrum} \end{cases}$$

$$Z(E,N,V) = \begin{cases} \text{tr}\left\{\delta_{E,\hat{H}}\right\} \; ; & \text{discrete spectrum} \\ \text{tr}\left\{\delta(E - \hat{H})\right\} \; ; & \text{continuous spectrum} \end{cases}$$

$$S(E,N,V) = -k_B \text{tr}\left\{\hat{\rho}\ln(\hat{\rho})\right\} = k_B \ln\left[Z(E,N,V)\right] \; .$$

DENSITY OPERATOR FOR THE CANONICAL ENSEMBLE

$$\hat{\rho}_T^{kG} = \frac{1}{Z(T,N,V)}\, e^{-\beta\hat{H}} \; ;$$
$$Z(T,N,V) = \text{tr}\left\{e^{-\beta\hat{H}}\right\} \; ;$$
$$F(T,N,V) = -k_B T \ln\left[Z(T,N,V)\right] \; .$$

DENSITY OPERATOR FOR THE GRAND CANONICAL ENSEMBLE

$$\hat{\rho}_T^{gkG} = \frac{1}{Z(T,\mu)}\, e^{-\beta(\hat{H}-\mu\hat{N})} \; ;$$
$$Z(T,\mu,V) = \text{tr}\left\{e^{-\beta(\hat{H}-\mu\hat{N})}\right\} \; ;$$
$$\Omega(T,\mu,V) = -k_B T \ln\left[Z(T,\mu,V)\right] \; .$$

5.3   Third law of thermodynamics

The third law of thermodynamics states that for all systems, in the limit $T \to 0$ entropy goes to a universal constant and is no longer extensive. For simplicity's sake we choose the microcanonical ensemble to compute the entropy

$$S(E, N, V) = -k_B \text{tr} \left\{ \hat{\rho}_{\text{E}}^{\text{mkG}} \ln \left[\hat{\rho}_{\text{E}}^{\text{mkG}} \right] \right\}$$
$$= k_B \ln \left[Z(E, N, V) = k_B \ln \left[\text{tr} \left\{ \delta_{\text{E}, \hat{\text{H}}} \right\} \right] \right]$$
$$= k_B \ln \left[\Gamma(E, N, V) \right] ,$$

with $\Gamma(E, N, V)$ representing the number of states of the energy E. For $T \to 0$ the internal energy becomes the energy of the ground state, E_0. Then for $T \to 0$ the entropy is given by

$$S \xrightarrow[T \to 0]{} k_B \ln \left[\Gamma(E_0 \right]$$

Entropy for $T \to 0$ is therefore given by the degeneracy of the ground state. Of course there are systems with non-degenerated ground state. For those systems entropy is zero. However, should the ground state be degenerate (as a rule this is caused by symmetries) small external perturbations, which are always present, the degeneracy will be lifted. Then for $T \to 0$ the entropy always goes to zero.

The third law of thermodynamics is also called **Nernst-Planck-Theorem**. H. Nernst had – on the basis of examinations of numerous chemical reactions – formulated thehypothesis that for $T = 0$ changes of the state of a system would not be followed by a change in entropy. Planck generalised this theorem and stated that for $T \to 0$ entropy becomes a constant that is independent from the system size and can therefore be set to be zero.

5.4   Example: Einstein-solids

5.4.1   Model

The oscillations of the atoms in a solid can be described by means of independent harmonic oscillators in three dimensions. The energy of a single oscillator is

$$E = \hbar \omega \left(n_x + n_y + n_z \right) + \frac{3}{2} \hbar \omega .$$

We shall put the zero point energy into the energy zero. As with a one-dimensional oscillator, the quantum numbers can assume the following values

$n_\alpha \in \mathcal{N}_0$. As the individual oscillators are independent their contributions to the energy add up.

$$E = \hbar\omega \underbrace{\sum_{i=1}^{\mathcal{N}} n_i}_{:=M}$$

$$E_M := \hbar\omega \, M \, ; \qquad M \in \mathcal{N}_0 \, .$$

The total energies are therefore quantised in integer multiples M of $\hbar\omega$.

5.4.2 Microcanonical ensemble

For a macroscopic energy, characterised by M, there are many microstates $\{n_i\}$. For the microcanonical ensemble we need the number Γ_M of those microstates.

Number of microstates

Therefore the goal is to distribute the total number of quanta, M, on $\mathcal{N} = 3N$ oscillators (places). The quanta are indistinguishable, however the lattice points are certainly not. Thus the task is to distribute M objects into $\mathcal{N}$ boxes. This problem was already discussed in the lecture 'Probability theory, Statistics and Data analysis'. The solution was

$$\Gamma_M = \binom{\mathcal{N} + M - 1}{M} \, .$$

Entropy

Now the number of lattice points is again macroscopically $\mathcal{N} \gg 1$. Therefore we can substitute $\mathcal{N} - 1$ by $\mathcal{N}$ and use the Stirling formula to calculate the

entropy. We assume that $M \gg 1$.

$$
\begin{aligned}
S(E_M, N) = k_B \ln(\Gamma_M) &= k_B \left(\ln\left[(\mathcal{N} - 1 + \mathrm{M})!\right] - \ln\left[(\mathcal{N} - 1)!\right] - \ln\left[\mathrm{M}!\right] \right) \\
&\approx k_B \left((\mathcal{N} + M)\ln\left[\mathcal{N} + \mathrm{M}\right] + \mathcal{N} + M - \mathcal{N}\ln\left[\mathcal{N}\right] - \mathcal{N} - M \ln M - M \right) \\
&= k_B \left((\mathcal{N} + M)\ln\left[\mathcal{N} + \mathrm{M}\right] - \mathcal{N}\ln\left[\mathcal{N}\right] - M\ln\left[\mathrm{M}\right] \right) \\
&= k_B \left((\mathcal{N} + M)\left(\ln(\mathcal{N}) + \ln\left[1 + \frac{\mathrm{M}}{\mathcal{N}}\right] \right) - \mathcal{N}\ln(\mathcal{N}) - M\ln(M) \right) \\
&= k_B \left(\overbrace{\mathcal{N}\ln(\mathcal{N})}^{(1)} + M\ln(\mathcal{N}) + (\mathcal{N} + M)\ln\left[1 + \frac{\mathrm{M}}{\mathcal{N}}\right] - \overbrace{\mathcal{N}\ln(\mathcal{N})}^{(1)} - M\ln\left[\mathrm{M}\right] \right) \\
&= k_B \left(M\ln(\mathcal{N}) + (\mathcal{N} + M)\ln\left[1 + \frac{\mathrm{M}}{\mathcal{N}}\right] - M\ln\left[\mathrm{M}\right] \right) .
\end{aligned}
$$

The expression for the entropy is therefore

$$
S(E_M, N) = k_B \mathcal{N} \left((1 + \frac{M}{\mathcal{N}})\ln\left[1 + \frac{\mathrm{M}}{\mathcal{N}}\right] - \frac{M}{\mathcal{N}}\ln\left[\frac{\mathrm{M}}{\mathcal{N}}\right] \right) . \qquad (5.2)
$$

This means that entropy is extensive, as it should be!

Temperature

Temperature in the microcanonical ensemble is defined as

$$
\begin{aligned}
\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)\Big|_{\mathcal{N}} &= \frac{1}{\hbar\omega} \left(\frac{\partial S}{\partial M} \right)\Big|_{\mathcal{N}} \\
&= \frac{k_B}{\hbar\omega} \left(1 + \ln\left[1 + \frac{\mathrm{M}}{\mathcal{N}}\right] - 1 - \ln\left[\frac{\mathrm{M}}{\mathcal{N}}\right] \right) \\
&= \frac{k_B}{\hbar\omega} \ln\left[1 + \frac{\mathcal{N}}{\mathrm{M}}\right] .
\end{aligned}
$$

> #### TEMPERATURE
> #### (*Einstein solid*)
>
> $$\beta = \frac{1}{\hbar\omega} \ln\left[1 + \frac{\mathcal{N}}{M}\right] \; ; \tag{5.3}$$
>
> $$T(E_M, N) = \frac{\hbar\omega}{k_B}\left(\ln\left[1 + \frac{\mathcal{N}}{M}\right]\right)^{-1} . \tag{5.4}$$

Internal energy

First we solve equation (5.3) for M

$$\beta\hbar\omega = \ln\left[1 + \frac{\mathcal{N}}{M}\right]$$

$$\frac{\mathcal{N}}{M} = e^{\beta\hbar\omega} - 1$$

$$M = \frac{\mathcal{N}}{e^{\beta\hbar\omega} - 1} .$$

Then the internal energy as function of temperature reads

> #### INTERNAL ENERGY
> #### (*Einstein solid*)
>
> $$E_M(T) = \frac{\mathcal{N}\hbar\omega}{e^{\beta\hbar\omega} - 1} . \tag{5.5}$$

We see that the energy is extensive, as it should be. We can now convert the entropy $S(M, \mathcal{N})$ to $S(T, \mathcal{N})$ by replacing $M/\mathcal{N}$ by $1/(e^{\gamma} - 1)$ with $\gamma = \beta\hbar\omega$.

We use equation (5.2) [Page 128]

$$
\begin{aligned}
S(T,N) &= k_B\mathcal{N}\left((1 + \frac{M}{\mathcal{N}})\ln\left[1 + \frac{M}{\mathcal{N}} \right] - \frac{M}{\mathcal{N}}\ln\left[\frac{M}{\mathcal{N}} \right] \right)\\
&= k_B\mathcal{N}\left((1 + \frac{1}{e^\gamma - 1})\ln\left[1 + \frac{1}{e^\gamma - 1} \right] + \frac{1}{e^\gamma - 1}\ln\left[e^\gamma - 1 \right] \right)\\
&= k_B\mathcal{N}\left(\frac{e^\gamma}{e^\gamma - 1}\ln\left[\frac{e^\gamma}{e^\gamma - 1} \right] + \frac{1}{e^\gamma - 1}\ln\left[e^\gamma - 1 \right] \right)\\
&= k_B\mathcal{N}\left(\frac{e^\gamma}{e^\gamma - 1}\ln\left[e^\gamma \right] - \frac{e^\gamma - 1}{e^\gamma - 1}\ln\left[e^\gamma - 1 \right] \right)\\
&= k_B\mathcal{N}\left(\frac{\gamma e^\gamma}{e^\gamma - 1} - \ln\left[e^\gamma - 1 \right] \right)\\
&= k_B\mathcal{N}\left(\frac{\gamma e^\gamma}{e^\gamma - 1} - \ln\left[e^\gamma(1 - e^{-\gamma}) \right] \right)\\
&= k_B\mathcal{N}\left(\frac{\gamma e^\gamma}{e^\gamma - 1} - \gamma - \ln\left[1 - e^{-\gamma} \right] \right)\\
&= k_B\mathcal{N}\left(\frac{\gamma}{e^\gamma - 1} - \ln\left[1 - e^{-\gamma} \right] \right).
\end{aligned}
$$

Thus we have entropy as a function of the variables T and N.

<div style="border:1px solid">

ENTROPY
(*Einstein Solid*)

$$
S(T,\mathcal{N}) = k_B\mathcal{N}\left(-\ln\left[1 - e^{-\beta\hbar\omega} \right] + \frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} \right). \qquad (5.6)
$$

</div>

5.4.3   Canonical ensemble

As a general rule it is easier to use the canonical or grand canonical ensemble, as we will see in the case of the Einstein solid. The difference is, that now the energy and therefore the total number of quanta, M, is not fixed anymore. Therefore, the quantum numbers n_i for each oscillator can assume any value between zero and infinity.

Canonical partition function

The partition function is easy to calculate

$$Z(T, \mathcal{N}) = \text{tr} \left\{ e^{-\beta \hat{H}} \right\} = \sum_{\{n_i\}} e^{-\beta \hbar \omega \sum_i n_i}$$

$$= \prod_i \left(\sum_{n_i=0}^{\infty} e^{-\beta \hbar \omega n_i} \right).$$

CANONICAL PARTITION FUNCTION
(Einstein solid)

$$Z(T, N) = \left(\frac{1}{1 - e^{-\beta \hbar \omega}} \right)^{\mathcal{N}}.$$

Free energy

Therefore the free energy is

FREE ENERGY
(Einstein solid)

$$F(T, \mathcal{N}) = -k_B T \ln(Z) = k_B T \mathcal{N} \ln \left[1 - e^{-\beta \hbar \omega} \right].$$

Entropy

Next we calculate the entropy

$$
\begin{aligned}
S(T,\mathcal{N}) &= -\left(\frac{\partial F(T,\mathcal{N})}{\partial T}\right)\bigg|_{\mathcal{N}} \\
&= -k_B\mathcal{N}\left(\ln\left[1-\mathrm{e}^{-\beta\hbar\omega}\right] + T\frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\frac{\partial\beta}{\partial T}\right) \\
&= k_B\mathcal{N}\left(-\ln\left[1-\mathrm{e}^{-\beta\hbar\omega}\right] - T\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\left(\frac{-1}{kT^2}\right)\right) \\
&= k_B\mathcal{N}\left(-\ln\left[1-\mathrm{e}^{-\beta\hbar\omega}\right] + \frac{\beta\hbar\omega}{e^{\beta\hbar\omega}-1}\right).
\end{aligned}
$$

This is the same expression as in equation (5.6) [Page 130], which we calculated in the framework of the microcanonical ensemble. For $T \to 0$, and thus $\beta \to \infty$, the entropy becomes zero. This is in agreement with the third law of thermodynamics.

5.4.4   Internal energy

From the entropy we get the internal energy

$$
\begin{aligned}
U(T,\mathcal{N}) &= -\left(\frac{\partial\ln[Z]}{\partial\beta}\right)\bigg|_{\mathcal{N}} = \mathcal{N}\left(\frac{\partial\ln\left[1-\mathrm{e}^{-\beta\hbar\omega}\right]}{\partial\beta}\right)\bigg|_{\mathcal{N}} \\
&= \mathcal{N}\frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} = \mathcal{N}\hbar\omega\frac{1}{e^{\beta\hbar\omega}-1},
\end{aligned}
$$

which is again in agreement with the result for the microcanonical ensemble equation (5.5) [Page 129].
Classically, the result is $U = \mathcal{N}k_BT$. We see, that this result is recovered for in the classical limit $\hbar\omega \ll k_BT$.

Heat capacity

Next we calculate the heat capacity

$$
\begin{aligned}
C_V &= \left(\frac{\partial U(T,\mathcal{N})}{\partial T}\right)\bigg|_{\mathcal{N}} = \left(\frac{\partial U(T,\mathcal{N})}{\partial\beta}\right)\bigg|_{\mathcal{N}}\left(-\frac{1}{k_BT^2}\right) \\
&= \mathcal{N}k_B\beta^2\hbar\omega\frac{\hbar\omega e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}.
\end{aligned}
$$

<div style="text-align: center">

HEAT CAPACITY
(*Einstein solid*)

$$C_V = \mathcal{N} k_B (\beta \hbar \omega)^2 \, \frac{e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^2} \, .$$

</div>

For low temperatures $\beta \hbar \omega \gg 1$ the heat capacity approaches zero in an exponential way, as there is a minimum excitation energy. For very high temperatures $\beta \hbar \omega \ll 1$ the heat capacity behaves as follows

$$C_V \xrightarrow[T \to \infty]{} \mathcal{N} k_B (\beta \hbar \omega)^2 \frac{1 - \beta \hbar \omega}{(1 - 1 + \beta \hbar \omega)^2} = \mathcal{N} k_B (\beta \hbar \omega)^2 \frac{1}{(\beta \hbar \omega)^2} = \mathcal{N} k_B \, .$$

This is again the result for the classical case. Finally we calculate the pressure. As the free energy is independent of the volume, the pressure vanishes

$$p = - \left(\frac{\partial F}{\partial V} \right) \bigg|_{T,N} = 0 \, .$$

This is because the centers of mass of the oscillators do not perform any translational motion.

Chapter 6

Identical non-interacting quantum systems particles

For identical non-interacting quantumparticles numerous properties can be calculated analytically. Here it is crucial, that the Hamiltonian is a sum of single particle operators, which only differ in their particle index.

$$\hat{H}_N = \sum_{\nu=1}^{N} \hat{H}_\nu \ .$$

This operator describes, for example, a quantum mechanical particle within an external potential $V(x)$. The Hamiltonian therefore is

$$H_\nu = \frac{\hat{p}_\nu^2}{2m} + V(\hat{x}_\nu) \ .$$

$\hat{p}_\nu$ and $\hat{x}_\nu$ are momentum and position operator of the νth particle. Apart from the particle index all Hamiltonians are identical and therefore also have the same eigenvalues ε_i.

6.1 Distinguishable particles

For distinguishable particles it is possible to determine, which particle is in which eigenstate. The state vector

$$|i_1, \ldots, i_N\rangle$$

then gives the eigenstates in which the individual particles are. The total energy is then the sum over all particlest

$$E_N(\{i_\nu\}) = \sum_{\nu=1}^{N} \varepsilon_{i_\nu} \ .$$

In the case of identical distinguishable particles the canonical ensemble is especially suitable. In this case, as indicated in the example in Table (**??**), we only need to specify which particle occupies which quantum state and then sum over all such distributions

Quantum number	T_1	T_2	T_3	T_4	Occupation number
1		x			1
2	x			x	2
3					0
4	x	x	x	x	4
5	x	x			2
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
L	x	x		x	3

Table 6.1: *Occupation numbers of single particle energies for distinguishable particles.*

For this case we get the following canonical partition function

<div style="border:1px solid">

CANONICAL PARTITION FUNCTION
(*for identical distinguishable particles*)

$$Z(T, N, V) = \sum_{i_1=1}^{L} \dots \sum_{i_N=1}^{L} e^{-\beta \sum_{\nu=1}^{N} \varepsilon_{i_\nu}}$$

$$= \prod_{\nu=1}^{N} \sum_{i_\nu} e^{-\beta \varepsilon_{i_\nu}} = \left(\sum_{i} e^{-\beta \varepsilon_i} \right)^N$$

$$= Z^N(T, N = 1, V) \,.$$

</div>

This result already turned up for the Einstein solid.

On the basis of Table (6.1) we can see that single particle energies can be occupied by more than one particle. This number is called **occupation number**. For a given single particle energy ε and N distinguishable particles there are several possibilities $M(m|N)$ to reach an occupation number m. Obviously this is the binomial coefficient.

MULTIPLICITY OF OCCUPATION NUMBERS
(*for distinguishable particles*)

$$M(m|N) = \binom{N}{m} .$$

(6.1)

6.2 Indistinguishable particles

As Fermions and Bosons are indistinguishable identical partcles, in principle it is not possible anymore to determine, which particle occupies which quantum state. One can only indicate the occupation numbers of the single particle states. Thus the multiplicity $(m|N)$ from equation (6.1) [Page 136] becomes

MULTIPLICITY OF OCCUPATION NUMBERS
(*for indistinguishable particles*)

$$M(m|L) = 1 .$$

(6.2)

6.2.1 Second quantisation

A partition function runs over all possible occupation numbers m_i of the single particle niveaus. As the sum of the occupation numbers is equal to the number of particles

$$N = \sum_{i=1}^{L} m_i$$

the grand canonical ensemble is better suited[1].

---

[1]As all ensembles are equivalent one can choose the mathematically most convenien one.

6.2.2 Partition function of the grand canonical ensemble

In order to calculate the partition function in this ensemble, one only has to sum all possible configurations of occupation numbers $\{n_i\}$.

$$Z(T, \mu, V) = \text{tr}\left\{e^{-\beta(\hat{H}-\mu\hat{N})}\right\} = \sum_{\{n_i\}} e^{-\beta \sum_i(\varepsilon_i-\mu)n_i} = \sum_{\{n_i\}} \prod_{i=1}^{L} e^{-\beta (\varepsilon_i-\mu)n_i}$$

$$= \prod_{i=1}^{L} \underbrace{\left(\sum_n e^{-\beta(\varepsilon_i-\mu)n}\right)}_{:=Z_{\varepsilon_i}} = \prod_{i=1}^{L} Z_{\varepsilon_i} \ . \tag{6.3}$$

6.2.3 Grand canonical potential

First we determine the grand canonical potential.

$$\Omega(T, \mu, V) = -k_B T \ln\left[Z(T, \mu, V)\right]$$
$$= -k_B T \sum_i \ln\left[Z_{\varepsilon_i}\right] \ .$$

When calculating Z_ε, we have to distinguish between fermions and bosons. The sum over n runs over the values $n \in \{0, 1\}$ for fermions and over $n \in \mathcal{N}_0$ for bosons. Then we get

$$Z_\varepsilon(T, \mu) = 1 + e^{-\beta(\varepsilon-\mu)} \ ; \qquad \text{(Fermions)}$$
$$Z_\varepsilon(T, \mu) = (1 - e^{-\beta(\varepsilon-\mu)})^{-1} \ ; \qquad \text{(Bosons)}$$
$$\Rightarrow \qquad \ln\left[Z_\varepsilon(T, \mu)\right] = -\sigma\ln\left[1 - \sigma z e^{-\beta\varepsilon}\right] \ . \tag{6.4}$$

Here we used the following definition:

$$\text{Fugacity:} \quad z := e^{\mu\beta} \tag{6.5}$$

$$\sigma = \begin{cases} -1 & \text{for Fermions} \ , \\ +1 & \text{for Bosons} \ . \end{cases} \tag{6.6}$$

The sign σ corresponds to the sign that appears when exchanging two particles

---

GRAND CANONICAL POTENTIAL

$$\Omega(T, \mu, V) = k_B T \; \sigma \sum_i \ln \left[1 - \sigma z \mathrm{e}^{-\beta \varepsilon_\mathrm{i}} \right] . \qquad (6.7)$$

6.2.4 Internal energy

Now we also want to bring the thermodynamic expectation value of the Hamiltonian and the number operator into a similar form. The following applies for the internal energy:

$$U = \langle H \rangle_{T,\mu} = \frac{1}{Z(T, \mu, V)} \; \mathrm{tr} \left\{ \hat{\mathrm{H}} \mathrm{e}^{-\beta \hat{\mathrm{H}} + \beta \mu \hat{\mathrm{N}}} \right\} ,$$

We also find the following thermodynamic relationship confirmed:

$$U = - \left(\frac{\partial \ln(Z(T, \mu, V))}{\partial \beta} \right) \bigg|_{\mu, N} + \mu \langle \hat{N} \rangle$$

As in the classical case, the additional term comes from the factor β in front of the number of particles. To avoid this term, the fugacity z can be kept fixed when differentiating w.r.t. β. Then we get the universal result (also for interacting particles)

INTERNAL ENERGY
(*via partition function*)

$$U(T, \mu, V) = - \left(\frac{\partial \ln(Z(T, \mu, V))}{\partial \beta} \right) \bigg|_{z, N} .$$

It is not at all obvious that the computation of averages via derivatives works in the quantum case as well, as in the exponent of the Boltzmann factor contains a sum of two operators that may not commute. The prove that the approach is still correct can be found in the appendixAppendix (D) [Page

212]. For second order derivatives w.r.t. β, however, this is usually not so easy anymore. In that case one obtains time dependent correlation function.

Next we will calculation of the internal energy explicitly

$$
U = -\left(\frac{\partial \ln(Z)}{\partial \beta}\right)\Big|_{z,V} \stackrel{(6.3)}{=} -\sum_i \left(\frac{\partial \ln(Z_i)}{\partial \beta}\right)\Big|_{z,V}
$$

$$
= -\sum_{i=1}^{L} \frac{\left(\frac{\partial Z_{\varepsilon_i}}{\partial \beta}\right)\Big|_{z,V}}{Z_i} = \sum_{i=1}^{L} \varepsilon_i \underbrace{\sum_n n \frac{e^{-\beta(\varepsilon_i-\mu)n}}{Z_i}}_{\langle n_{\varepsilon_i}\rangle_{T,\mu}}
$$

$$
= \sum_{i=1}^{L} \varepsilon_i \langle n_{\varepsilon_i}\rangle_{T,\mu} \ .
$$

INTERNAL ENERGY

$$
U = \langle H \rangle = \sum_{i=1}^{L} \varepsilon_i \langle n_{\varepsilon_i}\rangle_{T,\mu} \ ; \tag{6.8}
$$

$$
\langle n_{\varepsilon_i}\rangle_{T,\mu} = \sum_n n \frac{e^{-\beta(\varepsilon_i-\mu)n}}{Z_{\varepsilon_i}} \ . \tag{6.9}
$$

6.2.5 Average particle number

Likewise, we can calculate the thermodynamic expectation value of the number operator from the partition function.

AVERAGE PARTICLE NUMBER
(*via partition function*)

$$\langle N \rangle_{T,\mu} = \frac{1}{Z(T,\mu,V)} \ \mathrm{tr}\left\{\hat{N}e^{-\beta\hat{H}+\beta\mu\hat{N}}\right\}$$
$$= \frac{1}{\beta}\left(\frac{\partial\ln(Z(T,\mu,V))}{\partial\mu}\right)\bigg|_{T,N}.$$

x

$$\ln(Z) = \sum_i \ln(Z(\varepsilon_i)) \qquad \Rightarrow$$

$$\langle N \rangle = \sum_{i=1}^{L} \underbrace{\frac{1}{\beta}\left(\frac{\partial\ln(Z(\varepsilon_i))}{\partial\mu}\right)\bigg|_{T,N}}_{=\langle n_{\varepsilon_i}\rangle_{T,\mu}}.$$

This corresponds to equation (6.9) [Page 139].

AVERAGE PARTICLE NUMBER

$$\langle N \rangle = \sum_{i=1}^{L} \langle n_{\varepsilon_i}\rangle_{T,\mu} \ . \tag{6.10}$$

6.3 Density of states

The sum over i for d-dimensional problems leads to d-dimensional sums or integrals[2] . However, it is obvious that the sums in Ω, U and $\langle N \rangle$ depend on

---

[2]In Appendix (E) [Page 214] an alternative derivation of the transition from sum to intgral can be found.

i only via ε_i. This can be used as follows: All three sums are of the form

$$Q = \sum_i f(\varepsilon_i) = \sum_i f(\varepsilon_i) \underbrace{\left(\int \delta(\varepsilon - \varepsilon_i) \, d\varepsilon \right)}_{=1}$$

$$= \int f(\varepsilon) \underbrace{\left(\sum_i \delta(\varepsilon - \varepsilon_i) \right)}_{\rho(\varepsilon)} d\varepsilon \ .$$

We have introduced the single particle density of states

SINGLE PARTICLE DENSITY OF STATES

$$\rho(\varepsilon) = \sum_i \delta(\varepsilon - E_i) \ .$$

Thus, the grand canonical potential, for instance, can be expressed as follows

$$\Omega(T, \mu, V) = k_B T \sigma \int \ln \left[1 - \sigma z e^{-\beta \varepsilon} \right] \rho(\varepsilon) d\varepsilon \ .$$

The logarithm is rather a hindrance for the purpose of integration. Thus we use integration by parts in order to get the derivative of the logarithm and the antiderivative of the partition function (distribution function):

$$\Omega(T, \mu, V) = -k_B T \sigma \int \left. \left(\frac{\partial}{\partial \varepsilon} \ln \left[1 - \sigma z e^{-\beta \varepsilon} \right] \right) \right|_{T,z} F_\rho(\varepsilon) d\varepsilon$$

$$= -k_B T \sigma \int \frac{(-\sigma z)(-\beta) e^{-\beta \varepsilon}}{1 - \sigma z e^{-\beta \varepsilon}} F_\rho(\varepsilon) d\varepsilon$$

$$= - \int \frac{z}{e^{\beta \varepsilon} - \sigma z} F_\rho(\varepsilon) d\varepsilon$$

$$= - \int \langle n_\varepsilon \rangle_{T,\mu} F_\rho(\varepsilon) \, d\varepsilon \ .$$

Thus Ω, U and $\langle N \rangle$ can be expressed by similar one dimensional integrals.

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GRAND CANONICAL VARIABLES

$$\Omega(T, \mu, V) = - \int \langle n_\varepsilon \rangle_{T,\mu} \, F_\rho(\varepsilon) \, d\varepsilon \; ; \qquad (6.11)$$

$$U = \int \varepsilon \, \langle n_\varepsilon \rangle_{T,\mu} \, \rho(\varepsilon) d\varepsilon \; ; \qquad (6.12)$$

$$\langle N \rangle = \int \langle n_\varepsilon \rangle_{T,\mu} \, \rho(\varepsilon) d\varepsilon \; . \qquad (6.13)$$

</div>

It should already be pointed out here that the introduction of the density of states is exact, but caution is required if other terms of the integrand diverge. Then one must take into account that the density of states is in fact a delta functional. The thermodynamic limit must be performed with great care. We will discuss this in the context of Bose gas.

6.4 Average occupation number of single particle states

A key quantity for non-interacting particles is the average occupation number of the single particle niveaux, which was defined in equation (6.4) [Page 137] and equation (6.9) [Page 139]

$$\langle n_\varepsilon \rangle_{T,\mu} = \sum_n n \frac{e^{-\beta(\varepsilon - \mu)n}}{Z_\varepsilon(T, \mu)} \; ;$$

$$Z_\varepsilon(T, \mu) = \sum_n e^{-\beta(\varepsilon - \mu)n} \; ; \Rightarrow$$

$$\langle n_\varepsilon \rangle_{T,\mu} = \frac{1}{\beta} \left(\frac{\partial \ln(Z_\varepsilon(T, \mu))}{\partial \mu} \right) \bigg|_{T,V} .$$

From equation (6.4) [Page 137] then follows

FERMI AND BOSE DISTRIBUTION

$$\langle n_\varepsilon \rangle_{T\mu} = \frac{z}{e^{\beta\varepsilon} - \sigma z} = \frac{1}{e^{\beta(\varepsilon-\mu)} - \sigma} \; ; \qquad\qquad (6.14)$$

$$\text{mit } \sigma = \begin{cases} -1 & \text{Fermionen} \\ +1 & \text{Bosonen} \end{cases}$$

These are the Fermi-Dirac and the Bose-Einstein distribution.

6.4.1 Fermi-Dirac distribution

For fermions the average occupation number of a single particle state with energy ε is

---

FERMI-DIRAC DISTRIBUTION

$$f_D(\varepsilon, T) := \langle n(\varepsilon_\nu) \rangle_T = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1} \; ; \qquad 0 \le f_D(\varepsilon) \le 1^{(*)}$$

$$f_D(\varepsilon, T) \xrightarrow[T\to 0]{} \Theta(\varepsilon < \mu) \; ;$$

$$f_D(\varepsilon = \mu, T) = \frac{1}{2} \; .$$

The inequation (*) follows, as the exponential function is always positive for arbitrary real arguments. Therefore there is no constraint for the chemical potential either.

The deviation from the two limit values 0 and 1 are

$$\varepsilon < \mu : \quad 1 - f_D(\varepsilon, T) = \frac{1}{1 + e^{-\beta(\varepsilon-\mu)}} = \frac{1}{1 + e^{\beta|\varepsilon-\mu|}} \quad < e^{-\beta|\varepsilon-\mu|} \; ;$$

$$\varepsilon > \mu : \quad f_D(\varepsilon, T) = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1} = \frac{1}{e^{\beta|\varepsilon-\mu|} + 1} \quad < e^{-\beta|\varepsilon-\mu|} \; .$$

This means that at $|\varepsilon - \mu| = k_B T$ the deviation from the limit (1 or 0) is already only $1/e$ Thus the deviation of the step function is constrained to
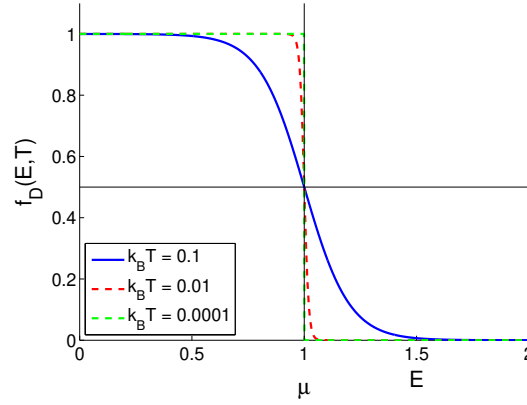
the area $k_B T$ around the Fermi level.

Figure 6.1: **Fermi-Dirac-Verteilung**

6.4.2 Bose-Einstein distribution

BOSE-EINSTEIN DISTRIBUTION

$$f_B(\varepsilon, T) := \langle n(\varepsilon) \rangle_T = \frac{1}{e^{\beta(\varepsilon - \mu)} - 1} \ .$$

As a negative occupation number is unphysical the chemical potential has to be smaller than the energy of the ground state ($\mu < \varepsilon_0$). We can always choose the zero point of energy such that $\varepsilon_0 = 0$. With this convention we have the constraint $\mu < 0$. As the chemical potential has to be chosen such that it it gives a desire average particle number, μ will adjust in the right way for self consistent calculations and avoid negative occupation numbers.

Chapter 7

Applications

7.1 The ideal quantum gas

The ideal quantum gas is the simplest quantum mechanical many-body system. Nevertheless it already exhibits interesting thermodynamic properties. It consists either of non-interacting Fermions or Bosons. The particles are confined to a cuboid and feel no other potential.

7.1.1 Density of state

Considering free non-relativistic quantum particles in a cuboid, the quantised single-particle energies are, as was already discussed

$$E_{\vec{l}} = \frac{1}{2m} \sum_{i=1}^{3} \left(\frac{2\pi\hbar l_i}{L_i}\right)^2 = \frac{1}{2m} \sum_{i=1}^{3} \left(\frac{hl_i}{L_i}\right)^2 .$$

In order to calculate the different quantities we need the single-particle density of states that takes the spin degeneracy

$$M_S := 2S + 1$$

into account The derivation of the density of states can be found in Appendix (F.1) [Page 218].
The easiest way to determine the dos is is via the distribution function.

Including spin degeneracy M_S, the distribution function is

$$
\begin{aligned}
F_d(\varepsilon) :=\ & M_S \sum_{\vec{l}} \theta \left[\frac{\hbar^2 \vec{k}^2(\vec{l})}{2m} < \varepsilon \right] \\
=\ & M_S \frac{V}{(2\pi)^d} \sum_{\vec{l}} \theta \left[\frac{\hbar^2 \vec{k}^2(\vec{l})}{2m} < \varepsilon \right] \triangle^d k \\
=\ & \frac{M_S V}{(2\pi)^d} \int \theta \left[\vec{k}^2 < \frac{2m\varepsilon}{\hbar^2} \right] d^d k \\
=\ & \frac{M_S V}{(2\pi)^d} V_d \left(R = \sqrt{2mE/\hbar^2} \right) \\
=\ & \frac{M_S V}{(2\pi)^d} \frac{(2m\varepsilon)^{\frac{d}{2}}}{\hbar^d} \frac{\pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2}+1)} \\
=\ & M_S V \left(\frac{2\pi m}{h^2} \right)^{\frac{d}{2}} \frac{2}{d\,\Gamma(\frac{d}{2})}\, \varepsilon^{\frac{d}{2}}\ .
\end{aligned}
$$

We get the density of states by differentiating w.r.t. ε.

$$
\begin{aligned}
\rho(\varepsilon) = \frac{d}{dE} F_d(\varepsilon) =\ & M_S V \left(\frac{2\pi m}{h^2} \right)^{\frac{d}{2}} \frac{2}{d\,\Gamma(\frac{d}{2})}\, \frac{d}{2}\, \varepsilon^{\frac{d}{2}-1} \\
=\ & M_S V \left(\frac{2\pi m}{h^2} \right)^{\frac{d}{2}} \frac{1}{\Gamma(\frac{d}{2})}\, \varepsilon^{\frac{d}{2}-1}\ .
\end{aligned}
$$

The result is

SINGLE-PARTICLE DENSITY OF STATES
(free non-relativistic particles)

$$
\rho(\varepsilon) = C_d\, \varepsilon^{\frac{d}{2}-1}\ ; \tag{7.1}
$$

$$
F_d(\varepsilon) = C_d\, \frac{2}{d}\, \varepsilon^{\frac{d}{2}}\ ; \tag{7.2}
$$

$$
C_d = M_S V \left(\frac{2\pi m}{h^2} \right)^{\frac{d}{2}} \frac{1}{\Gamma(\frac{d}{2})}\ . \tag{7.3}
$$

7.1.2 Grand canonical potential

Now we are able to use equation (6.11) [Page 142] and equation (6.14) [Page 143] to calculate the grand canonical potential.

$$\Omega(T,\mu,V) = -\int \langle n_\varepsilon\rangle_{T,\mu} \, F_\rho(\varepsilon) \, d\varepsilon = -\frac{2C_d}{d} \int \frac{z}{e^{\beta\varepsilon} - \sigma z} \, \varepsilon^{\frac{d}{2}} \, d\varepsilon \ . \qquad (7.4)$$

Substituting $\beta\varepsilon = t$ we get

$$\beta\Omega(T,\mu,V) = -\frac{2C_d}{d} \, (k_B T)^{\frac{d}{2}} \underbrace{\int \frac{z}{e^t - \sigma z} \, t^{\frac{d}{2}+1} \, \frac{dt}{t}}_{:=\Gamma(\frac{d}{2}+1) \, g^\sigma_{\frac{d}{2}+1}(z)}$$

$$\overset{(7.3)}{=} -M_S V \left(\frac{2\pi m}{h^2}\right)^{\frac{d}{2}} \frac{2}{d\,\Gamma(\frac{d}{2})} \, (k_B T)^{\frac{d}{2}} \, \Gamma(\frac{d}{2}+1) \, g^\sigma_{\frac{d}{2}+1}(z)$$

$$= -M_S V \left(\frac{2\pi m}{h^2\beta}\right)^{\frac{d}{2}} \, g^\sigma_{\frac{d}{2}+1}(z) \ .$$

The remaining integral will appear on several occasions. Because of its similarity to the gamma function we will call it *quantum mechanical gamma function* and formulate it as follows

---

> QUANTUM MECHANICAL GAMMA FUNCTION
> *(and recursion formula)*
>
> $$g_l^{(\sigma)}(z) := \frac{1}{\Gamma(l)} \int \frac{z}{e^t - \sigma z} \, t^l \, \frac{dt}{t} \ ; \qquad (7.5)$$
>
> $$z\frac{dg_l^\sigma(z)}{dz} = g^\sigma_{l-1}(z) \ ; \qquad (l > 1) \ . \qquad (7.6)$$

The recursion formula is derived in Appendix (G.1) [Page 220]. Further properties of $g_l^{(\sigma)}(z)$ shall be discussed later on. Thus we can now write the grand canonical potential as

---

GRAND CANONICAL POTENTIAL
(*bosonic correction term is not yet introduced*)

$$\beta \, \Omega(T, \mu, V) = -M_S V \, \lambda_T^{-d} \, g_{\frac{d}{2}+1}^{\sigma}(z) \; ; \tag{7.7}$$

$$\lambda_T := \sqrt{\frac{2\pi\beta\hbar^2}{m}} \; . \qquad \text{(thermal de Broglie wavelength)} \tag{7.8}$$

Again we encountered the thermal de Broglie wavelength.

7.1.3   Pressure

From $\Omega = -pV$ we directly get

PRESSURE
(*bosonic correction term is not yet introduced*)

$$\beta p = M_S \lambda_T^{-d} g_{\frac{d}{2}+1}^{\sigma}(z) \; . \tag{7.9}$$

7.1.4   Average number of particles

In order to calculate the average number of particles, equation (6.13) [Page 142] is used. The calculation is similar to that for the grand canonical potential

$$\langle N \rangle = \int \langle n_\varepsilon \rangle_{T,\mu} \, \rho(\varepsilon) \, d\varepsilon$$

$$= C_d \int \frac{z}{e^{\beta\varepsilon} - \sigma z} \, \varepsilon^{\frac{d}{2}} \, \frac{d\varepsilon}{\varepsilon} \; .$$

Substituting $\beta\varepsilon = t$ we get

$$\langle N \rangle = C_d \, (k_B T)^{\frac{d}{2}} \underbrace{\int \frac{z}{e^t - \sigma z} \, t^{\frac{d}{2}} \frac{dt}{t}}_{:=\Gamma(\frac{d}{2}) \, g^{\sigma}_{\frac{d}{2}}(z)}$$

$$\stackrel{(7.3)}{=} M_S V \left(\frac{2\pi m}{h^2}\right)^{\frac{d}{2}} \frac{1}{\Gamma(\frac{d}{2})} (k_B T)^{\frac{d}{2}} \Gamma(\frac{d}{2}) \, g^{\sigma}_{\frac{d}{2}}(z)$$

$$n := \frac{\langle N \rangle_{T,\mu}}{V} = M_S \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{d}{2}} g^{\sigma}_{\frac{d}{2}}(z) \; .$$

Thus the final result is

Average number of particles
(*bosonic correction term is not yet introduced*)

$$n(T, z) := n(T, \mu(z)) = M_S \lambda_T^{-d} g^{\sigma}_{d/2}(z) \; . \tag{7.10}$$

This equation can be – even though not easily – inverted, yielding the following result:

$$z = z(n, T) \; .$$

This is plugged into the equation for the pressure, yielding the quation of state for the ideal quantum gas.

Equation of state
(*bosonic correction term is not yet considered*)

$$\beta p = M_S \, \lambda_T^{-d} g^{\sigma}_{\frac{d}{2}+1}(z(n, T)) \; . \tag{7.11}$$

7.1.5 Classical limit

Now we shall consider the classical limit of high temperatures and/or low densities – i.e. $z \ll 1$. In that case we use the leading order of the series ex-

pansion of equation (G.1) [Page 221], which is $g_l^\sigma(z) = z + O(z^2)$. The effects, that the terms of higher order cause, are subject of subsequent lectures. At first we consider the density according to equation (7.10) [Page 149]

$$n = M_S \lambda_T^{-d} g_{d/2}^\sigma(z) = M_S \lambda_T^{-d} z \qquad \Rightarrow$$

$$z = \frac{n \lambda_T^d}{M_S} \ .$$

This result is plugged into the expression for pressure (equation (7.11) [Page 149])

$$\beta p = M_S \lambda_T^{-d} g_{\frac{d}{2}+1}^\sigma(z) = M_S \lambda_T^{-d} z = n \ ;$$

$$\Rightarrow \qquad pV = N k_B T \ .$$

This is the well known result for classical free particles. Classically there is no difference between Fermions and Bosons. In the classical limit the caloric equation of state results in

$$U = \frac{3}{2} pV = \frac{3N}{2} k_B T \ .$$

For the occupation of the single-particle levels we obtain in the classical limit

$$\langle n_k \rangle = \frac{z}{e^{\beta E(k')} - \sigma z} = z e^{-\beta E(k)} \frac{1}{1 - \sigma z e^{-\beta E(k)}} \xrightarrow[z \ll 1]{} e^{-\beta(E(k)-\mu)} + O(z^2) \ .$$

Thus we get the classical Boltzmann distribution for both particle-statistics.

7.2   The ideal Bose gas

As fermionic systems will be discussed extensively in solid state physics, here we shall concern ourselves more in depth with bosonic systems. Bosons exhibit interesting macroscopic quantum phenomena, which are a result that the occupation number can grow up to infinity. Therefore we shall discuss the ideal Bose gas in detail.

7.2.1   Bose-Einstein condensation (BEC)

As it was already hinted at, there is a small complication for Bosons. In order to understand it, we will consider the occupation numbers of the ground state and the first excited state at $T \to 0$. The Bose-Einstein distribution has the form

$$f_B(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} - 1} \ .$$

Therefore, for the ground state, for which we have chosen $\varepsilon_0 = 0$, the following applies:

$$f_B(\varepsilon_0) = \frac{1}{e^{-\beta\mu} - 1} \, .$$

In the case that the thermodynamic limit $\mu \ leadsto 0$, this contribution to the thermodynamic expectation values cannot be addressed via the density of states as we did before. This is a consequence of the importance of the details of the limit $V \to \infty$.

In order to clarify the problem and to demonstrate the correct approach, we shall consider the original expression for the number of particle in equation (6.10) [Page 140] once again. Here we deal with the problematic term ($\varepsilon_0 = 0$) separately

$$\langle N \rangle = \sum_{i=0}^{L} \langle n_{\varepsilon_i} \rangle_{T,\mu} = \sum_{i=0}^{L} \frac{z}{e^{\beta\varepsilon_i} - z}$$
$$= \frac{z}{1 - z} + \sum_{i=1}^{L} \frac{z}{e^{\beta\varepsilon_i} - z} \, .$$

The contribution of the higher single-particle energies are unproblematic, as is shown in Appendix (H.1) [Page 223]. Therefore we can again convert the remaining sum into an integral via the single-particle density of states

$$\langle N \rangle = \frac{1}{z^{-1} - 1} + \frac{V}{(2\pi)^d} \int \frac{z}{e^{\beta\varepsilon} - z} \, \rho(\varepsilon) \, d\varepsilon.$$

Actually the term $\varepsilon = 0$ would have to be omitted from the integral, but in the thermodynamic limit its contribution tends to zero. In particular, this is the reason why converting it into an integral and using the continuous density of states without the additional term comes out with something wrong. If one takes the integral from equation (7.10) [Page 149], one obtains

AVERAGE DENSITY
(for Bosons)

$$\tilde{n}(T,z) := \frac{n(T,z)}{M_S} = \underbrace{\frac{1}{V}\frac{1}{z^{-1}-1}}_{\tilde{n}_0} + \underbrace{\lambda_1^{-d}\, T^{d/2}\, g_{d/2}^{+1}(z)}_{:=\tilde{n}_n(T,z)} \; ;$$

$$\lambda_1 := \sqrt{2\pi\frac{\hbar^2}{mk_B}}\ .$$

The particles in the ground state are called condensate. The contribution of the integral is denoted by $n_n(T,z)$. the index stands for 'normal'. In order that the occupation numbers of the one-particle levels cannot assume unphysical (negative) values, $-\infty < \mu < \min_i \varepsilon_i = 0$ must be true. It follows that $0 < z < 1$. We will use this to further evaluate the function $g_l^{+1}(z)$. The details of the calculation are found in Appendix (G.3) [Page 221]. The results are

POLYLOGARITHM
(de Jonquière function)

$$g_l^{+1}(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^l}\ . \tag{7.12}$$

This function has the following properties:

$$g_l^{+1}(z) \geq 0\ ;$$
$$g_l^{+1}(0) = 0\ ;$$
$$\frac{d}{dz}g_l^{+1}(z) \stackrel{(7.12)}{=} \frac{1}{z}g_{l-1}^{+1}(z) > 0\ ;$$
$$g_l^{+1}(1) = \zeta(l)\ .$$

This mean that $g_l^{+1}(z)$ starts at zero for $z = 0$, is nondecreasing and within the interval $0 < z < 1$ on the right border the maximum value $\zeta(l)$ is given

by the Riemann zeta function. Especially the following applies:

$$\zeta(3/2) = 2.612 \; ; \qquad\qquad \zeta(5/2) = 1.3415 \; .$$

In the following, we will first consider three-dimensional systems $(d = 3)$ for which the following applies:

AVERAGE DENSITY
(for Bosons in 3d)

$$\tilde{n}(T, z) := \tilde{n}_0 + \tilde{n}_n(z) \; ; \qquad\qquad (7.13a)$$

$$\tilde{n}_0 := \frac{1}{V} \frac{z}{1 - z} \; ; \qquad\qquad (7.13b)$$

$$\tilde{n}_n(z) := \lambda_1^{-3} \, T^{3/2} \, g_{3/2}^{+1}(z) \; . \qquad\qquad (7.13c)$$

Therefore, for the physically allowed values of z, we have $g_{3/2}^1(z) \leq \zeta(3/2)$. Thus, for the contribution $\tilde{n}_n(z) \leq \tilde{n}_C$ of the particles in the normal state (contribution of the integral), there is an upper limit $\tilde{n}_C$:

CRITICAL DENSITY

$$\tilde{n}_C := \tilde{n}_n(T, z = 1) \; ; \qquad\qquad (7.14)$$

$$= \lambda_T^{-3} \, \zeta(3/2) \; . \qquad\qquad (7.15)$$

Therefore, Bose condensation sets in if

$$\text{either} \qquad \tilde{n} \geq \tilde{n}_C = \lambda_T^{-3}\zeta(3/2) \qquad\qquad (7.16a)$$

$$\text{or} \qquad \lambda_T^3 \geq \frac{\zeta(3/2)}{\tilde{n}} = \zeta(3/2) \underbrace{\frac{V}{\tilde{N}}}_{:=v} = \zeta(3/2) \, r^3 \; . \qquad\qquad (7.16b)$$

Here v is the average volume per particle and r is the average distance between particles. Bose condensation therefore starts when the thermal de Broglie wavelength exceeds the average distance between particles.
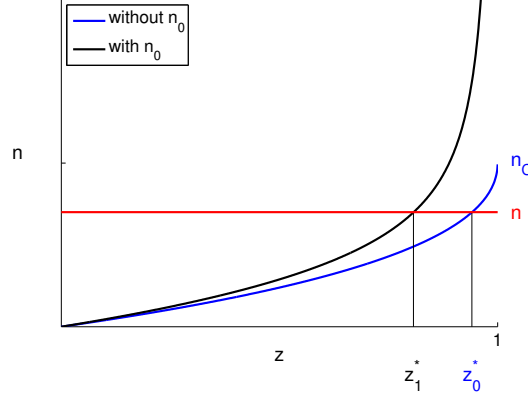
A) We shall start with $n < \tilde{n}_C$:

Figure 7.1: *Density as a function of fuagcity z. The blue graph is the result without condensate contribution ($\tilde{n}_n(T, z)$) the black one contains the condensate fraction.*

As can be seen in Figure 7.1, for $n < \tilde{n}_C$ there is always a solution for $n_n(T, z_0^*) = n$, even without the condensate contribution. Hecne

$$z_0^* < 1 \ . \tag{7.17}$$

The real solution for finite V is z_1^*. Now the additional term is nondecreasing:

$$\frac{d}{dz} \frac{1}{1-z} = \frac{1}{(1-z)^2} > 0 \ .$$

Thus both contributions in equation (7.13) [Page 153] are positive and monotonically nondecreasing. On the one hand, for all $V < \infty$ we have

$$z_1^* < z_0^* < 1 \ .$$

On the other hand it therefore follows that

$$\tilde{n}_0 = \frac{1}{V} \frac{z_1^*}{1 - z_1^*} \overset{z_1^* < z_0^*}{<} \frac{1}{V} \frac{z_0^*}{1 - z_0^*} \ .$$

Because of $z_0^* < 1$ (equation (7.17) [Page 154]), $z_0^*/(1-z_0^*)$ is a finite constant C^* independent from V. Finally we get

$$\tilde{n}_0 < \frac{C^*}{V} \xrightarrow[V \to \infty]{} 0 \ .$$

Therefore, in this case the condensate fraction vanishes in the thermodynamic limit and the chemical potential is uniquely determined by z_0^*.

For $\tilde{n} < \tilde{n}_C$ we have $\tilde{n}_0 = 0$.
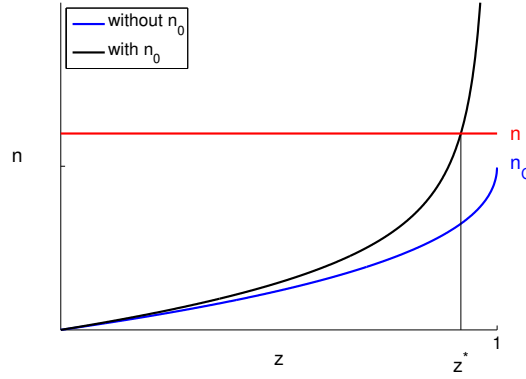
B) Now we consider $\tilde{n} > \tilde{n}_C$:

Figure 7.2: *Density as a function of fugacity z. The blue graph is the result without condensate contribution ($\tilde{n}_n(T, z)$), the black graph includes the condensate fraction.*

In this case we will show that the fugacity goes to 1 and the chemical potential goes to 0 and also that we have

$$\tilde{n}_0 = \tilde{n} - \tilde{n}_C > 0$$

in the thermodynamic limit, i.e. for $V \to \infty$.

For $\tilde{n} > \tilde{n}_C$, $\tilde{n}_0 > 0$ has to be true. The state ε_0 is macroscopically occupied. Thus we have Bose condensation.

Proof

The fugacity z^* follows from

$$\tilde{n} = \frac{1}{V} \frac{z^*}{1 - z^*} + \tilde{n}_n(T, z^*) \, . \tag{*}$$

We can see in the figure that $z^* \xrightarrow[V \to \infty]{} 1$. This results from the fact that the blue graph makes no contribution and the black graph approaches the vertical straight line at $z = 1$.

Mathematically one can look at that as follows: From (*) we get

$$\tilde{n} = \frac{1}{V}\frac{z^*}{1-z^*} + \tilde{n}_n(T, z^*) < \frac{1}{V}\frac{z^*}{1-z^*} + \underbrace{n_n(T, 1)}_{=\tilde{n}_C}$$

$$\Rightarrow \qquad (\tilde{n} - \tilde{n}_C) < \frac{1}{V}\frac{z^*}{1-z^*}$$

$$(\tilde{n} - \tilde{n}_C)(1 - z^*) < \frac{1}{V}\, z^*$$

$$(\tilde{n} - \tilde{n}_C) < z^*\left(\frac{1}{V} + (\tilde{n} - \tilde{n}_C)\right)$$

$$\frac{(n - \tilde{n}_C)}{\frac{1}{V} + (\tilde{n} - \tilde{n}_C)} < z^* \leq 1\,.$$

The last inequation is a consequence of the definition of z. For $V \to \infty$ the left side goes to 1 and therefore we get $z^* \to 1$

q.e.d. ✓

This means that, because of $z^* = e^{\beta\mu^*}$, we have $\beta\mu^* \xrightarrow[V\to\infty]{} 0$.

Now we will perform a series expansion in μ^* for the condensate term in the density

$$\tilde{n} = \frac{1}{V}\frac{z^*}{1-z^*} + \tilde{n}_C$$

$$= \frac{1}{V}\frac{1+\beta\mu^*}{(-\beta\mu^*)} + O(\mu^*) + \tilde{n}_C$$

$$= \frac{1}{V}\frac{1}{(-\beta\mu^*)} + \left(\tilde{n}_C - \frac{1}{V}\right) + O(\beta\mu^*)$$

Then

$$\tilde{n} - \tilde{n}_C - \frac{1}{V} = \frac{1}{V}\frac{1}{(-\beta\mu^*)} + O(\beta\mu^*)$$

$$\beta\mu^* = -\frac{1}{V(\tilde{n} - \tilde{n}_C + \frac{1}{V})} + O\left((\mu^*)^2\right)$$

$$\beta\mu^* = -\frac{1}{V(\tilde{n} - \tilde{n}_C)} + O(V^{-2}) + O\left((\mu^*)^2\right)\,. \qquad (*)$$

In leading order μ^* goes to zero as

$$\beta\mu^* = -\frac{1}{V}\frac{1}{\tilde{n} - \tilde{n}_C}$$

Therefore, both terms that were omitted in (*) are of the order $O(V^{-2})$. From this we get the condensate fraction

$$\tilde{n}_0 = \frac{1}{V}\frac{z^*}{1-z^*} = \frac{1}{V}\frac{1+\beta\mu^*}{(-\beta\mu^*)} = \frac{1}{V}\frac{1}{(-\beta\mu^*)} - \frac{1}{V} = (\tilde{n}-\tilde{n}_C) - \frac{1}{V}$$
$$= (\tilde{n}-\tilde{n}_C) - \frac{1}{V} \ .$$

IN THE THERMODYNAMIC LIMIT THE FOLLOWING APPLIES
(*in the condensation phase, i.e. $T < T_C$ or $n > \tilde{n}_C$*)

$$\tilde{n}_0 = \tilde{n} - \tilde{n}_C - \frac{1}{V} \xrightarrow[V\to\infty]{} \tilde{n} - \tilde{n}_C \ ;$$
$$\beta\mu^* = -\frac{1}{V}\frac{1}{\tilde{n} - \tilde{n}_C} \xrightarrow[V\to\infty]{} 0 \ ; \qquad (7.18)$$
$$z^* = 1 + \beta\mu^* \xrightarrow[V\to\infty]{} 1 \ .$$

T_C will be defined later on.

There is no Bose condensation in 1d and 2d

The reason, why there is no Bose-Einstein condensation in 1d and 2d is simple. According to equation (7.10) [Page 149] the regular density is

$$\tilde{n}_n(z) = \Lambda_T^{-d} g_{d/2}^1(z) \ .$$

We had universally shown that $g_{d/2}^1(z)$ is a nondecreasing function in the variable z. This function corresponds to $\zeta(d/2)$ for $z = 1$. From Table (G.5) we infer that

$$\zeta(1/2) = \zeta(2/2) = \infty \ .$$

Thus for all densities $\tilde{n}$ a solution for the equation

$$\tilde{n}_n(z^*) = \tilde{n} \ .$$

exists. The rest of the argumentation is the same as in Section (7.2.1) [Page 154]. Therefore, also in the thermodynamic limit we have $z^* < 1$. As a consequence of this the correction term vanishes in the thermodynamic with $1/V$.

Is BEC a trivial thing?

Didn't we actually make a trivial observation? As the temperature decreases, the number of bosons in the state of minimum single particle energy $\varepsilon_0 = 0$ increases due to the Bose distribution. We obtain a typical temperature for this from the condition

$$\beta(\varepsilon_1 - \varepsilon_0) = \beta\varepsilon_1 \geq 1$$

$$\Rightarrow \qquad k_B T \leq \varepsilon_1 = \frac{\left(\frac{2\pi\hbar}{L}\right)^2}{2m} = \frac{2\pi\hbar^2}{m}\frac{\pi}{L^2} \; ;$$

$$\text{or rather} \qquad 1 \leq \frac{2\pi\hbar^2\beta}{m}\frac{\pi}{L^2} = \frac{\lambda_T^2}{L^2}\pi$$

$$\text{hence} \qquad L \leq \sqrt{\pi}\lambda_T \; . \tag{7.19}$$

This transition takes place when the thermal de Broglie wavelength exceeds the size of the system.
Bose condensation, however, occurs when the de Broglie wavelength exceeds the average distance between particles.
A smaller wavelength means higher temperature and therefore Bose condensation already occurs at much higher temperatures. We reconsider the two conditions for the transitions

$$\text{eq.(7.16b)} : \qquad\qquad \lambda_{T_C} = \left(\zeta(3/2)\right)^{\frac{1}{3}} r$$

$$\text{eq.(7.19)} : \qquad\qquad \lambda_{T_B} = \frac{L}{\sqrt{\pi}}$$

Since $\lambda_T = const/\sqrt{T}$ we find for the ratio of the corresponding temperatures

$$\frac{T_C}{T_B} = \frac{\lambda_{T_B}^2}{\lambda_C^2} \approx \frac{L^2}{r^2} = \left(\frac{V}{V/N}\right)^{2/3} = N^{2/3} \approx 10^{\frac{2\cdot24}{3}} = 10^{16} \; .$$

We will see that Bose condensation occurs for $O(1K)$, whereas the trivial tranistion is to be expected only at $10^{-16}K$. This means that BEC is a real phase transition.
BEX is a real phase transition

Different conditions for BEC

In equation (7.14) [Page 153] we had the condition for BEC

$$\tilde{n} > \tilde{n}_C = \Lambda \, T^{3/2} \; .$$

Two conditions can be derived from this

CONDITIONS FOR CONDENSATION

$$\tilde{n} > \tilde{n}_C(T) \qquad\qquad := \Lambda\, T^{3/2}\ ; \qquad (7.20)$$

$$T < T_C(\tilde{n}) \qquad\qquad := \left(\frac{\tilde{n}}{\Lambda}\right)^{2/3}\ ; \qquad (7.21)$$

$$\Lambda = \lambda_1^{-3}\, \zeta(3/2)\ ; \qquad\qquad\qquad (7.22)$$

$$\zeta(3/2)\, T_C^{3/2} = \tilde{n}\lambda_1^3\ . \qquad\qquad\qquad (7.23)$$

For $T < T_C$ we have $z = 1$ in the thermodynamic limit (see equation (7.18) [Page 157]) and for the condensate fraction we have

$$\tilde{n}_0 = \tilde{n} - \tilde{n}_C(T) = \tilde{n} - \Lambda T^{3/2}$$

$$= \tilde{n}\left[1 - \left(\frac{T}{(\tilde{n}/\Lambda)^{2/3}}\right)^{3/2}\right] \overset{(7.21)}{=} \tilde{n}\left[1 - \left(\frac{T}{T_C}\right)^{3/2}\right]\ .$$

With this we have the

TEMPERATURE DEPENDENCE OF THE CONDENSATE FRACTION

$$\tilde{n}_0 = \tilde{n}\left[1 - \left(\frac{T}{T_C}\right)^{3/2}\right]\ .$$

This means that below T_C a macroscopic number of particles condense in the ground state ($k = 0$). We see that the condensate fraction becomes the total density for $T \to 0$. All particles, therefore, condense in the ground state. For $T < T_C$ the density of the normal particles of the fluid is

$$\tilde{n}_n := \tilde{n} - \tilde{n}_0 = \lambda_T^{-3}\zeta(3/2) = \Lambda T^{3/2}\ . \qquad (7.24)$$

With the values for ^{4}He, i.e. a density of $\rho = 75.4\ kg\ m^{-3}$, a mass of $m_{^4\text{He}} = 6.66 10^{-27} kg$ and $\zeta(5/2) = 1.3415$ the transition temperature for ^{4}He is $3.13 K$. This is surprisingly close to the value for the λ transition in ^{4}He ($T_\lambda = 2.18 K$). At this point, helium has a phase transition from a superfluid to a normal fluid. The physical properties of ^{4}He are fascinating, but would take too long to discuss in this lecture.
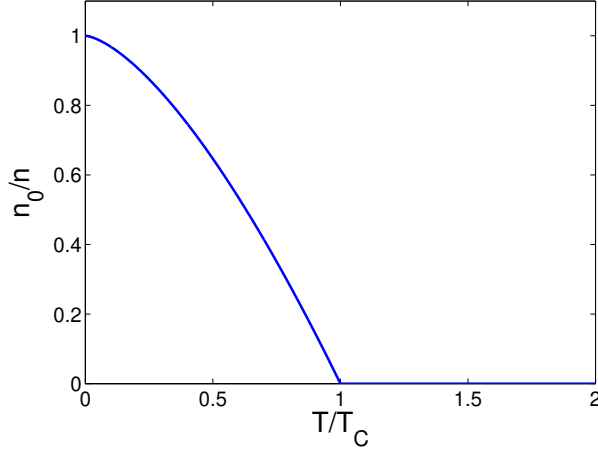
Figure 7.3: *Fraction of Bosons in the single-particle ground state (condensate fraction).*

For $T > T_C$ the condensate fraction vanishes proportional to V^{-1} and therefore we have

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DENSITY
(outside the condensation phase, i.e. especially $T > T_C$)

$$\tilde{n}(T, z) = \lambda_1^{-3} \, T^{3/2} \, g_{3/2}^1(z) \; ; \tag{7.25}$$

$$\tilde{n}_0 = 0 \; . \tag{7.26}$$

</div>

7.2.2   Grand canonical potential

In equation (7.7) [Page 148] we had already calculated the grand canonical potential without special consideration of the ε_0 terms. The result was

$$\frac{\beta \, \Omega(T, \mu, V)}{V} = -M_S \, \lambda_1^{-3} \, T^{3/2} \, g_{\frac{5}{2}}^\sigma(z) \; . \tag{7.27}$$

This contribution to the grand canonical potential is extensive. To this result of the regular phase the $\varepsilon_0 = 0$ term

$$\frac{\beta \Omega_{\varepsilon_0}}{V} = M_S \, \frac{\ln(1 - z)}{V}$$

from equation (6.7) [Page 138] is added. Outside the condensate phase we have $z < 1$. This contribution yields no extensive contribution to the potential and can be neglected in comparison to equation (7.27) [Page 160]. Within the condensation phase

$$1 - z = |\beta\mu| = \frac{(\tilde{n}_C - \tilde{n}_0)}{V} \; ; \text{und somit} \; \frac{\beta\Omega_{\varepsilon_0}}{V} \propto \frac{\ln(V)}{V} \xrightarrow[V\to\infty]{} 0 \; .$$

applies. The correction term therefore vanishes in the thermodynamic limit.

Caution is required here: If one intends to use the large canonical potential to calculate other thermodynamic quantities, such as the number of particles, by partial derivation, one must not yet omit the correction term. The reason for this is that when differentiating, it can have a form that does not disappear in the thermodynamic limit! This means that the thermodynamic limit should only be calculated when the final result is available.

Try yourself to compute the average particle number form the derivative of Ω w.r.t. the chemical potential μ. it is already qualitatively clear that when we use Ω without the condensate term, we cannot get the condensate fraction.

7.2.3   Pressure

Because of $(p = -\Omega/V)$, we immediately get the pressure. Here the form of the condensate term is obviously unimportant. This is evident, as the particles in the condensate do not have any momentum $(k = 0)$. Nevertheless, pressure will show important features at the phase transition. The pressure is therefore given by equation (7.27) [Page 160]

PRESSURE AS A FUNCTION OF T AND z

$$p(T, z) = M_S \begin{cases} k_B \; \lambda_1^{-3} \; g_{5/2}^1(z) \; T^{5/2} \; ; & \text{outside the condensate phase} \\ k_B \; \lambda_1^{-3}\zeta(5/2) \; T^{5/2} \; ; & \text{within the condensate phase} \end{cases} .$$

$$(7.28)$$

As a matter of fact, the first equation is also valid in the condensate phase, but here $z =$.

p-T phase diagram

Since $g^1_{5/2}(z)$ is a nondecreasing function, the pressure increases with increasing z up to a maximum value for $z = 1$. At this point the condensation phase is entered and the pressure does not change any more.. This also means, that for an arbitrary but fixed temperature T the pressure cannot exceed the critical pressure:

CRITICAL PRESSURE (VAPOUR PRESSURE)
(*at a fixed temperature*)

$$p_C(T) = M_S \, k_B \, \lambda_1^{-3} \zeta(5/2) \; T^{5/2} \; . \tag{7.29}$$

This pressure is also called **vapor pressure**. The resulting p-T phase diagram is plotted in Figure 7.4.
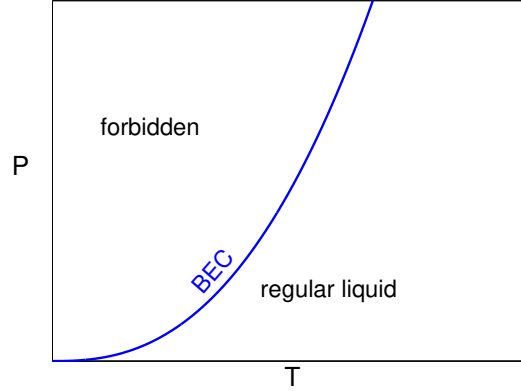
Figure 7.4: *p-T phase diagram. The area above the blue line is inaccessible. In the lower area, for pairs of values of p and T a regular fluid is present. Exactly on the blue line there is the two-phase area for which a mixture of regular fluid and condensate exists.*

In order to express the pressure as a function of temperature and density (equation of state), we first equation (7.25) [Page 160] have determine $z(T, n)$. The result is then plugged into $p(T, z(n))$ resulting in $p(T, n)$. Numerically, is, however, easier to $p(T, z)$ and $n(T, z)$ for a given z and draw a mark at the point (p, n). The $p - n$ diagram exhibits an interesting behaviour. Instead of n we use $v = 1/n$, i.e. the volume per particle and we will study the $p - v$ diagram.

Pressure as a function of density

For every temperature T there is a critical density $\tilde{n}_C = \Lambda T^{3/2}$. Thus for an arbitrary but fixed temperature there always is a transition into the condensation phase.

Outside the condensate phase $(0 < z < 1)$ is valid for fixed T and

$$\frac{\partial \tilde{n}(T, z)}{\partial z} = \lambda_T^{-3} \frac{d}{dz} g_{3/2}^1(z) = \lambda_T^{-3} \frac{g_{1/2}^1(z)}{z} > 0 \ .$$

Then

$$\left.\frac{\partial p}{\partial \tilde{n}}\right|_T = \left.\frac{\partial p}{\partial z}\right|_T \left.\frac{\partial z}{\partial \tilde{n}}\right|_T = k_B \Lambda \ T^{5/2} \frac{dg_{5/2}^1(z)}{dz} \frac{dz}{d\tilde{n}}$$

$$= k_B \Lambda \ T^{5/2} \underbrace{\frac{g_{3/2}^1(z)}{z} \frac{dz}{d\tilde{n}}}_{>0} > 0 \ .$$

The pressure therefore increases with increasing density (or decreasing v), as one would intuitively assume for reasons of stability.

Within the condensation phase, however, for fixed temperature the pressure is independent of the density (see equation (7.28) [Page 161]). This means that when the volume is reduced or the number of particles is increased the pressure does not increase anymore. In other words:

The specific density of the condensate is $n_C = \infty$.
Respectively the specific volume is $v_C = 0$.
How does the p-v- diagram look like in the classical case?
For the transition point the following applies:

$$p_C = d_p T^{5/2} \ ; \qquad\qquad (equation(7.29)[Page162])$$
$$\tilde{n}_C = d_n T^{3/2} \ ; \qquad\qquad (equation(7.20)[Page159]) \ .$$

This yields a phase boundary at

$$\frac{p}{d_p} = \left(\frac{d_n}{\tilde{n}}\right)^{-5/3}$$

This is the dashed line in Figure 7.5. In the condensate phase a mixture of phases is present.

7.2.4 Landau criterion

We shall now consider the physical reason for the occurrence of frictionless flow of a bosonic liquid. We consider a macroscopic object of mass M moving
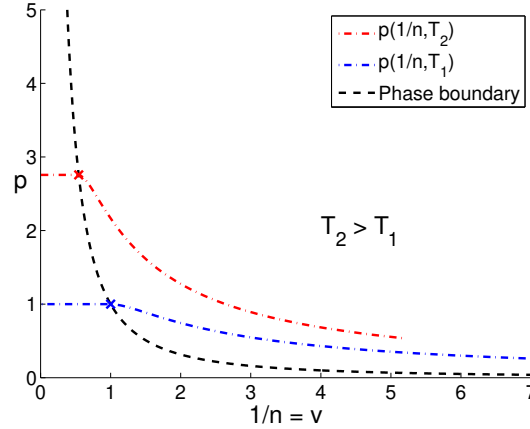
Figure 7.5: *Pressure as a function of the inverse density or the specific voume. For a fixed number of particles this corresponds to the p-T diagram. The dashed line is the phase boundary. Below it is the condensate phase.*

with velocity $\vec{V}$ in a fluid. The momentum of the object is therefore $\vec{P} = M\vec{V}$ and its kinetic energy is $E_{kin} = M\vec{V}^2/2$. We assume that the motion of th e macroscopic object causes an excitation with wave vector $\vec{k}$ in the liquid. The momentum of this quasiparticle is then $\vec{p} = \hbar\vec{k}$ and its energy is described by a dispersion $E(\vec{k})$. After the excitation of the quasiparticle, the macroscopic object has velocity $\vec{V}'$ or rather momentum $\vec{P}' = M\vec{V}'$ and its kinetic energy is $E'_{kin} = M\vec{V}'^2/2$. Due to the momentum conservation, the following applies

$$M\vec{V} = M\vec{V}' + \hbar\vec{k}$$

$$\Rightarrow \qquad \vec{V}' = \vec{V} - \frac{\hbar\vec{k}}{M} \tag{*}$$

and because of energy conservation we have

$$\frac{1}{2}M\vec{V}^2 = \frac{1}{2}M\vec{V}'^2 + E(\vec{k}) \ .$$

Along with (*) we can express the first term on the right hand site as follows

$$\frac{1}{2}M\vec{V}'^2 \stackrel{(*)}{=} \frac{1}{2}M\left(\vec{V}^2 + \left(\frac{\hbar}{M}\right)^2\vec{k}^2 - 2\frac{\hbar}{M}\vec{V}\vec{K}\right)$$

$$= \frac{1}{2}M\vec{V}^2 + \frac{\hbar^2\vec{k}^2}{2M} - \hbar\vec{k}\vec{V} \ .$$

Therefore we get

$$\hbar \vec{k}\vec{V} = \underbrace{\frac{1}{2}M\vec{V}^2 - \frac{1}{2}M\vec{V}'^2}_{E(\vec{k})} + \frac{\hbar^2\vec{k}^2}{2M} \ .$$

$$= E(\vec{k}) + \frac{\hbar^2\vec{k}^2}{2M} \ .$$

From this we can derive the following inequality:

$$\hbar|\vec{k}|\,|\vec{V}| \geq \hbar\vec{k}\vec{V} = E(\vec{k}) + \frac{\hbar^2\vec{k}^2}{2M} \geq E(\vec{k})$$

$$\text{or rather} \qquad |\vec{V}| \geq \frac{E(\vec{k})}{\hbar|\vec{k}|} \ .$$

If this inequality is cannot be fulfilled, then there will no excitation in the fluid and in turn the macroscopic particle will not lose energy. Hence it will move frictionless. There is an excitation in the fluid for which the right side is minimal. For this we define

$$V_{cr} = \min_{\vec{k}} \frac{E(\vec{k})}{\hbar|\vec{k}|} \ . \tag{7.30}$$

Therefore there will be no dissipation possible if $|\vec{V}| < V_{min}$. Put differently, dissipation is only possible if the velocity of the macroscopic particle exceeds V_{min}

CONDITION FOR DISSIPATION

$$|\vec{V}| \geq V_{cr} = \min_{\vec{k}} \frac{E(\vec{k})}{\hbar|\vec{k}|} \ .$$

This critical velocity was first derived by Landau. If we have the dispersion of an ideal Bose gas ($E(\vec{k}) \propto k^2$), the right side of the equation is zero. Therefore it is always possible to generate dissipative processes.

Consequently the ideal Bose gas is not superfluid, even with BEC.

When taking into consideration the interactions of the Bosons, the lower excitations (phonons) have a linear dispersion $E(\vec{k}) = c\hbar|\vec{k}|$. Then the critical

velocity is the same as the phonon velocity.

$$V_{cr} = c \ .$$

For superfluid Helium, however, the dispersion relation $E(\vec{k})$ starts with a linear photon dispersion, but then at a higher wave vector $\vec{k}$, a socalled roton minimum exists. R. Feynman discussed the origin in some of his papers. For $\vec{k}$ at the roton minimum we have $E(\vec{k}_{rot}) < \hbar c |\vec{k}|$. Therefore we find

$$V_{cr} = \min_{\vec{k}} \frac{E(\vec{k})}{\hbar |\vec{k}|} = \frac{E(\vec{k}_{rot})}{\hbar |\vec{k}_{rot}|} < \frac{\hbar c |\vec{k}_{rot}|}{\hbar |\vec{k}_{rot}|} = c$$

that the critical velocity V_{cr} is smaller than the phonon velocity c. However, a quantitative comparison with experiments shows that the resulting Landau velocity V_{cr} is too large for superfluid helium. When deriving the Landau criterion, the formation of vortexes is neglected. This would lead to a further reduction of the critical velocity.
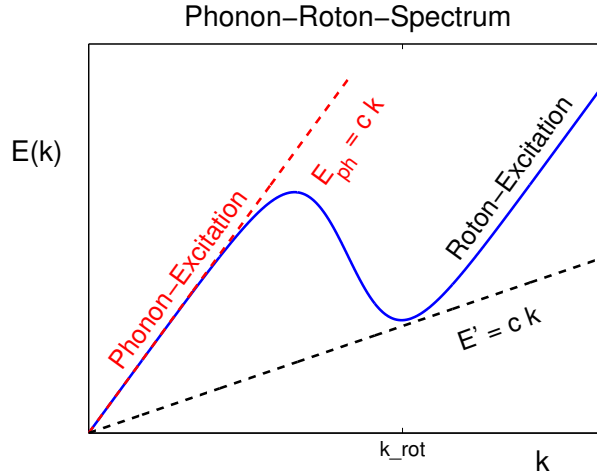

Figure 7.6: Phonon-roton dispersion

7.2.5   Thermodynamic potentials

Internal energy

We can get the internal energy from equation (6.12) [Page 142] as

$$U = \int \varepsilon \frac{z}{e^{\beta \varepsilon} - z} \rho(\varepsilon) \ d\varepsilon$$

$$= C_d \int \frac{z}{e^{\beta \varepsilon} - z} \varepsilon^{\frac{d}{2}} d\varepsilon \ .$$

Comparing that with equation (7.4) [Page 147] we find that

$$U = -\frac{d}{2}\Omega = \frac{d}{2}pV .$$

For three dimensions we thus have the

CALORIC EQUATION OF STATE

$$U = \frac{3}{2}pV .$$

This is the same relation as in the classical case. Inserting the result for the pressure, which was

$$p(T, z) = M_S k_B \, \lambda_1^{-3} \, T^{5/2} \, g_{5/2}^1(z)$$

we get

$$\frac{U}{Nk_B} = \frac{3}{2}\frac{V}{N}\frac{p}{k_B}$$

$$= \frac{3}{2}\underbrace{\frac{V}{N}}_{=1/\tilde{n}}M_S \, \lambda_1^{-3} \, T^{5/2} \, g_{5/2}^1(z) .$$

Finally, we obtain

$$\frac{U}{Nk_B} = \frac{3T}{2} \cdot \frac{\lambda_T^{-3} \, g_{5/2}^1(z)}{\tilde{n}} . \tag{7.31}$$

In the condensate phase we have $z = 1$. As a reminder: In the classical model the result was $U/(Nk_B) = \frac{3}{2}T$.

Heat capacity (specific heat)

Based on equation (7.31) [Page 167] we can now calculate the heat capacity.

$$\frac{C_V}{Nk_B} := \left.\frac{\partial(U/Nk_B)}{\partial T}\right|_{V,N} = \left.\frac{\partial}{\partial T}\left(\frac{3}{2\tilde{n}}\lambda_1^{-3}T^{5/2} \, g_{5/2}^1(z)\right)\right|_{V,N} .$$

As V and N are kept constant, the density $\tilde{n}$ is constant too. Therefore we get

$$\frac{C_V}{k_B N} = \frac{3}{2\tilde{n}} \, \lambda_1^{-3} \, \left.\frac{\partial}{\partial T}\left(T^{5/2} \, g_{5/2}^1(z)\right)\right|_{V,N} . \tag{7.32}$$

We shall seperately evaluate this formula for the two ranges of temperature $T \lessgtr T_C$.

A) $\mathbf{T < T_C}$

For $T < T_C$ we have $z \equiv 1$ and from equation (7.32) [Page 167] follows

$$\frac{C_V}{Nk_B} = \frac{5}{2}\frac{3}{2\tilde{n}}\lambda_1^{-3}T^{3/2}\,g_{5/2}^1(1) = \frac{15}{4\tilde{n}}\zeta(5/2)\lambda_1^{-3}T^{3/2}\;.$$

Equation (7.21) [Page 159] says

$$\tilde{n} = \lambda_1^{-3}\zeta(3/2)T_C^{3/2}$$

Therefore we get

$$\frac{C_V}{Nk_B} = \underbrace{\frac{15}{4}\frac{\zeta(5/2)}{\zeta(3/2)}}_{=1.925}\left(\frac{T}{T_C}\right)^{3/2}\;. \tag{7.33}$$

As a reminder: In the classical case the result was $\frac{C_V}{Nk_B} = \frac{3}{2}$.

B) $\mathbf{T > T_C}$

For $T > T_C$ also z contributes to the derivative

$$\frac{C_V}{Nk_B} = \frac{15}{4\tilde{n}}\underbrace{\lambda_1^{-3}T^{3/2}}_{\lambda_T^{-3}}\,g_{5/2}^1(z) + \frac{3}{2\tilde{n}}\underbrace{\lambda_1^{-3}T^{5/2}}_{=T\lambda_T^{-3}}\,\underbrace{\frac{d}{dz}g_{5/2}^1(z)}_{\overset{(7.6)}{=}g_{3/2}^1(z)\,/z}\,\frac{dz}{dT}\bigg|_{V,N}$$

$$= \frac{15}{4}\frac{\lambda_T^{-3}\,g_{5/2}^1(z)}{\tilde{n}} + \frac{3}{2}T\,\frac{\lambda_T^{-3}\,g_{3/2}^1(z)}{\tilde{n}}\,\frac{z'}{z}\;.$$

Based on equation (7.25) [Page 160] $[\tilde{n} = \lambda_T^{-3}g_{3/2}^1(z)]$ this expression can be simplified further:

$$\frac{C_V}{Nk_B} = \frac{15}{4}\frac{g_{5/2}^1(z)}{g_{3/2}^1(z)} + \frac{3}{2}\,T\,\frac{z'}{z}\;.$$

Now we merely need z'/z. BUT: The fugacity not only depends on β, but also on μ. As N is kept fixed, μ has to change with temperature. With

equation (7.25) [Page 160], from $n = N/V = konst$ again follows

$$0 = \frac{d\tilde{n}}{dT} = \frac{d}{dT}\lambda_T^{-3}g_{3/2}^1(z) = \lambda_1^{-3}\frac{d}{dT}T^{3/2}g_{3/2}^1(z)$$

$$= \lambda_1^{-3}\left(\frac{3}{2}T^{1/2}g_{3/2}^1(z) + T^{3/2}\frac{d}{dz}g_{3/2}^1(z)z'\right)$$

$$= \lambda_1^{-3}\left(\frac{3}{2}T^{1/2}g_{3/2}^1(z) + T^{3/2}g_{1/2}^1(z)\frac{z'}{z}\right) ;$$

$$\Rightarrow \quad \frac{z'}{z} = -\frac{3}{2T}\frac{g_{3/2}^1(z)}{g_{1/2}^1(z)} .$$

Thus we have the final result

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Heat capacity

$$\frac{C_V}{Nk_B} = \begin{cases} \frac{15}{4}\frac{g_{5/2}^1(z)}{g_{3/2}^1(z)} - \frac{9}{4}\frac{g_{3/2}^1(z)}{g_{1/2}^1(z)} & \text{for } T > T_C \quad (a) \\[2ex] \frac{15}{4}\frac{\zeta(5/2)}{\zeta(3/2)}\left(\frac{T}{T_C}\right)^{3/2} & \text{for } T \leq T_C \quad (b) \end{cases} \tag{7.34}$$

$$\frac{15}{4}\frac{\zeta(5/2)}{\zeta(3/2)} = 1.925 .$$

</div>

We now want to plot $C_V(T)$ as function of T. For $T \leq T_C$ the expression in equation (7.34) [Page 169] is simple and universally valid independent of the density.

Now we turn to the case $T > T_c$ and a fixed density $\tilde{n}$. Here we have no condensate and the density is given by

$$\tilde{n} = \lambda_1^{-3}T^{3/2}g_{3/2}^1(z) .$$

If $\tilde{n}$ is fixed this equation gives the dependence of μ on T. From this equation we can also derive how z behaves for $T \to \infty$ if $\tilde{n}$ is kept fixed. For $T \to \infty$ the right hand site would also go to infinity, unless $g_{3/2}^1(z)$ goes to zero. That in turn means that $z \to 0$.

In addition, we obtain for for $T = T_C$ and still the same density we have ($z = 1!!$)

$$\tilde{n} = \lambda_1^{-3}T_C^{3/2}g_{3/2}^1(1) .$$

Dividing the two equations yields

$$1 = \left(\frac{T}{T_C}\right)^{3/2} \frac{g_{3/2}^1(z)}{\zeta(3/2)} \; ; \qquad \Rightarrow \frac{T}{T_C} = \left[\frac{g_{3/2}^1(z)}{\zeta(3/2)}\right]^{-2/3} . \tag{7.35}$$

This equation tells us how T depends on z or rather μ. For later use we rewrite this expression as

$$g_{3/2}^1(z) = \zeta(3/2)\left(\frac{T}{T_C}\right)^{-3/2} . \tag{7.36}$$

For $z \ll 1$ the left hand site can be replaced by z and we have

$$z \ll 1 \; \Rightarrow \qquad z = \zeta(3/2)\left(\frac{T}{T_C}\right)^{-3/2} . \tag{7.37}$$

In order to plot the specific heat for $T \geq T_C$ we use the following approach: We choose a value $z \in (0, 1)$. From equation (7.35) [Page 170] we then calculate the corresponding temperature and evaluate C_V for z and this temperature according to equation (7.34) [Page 169] a). For the limit $T \to \infty$
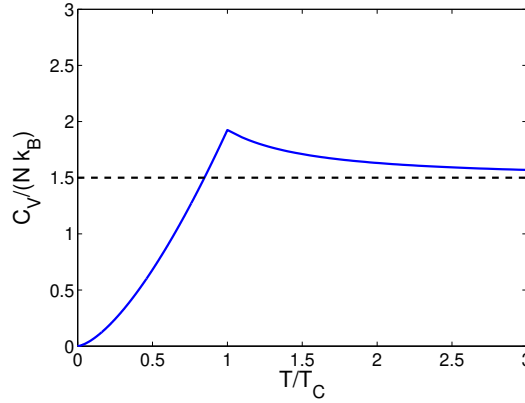
Figure 7.7: Heat capacity of the ideal Bose gas. Dashed line: Classical result

or rather $\beta \to 0$. From the previous slide we know that we then have $z \to 0$. For small values of z we have $g_l(z) \approx z$ and therefore in this limit we get

$$\frac{C_V}{Nk_B} \xrightarrow[T \to \infty]{} \frac{15}{4} - \frac{9}{4} = \frac{3}{2}.$$

This is the result for the classical ideal gas for which $U = \frac{3}{2}Nk_BT$. The specific heat depicted in the figure is similar to that of ^{4}He. However the latter diverges at T_C.

7.2.6 Entropy and latent heat

Starting from

$$\frac{\Omega(Z(V,\mu,T)}{Vk_BM_S} = -T\lambda_T^{-3}g_{5/2}^1(z) + \frac{T}{V}\ln(1-z)$$

$$= -T^{5/2}\lambda_1^{-3}g_{5/2}^1(z) + \frac{T}{V}\ln(1-z)$$

we calculate the entropy via $S = -\frac{\partial\Omega}{\partial T}\big|_{\mu,V}$

$$\frac{S}{Vk_BM_S} = \frac{\partial}{\partial T}\left(T^{5/2}\lambda_1^{-3}g_{5/2}^1(z)\right)\bigg|_{\mu,V} - \frac{\partial}{\partial T}\left(\frac{T}{V}\ln(1-z)\right)\bigg|_{\mu,V}. \tag{7.38}$$

The last term in equation (7.38) [Page 171] vanishes in the thermodynamic limit.

$$\frac{\partial}{\partial T}\left(\frac{T}{V}\ln(1-z)\right)\bigg|_{\mu,V} = \frac{\ln(1-z)}{V} - \frac{T}{V(1-z)}\frac{\partial z}{\partial\beta}\frac{d\beta}{dT}$$

$$= \frac{\ln(1-z)}{V} + \frac{T}{V(1-z)}z\frac{1}{k_BT^2}$$

it has been proven for the grand canonical potential that the first term vanishes in the thermodynamic limit. The second vanishes for the following reasons: For $T > T_C$ we have $z < 1$. Then it vanishes with $1/V$. For $T \le T_C$ $z = 1 + O(V^{-1})$ applies and we have $V(1-z) \to const$, but $\mu \to 0$.
This also means, as the correction term originates from the condensate:

The condensate does not contribute to the entropy.
The entropy of the condensate is zero.

Therefore only the first term of equation (7.38) [Page 171] remains.

$$\frac{S}{Vk_BM_S} = \frac{\partial}{\partial T}\left(T^{5/2}\lambda_1^{-3}g_{5/2}^1(z)\right)\bigg|_{\mu,V}. \tag{7.39}$$

Again, we discuss the two temperature ranges sepertately.

A) $T < T_C$

In the thermodynamic we here have $z = 1$, which is independent of T. With that we get

$$\frac{S}{Vk_BM_S} = \frac{5}{2}T^{3/2}\lambda_1^{-3}g_{5/2}^1(1) = \frac{5}{2}\lambda_T^{-3}\zeta(5/2) , \tag{7.40}$$

or

$$\frac{S}{k_B} = V \ M_S \ \lambda_T^{-3} \cdot \frac{5}{2}\zeta(5/2) \ .$$

From equation (7.24) [Page 159] we know that in the condensate the density of particles in the normal phase is $n_n = M_S\lambda_T^{-3}\zeta(3/2)$. Thus we have

$$\frac{S}{k_B} = \frac{5}{2}\frac{\zeta(5/2)}{\zeta(3/2)} \cdot N_n(T) \ ,$$

With $N_n(T)$ being the total number of particles that are not part of the condensate. This means that in the regular state the entropy per particle is

$$\frac{S}{N_n} = \frac{5}{2}\frac{\zeta(5/2)}{\zeta(3/2)} \ k_B \ .$$

As the entropy of the particles in the condensate is zero, the difference in entropy between a single particle in the condensate and one in the regular state is

$$\frac{\Delta S}{N_n} = \frac{5}{2}\frac{\zeta(5/2)}{\zeta(3/2)} \ k_B \ .$$

That leads to

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LATENT HEAT
(per particle)

$$L := T\frac{\Delta S}{N} = \frac{5}{2} \ \frac{\zeta(5/2)}{\zeta(3/2)} \ k_B T \ . \tag{7.41}$$

</div>

This is the energy released when a **normal particle** is converted into a **condensed particle**.
Thus we get a **mixed phase**, in which two phases coexist, as they do in a **first order phase transitions** (for example: water $\leftrightarrow$ ice)

B) Clausius-Clapeyron relation

In the coexistence region of a phase transition, the Clausius-Clapeyron equation should apply. For this we need the derivative of the vapour pressure

as a function of temperature. With the vapour pressure from equation (**??**) [Page **??**] this derivation is

$$p_C(T) = M_S \, k_B \, \lambda_1^{-3} \zeta(5/2) \; T^{5/2} \; ;$$

$$\frac{dp_C(T)}{dT} = \frac{5}{2} \, M_S \, k_B \, \lambda_1^{-3} \zeta(5/2) \; T^{3/2} = \frac{5}{2} \, M_S \, k_B \, \lambda_T^{-3} \zeta(5/2) \; .$$

Using equation (7.20) [Page 159]

$$n_C = M_S \lambda_T^{-3} \zeta(3/2)$$

the right hand side of the above equation can be rewritten to

$$\frac{dp_C(T)}{dT} = \frac{5}{2} \, \frac{\zeta(5/2)}{\zeta(3/2)} \, k_B \, n_C$$

and this in turn can be rewritten into

$$\frac{dp_C(T)}{dT} = \frac{L}{T} \, n_C \; .$$

using equation (7.41) [Page 172]. Eventually we need the difference between the specific volumes and both coexisting phases.

$$\Delta v = v_C - 0 = \frac{1}{n_C} \; .$$

Thus the slope of the coexistence curve is given by

CLAUSIUS-CLAPEYRON RELATION
(*for ideal Bosons*)

$$\frac{dp_C(T)}{dT} = \frac{\Delta s}{\Delta v} = \frac{L}{T\Delta v} \; .$$

C) Finally we consider the temperature range $T > T_C$

Above T_C we have $z < 1$. The fugacity also contributes to the derivative in equation (7.38) [Page 171].

$$
\begin{aligned}
\frac{S}{Vk_BM_S} &= \frac{\partial}{\partial T}\left(T^{5/2}\,\lambda_1^{-3}g_{5/2}^1(z)\right)\\
&= \frac{5}{2}\lambda_T^{-3}g_{5/2}^1(z) + \lambda_1^{-3}\,T^{5/2}\underbrace{\left(\frac{d}{dz}g_{5/2}^1(z)\right)}_{\overset{(7.6)}{=}g_{3/2}^1(z)\,/z}\frac{dz}{dT}\\
&= \frac{5}{2}\lambda_T^{-3}g_{5/2}^1(z) + \lambda_T^{-3}\,T\,g_{3/2}(z)z^{-1}\,z\frac{(-\mu)}{k_BT^2}\\
&= \frac{5}{2}\lambda_T^{-3}g_{5/2}^1(z) + \underbrace{\lambda_T^{-3}g_{3/2}(z)}_{\tilde{n}}\frac{(-\mu T)}{k_BT^2}\\
&= \frac{5}{2}\lambda_T^{-3}g_{5/2}^1(z) - \beta\mu\tilde{n}\ .
\end{aligned}
$$

Comparing this resulult with the result for the condensate phase from equation (7.40) [Page 171] we get

$$
\frac{S}{Vk_BM_S} = \begin{cases}\frac{5}{2}\lambda_T^{-3}g_{5/2}^1(1) & \text{for } T \le T_C\\ \frac{5}{2}\lambda_T^{-3}g_{5/2}^1(z) - \beta\mu\tilde{n} & \text{for } T > T_C\end{cases}
$$

and realise, that we can synthesise them, as we have $T \le T_C$ $z = 1$ and $\mu = 0$. Together with $\mu\beta = \ln[z]$ we get the

---

ENTROPY OF THE IDEAL BOSE GAS

$$
\frac{S}{Vk_BM_S} = \frac{5}{2}\lambda_T^{-3}g_{5/2}^1(z) - \ln[z]\tilde{n}\ .
$$

In order to plot the entropy as a function of temperature we proceed in a similar way as we did for the specific het. For $T \le T_C$ we use

$$
\frac{S}{Vk_BM_S} = \frac{5}{2}\lambda_1^{-3}\zeta(5/2)T^{3/2}\ .
$$

We can rewrite this term using the definitions of T_C from equation (7.21) [Page 159].

$$T_C^{-3/2} := \left\{ \left(\frac{\tilde{n}}{\Lambda} \right)^{2/3} \right\}^{-3/2} = \frac{\Lambda}{\tilde{n}} = \frac{\lambda_1^{-3} \zeta(3/2)}{\tilde{n}}$$

$$\Rightarrow \qquad \lambda_1^{-3} = \frac{\tilde{n} \, T_C^{-3/2}}{\zeta(3/2)} \; .$$

Thus the following is also valid:

$$\frac{S}{V k_B M_S} = \tilde{n} \, \frac{5}{2} \frac{\zeta(5/2)}{\zeta(3/2)} \left(\frac{T}{T_C} \right)^{3/2} \; .$$

For the region $T > T_C$ we choose an allowed value for the fugacity ($z \in (0,1)$). Then we use equation (7.35) [Page 170]

$$\frac{T}{T_C} = \left[\frac{g_{3/2}^1(z)}{\zeta(3/2)} \right]^{-2/3} \tag{7.42}$$

to calculate the corresponding temperature T/T_C, which we use as the value of the abscissa in the graph. Furthermore, int the expression for the entropy

$$\frac{S}{V k_B M_S} = \frac{5}{2} \lambda_T^{-3} g_{5/2}^1(z) - \ln[z] \tilde{n}$$

we will eliminate the thermal de Broglie wavelength. For $T > T_C$ we use equation (7.25) [Page 160], which says

$$\tilde{n} = \lambda_T^{-3} g_{3/2}^1(z) \Rightarrow \qquad \lambda_T^{-3} = \frac{\tilde{n}}{g_{3/2}^1(z)} \; .$$

The expression for entropy thus contains only the fugacity and the density.

$$\frac{S}{V k_B M_S} = \tilde{n} \left(\frac{5}{2} \frac{g_{5/2}^1(z)}{g_{3/2}^1(z)} - \ln[z] \right) ; \tag{7.43}$$

or rather: $\qquad \dfrac{S}{N k_B M_S} = \dfrac{5}{2} \dfrac{g_{5/2}^1(z)}{g_{3/2}^1(z)} - \ln[z] \; . \tag{7.44}$

Now we can easily plot a mark at the data pair $S/N, T/T_C$, which corresponds to the chosen z-value. Finally, we repeat the procedure for enough z-values to obtain a smooth curve. The resulting graph is depicted in Figure 7.8. Again, the comparison with the classical result is interesting. To this end we
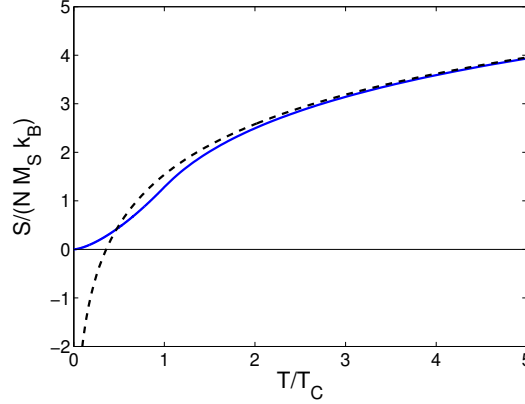
Figure 7.8: Entropy of an ideal Bose gas. Dashed line: classical result

recall equation (7.36) [Page 170]

$$g_{3/2}^1(z) = \zeta(3/2)\left(\frac{T}{T_C}\right)^{-3/2} .$$

For $\frac{T}{T_C} \gg 1$ we obtain

$$g_{3/2}^1(z) \to 0 \Rightarrow \qquad z \to 0$$

$$\Rightarrow \qquad \frac{g_{5/2}^1(z)}{g_{3/2}^1(z)} \to 1 .$$

We replace the argument of the logarithm in equation (7.44) [Page 175] – z – according to equation (7.37) [Page 170] with $\zeta(3/2)(T/T_C)^{-3/2}$ and obtain

$$\frac{S}{Vk_BM_S} = \frac{5}{2} + \frac{3}{2}\ln\left[\frac{T}{T_C}\right] - \ln\left[\zeta(3/2)\right] . \tag{7.45}$$

Classically we had

$$\frac{S}{k_BN} = \ln\left(\frac{T^{\frac{d}{2}}}{n\lambda_1^d}\right) + \frac{d+2}{2}$$

$$\text{for } d = 3 \Rightarrow \qquad = \ln\left(\frac{T^{\frac{3}{2}}}{n\lambda_1^3}\right) + \frac{5}{2} .$$

Via equation (7.23) [Page 159] we can now replace the combination of parameters $\tilde{n}\lambda_1^3$ with $\zeta(3/2)T_C^{3/2}$. That leads to

$$\frac{S}{Nk_BM_S} = \frac{5}{2} + \frac{3}{2}\ln\left[\frac{T}{T_C}\right] - \ln\left[\zeta(3/2)\right] ,$$

in agreement with the above limit of the quantum mechanical result in equation (7.45) [Page 176]. Here T_C is just a combination of parameters, which can be used, although there is no phase transition in the classical system.
In Figure 7.8 we also see that the quantum mechanical result approaches the classical result for $T/T_C > 1$. We also find that the classical result becomes invalid for low temperatures, and there the discrepancy is as large as it can be. In the classical case the entropy diverges, while in the quantum case it is zero.

7.2.7 Is ^{4}He an ideal Bose gas?

Finally we will discuss, how well liquid ^{4}He can be described by an ideal Bose gas. The subject of Bose condensation and superfluidity has already led to two Nobel prices:

- 2003: Alexei Abrikossow, Witali Ginsburg, Anthony James Leggett **for groundbreakin work on the theory of superconductors and superfluids**.

- 2001: Eric A. Cornell, Wolfgang Ketterle, Carl E. Wieman **for producing Bose-Einstein condensation in diluted gases of alkali atoms and for early fundamental studies on the properties of condensates**.

Liquid helium is an extraordinary liquid, whih can exist in two phases: Normal helium (He I) or superfluid helium (He II). Those two phases are seperated by the so called lambda phase transition, which is located at approximately $T = 2.2K$. Experimentally, one finds a logarithmic divergence at
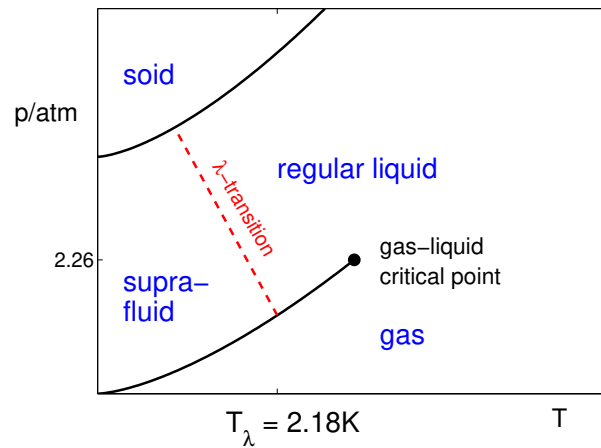

Figure 7.9: Phase diagram of ^{4}He.

T_C.

Is it a valid assumption that the transition can be described with the BEC transition of ideal Bosons, even when it is modified by two-particle interaction? The good agreement of the transition temperature that we have calculated for ^{4}He and $T_C = 3.13K$ in the ideal Bose gas model, seems to suggest that. Also the circumstance that two phases coexist coincides: A superflid phase corresponding to the the Bose-Einstein condensate and a regular phase, corresponding to the atoms in excited states.

Also the observation of the particles in the superfluid phase having no entropy is the same.

However, there is also:

- ^{3}He also becomes superfluid for low temperatures. Hwever, here we have a system of Fermions, for which there is no Bose-Einstein condensation in its basic form.

- The λ transition is no first ordeer phase transition and thus we cannot have pure Bose-Einstein condensation.

- BEC: in the P-T plane $P_C \propto T^{5/2}$ increases while the λ line decreases with temperature.

- The arguments of Landau that ideal Bose gases cannot become superfluid. One can even show that superfluidity only occurs for interacting Bosons.

7.2.8   BEC in laser cooled atoms in a magnetic trap

The exact theoretical discussion of ^{4}He is difficult, as the high density causes very strong interaction. It is substantially easier for a system of lower density and weaker interaction. This is the case for BEC in a magnetically trapped, laser cooled, diluted atomic gases. Because of their magnetic moments, neutral alkali atoms can be trapped with a suitable magnetic field and subsequently be cooled with lasers.

- Alkali atoms have one valence electron (s-orbital), which is important for laser cooling.

- Isotopes, for which the total spin of electron and nucleus is an integer and for which Bose statistics applies, are used.

- All atoms have a magnetic moment, which is essential for magnetic confinement.

The first experiments that were awarded with a Nobe price in phyiscs [1] used rubidium atoms ($A = 86$) and sodium atoms ($A = 23$).

How was BEC observed in those systems? The magnetic trap confines the atoms within a parabolic potential (harmonic oscillator). The ground state of the harmonic oscillator extends over $a_0 = (\hbar/m\omega)^{1/2}$. The extent of the νth excited state is approximately $R_\nu = \nu^{1/2}a_0$. The number of thermally occupied levels is $\nu_{max} = \frac{k_B T}{\hbar\omega}$ without BEC. Thus the dimensions without BEC would be

$$R_T = \sqrt{\frac{k_B T}{\hbar\omega}}\, a_0 \gg a_0 \ .$$

For $T > T_C$ one therefore sees a nearly homogenous density distribution of the radius $R_{T_C} \gg a_0$. Below T_C, however, a finite portion of the Boson cloud is in the ground state, which extends over a_0. For decreasing temperatures (for $T < T_C$), one observes an increasing rise of a sharp peak in the center in the experiments.

By now it is possible to trap 100 to 10^{10} within a relatively small volume. With this one can reach very low temperatures of $T = 10^{-8}K - 5 \cdot 10^{-5}K$ and low densities of $n = (10^{11} - 10^{15})\text{cm}^{-3}$ (instead of 10^{24}).

The magnetic field that is used creates a harmonic potential, which we shall – for the sake of simplicity – assume to be isotropic.

$$V(\vec{x}) = \frac{m\omega^2}{2}\vec{x}^{\,2} \ .$$

Then we get the well known quantised energies

$$E_{\vec{l}} = \hbar\omega \sum_{i=1}^{d} l_i \ ,$$

Here we absorb the zero point energy into the chemical potential. The quantum numbers are $l_i \in \mathbb{N}_0$. The calculation of T_C is very similar to that of free bosons. For condensation to occur, the fugacity in the thermodynamic limit must be $z = 1$, since only then we have a macroscopic occupation of n_0. The transition temperature is the temperature for which $z = 1$ first occurs and where the total number of particles is still in the regular state. Thus we have the condition

$$\tilde{N} = \tilde{N}_n(T_C, z = 1) \ .$$

[1] Nobel price for physics 2001: Wolfgang Ketterle, Eric A. Cornell und Carl E. Wieman: *for producing Bose-Einstein condensation in diluted gases of alkali atoms and for early fundamental studies on the properties of condensates.*

As a reminder: $\tilde{N} = N/(2S + 1)$. The number of Bosons $\tilde{N}_n$ in the regular state is determined by equation (6.10) [Page 140] without special treatment of the ε_0-term.

$$N_n(T_C, z = 1) = \sum_{l_1,..,l_d=0}^{\infty} \frac{1}{e^{\beta_C \hbar \omega \sum_i l_i} - 1} \ .$$

Since the calculation of the density of states is a bit more elaborate, we will apply another method that uses the sum formula outlined in Appendix (E) [Page 214]. In the case at hand we have $\delta_i = \frac{\hbar \omega}{k_B T_C}$ and

$$\Delta V = \left(\frac{\hbar \omega}{k_B T_C} \right)^d$$

With equation (E.3) [Page 217] we convert the sum into an integral.

$$\tilde{N} \stackrel{!}{=} \left(\frac{k_B T_C}{\hbar \omega} \right)^d \int_0^{\infty} \cdots \int_0^{\infty} \frac{1}{e^{\sum_i x_i} - 1} d^d x \ . \tag{7.46}$$

The relative uncertainty for this is – according to Appendix (E) [Page 214] – of the order

$$\delta = \frac{\hbar \omega}{k_B T_C} \ . \tag{7.47}$$

The experimental values for ω are in the range of $(100 - 1000)s^{-1}$ and $T_C = O(10^{-7}K)$. Thus we get an estimate for δ

$$\delta = \frac{\hbar \omega}{k_B T_C} \lesssim \frac{1.1 \cdot 10^{-34} \cdot 10^3}{1.4 \cdot 10^{-23} \cdot 10^{-7}} = 8 \cdot 10^{-2} \ .$$

Thus δ is still small enough to allow the approximation of the sum with the simple integral. We will now calculate the integral of equation (7.46) [Page 180].

$$\tilde{N} = \left(\frac{k_B T_C}{\hbar \omega} \right)^d \int_0^{\infty} \cdots \int_0^{\infty} \frac{e^{-\sum_l x_i}}{1 - e^{-\sum_l x_i}} \ d^d x$$

$$= \left(\frac{k_B T_C}{\hbar \omega} \right)^d \sum_{m=0}^{\infty} \int_0^{\infty} \cdots \int_0^{\infty} e^{-(m+1) \sum_l x_l} \ d^d x$$

$$= \left(\frac{k_B T_C}{\hbar \omega} \right)^d \sum_{m=0}^{\infty} \left(\int_0^{\infty} e^{-(m+1) \, x} \ dx \right)^d$$

$$= \left(\frac{k_B T_C}{\hbar \omega} \right)^d \sum_{m=0}^{\infty} \left(\frac{1}{m+1} \right)^d \ .$$

So the result we are looking for is:

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<center>TRANSITION TEMPERATURE
(*for BEC in a harmonic trap*)</center>

$$\tilde{N} = \left(\frac{k_B T_C}{\hbar \omega}\right)^d \zeta(d) \tag{7.48}$$

$$\frac{k_B T_C}{\hbar \omega} = \left(\frac{\tilde{N}}{\zeta(d)}\right)^{1/d} \tag{7.49}$$

</div>

An important property is that BEC now also exists for $d = 2$, as we now have $\zeta(3) = 1.2021$ and $\zeta(2) = 1.6449$ with only $\zeta(1) = \infty$.

The transition temperatures one gets for given experimental number of particles and trap frquency ω are in the range of nano- and micro Kelvin. Of course this is a crude estimate, as the interaction between particles was neglected. The values, however, are again of the right order of magnitude.

equation (7.48) [Page 181] gives the appearance that a different universal power law is at work for T_C than for equation (7.21) [Page 159] due to the changed confinement potential. There we had found the following dependence for $d = 3$:

$$\tilde{n} = \lambda_{T_C}^{-3} \zeta(\frac{3}{2})$$

This impression, however, is deceiveng, as on the left side of equation (7.48) [Page 181] stands not only the density,but the whole number of particles. For the harmonic oscillator there exists no fixed volume. However, we can estimate the volume as follows: According to QM I the average quadratic radial expansion of the ocillators is

$$\langle r^2 \rangle_n := 3\langle x^2 \rangle_n = 3a_0^2 n \; ;$$
$$a_0^2 := \frac{\hbar}{m\omega} \; .$$

We are interested in the expansion at temperature T_C. The corresponding thermodynamic expectation value for r^2 results in

$$\langle r^2 \rangle_{T_C} = 3a_0^2 \langle n \rangle_{T_C} = \frac{3a_0^2}{e^{\beta_C \hbar\omega} - 1} \overset{\beta_C \hbar\omega \ll 1}{=} \frac{3a_0^2 k_B T_C}{\hbar\omega} \; .$$

In the end we thus get the average volume at T_C.

$$\langle V \rangle_{T_C} = \frac{4\pi}{3} \langle r^2 \rangle_{T_C}^{3/2} = \frac{4\pi a_0^3 3^{3/2}}{3} \left(\frac{k_B T_C}{\hbar \omega} \right)^{3/2}$$

$$\Rightarrow \qquad \left(\frac{k_B T_C}{\hbar \omega} \right)^{3/2} = \frac{\langle V \rangle_{T_C}}{4\pi \sqrt{3} a_0^3} \; .$$

Plugging this into equation (7.48) [Page 181] for $d = 3$ we get

$$\tilde{N} = \left(\frac{k_B T_C}{\hbar \omega} \right)^{3/2} \left(\frac{k_B T_C}{\hbar \omega} \right)^{3/2} \zeta(3) = \frac{V}{4\pi \sqrt{3} a_0^3} \left(\frac{k_B T_C}{\hbar \omega} \right)^{3/2} \zeta(3)$$

$$\tilde{n} = \frac{(2\pi)^{3/2}}{4\pi \sqrt{3}} \left(\frac{k_B T_C}{2\pi a_0^2 \hbar \omega} \right)^{3/2} \zeta(3) = \frac{\sqrt{2\pi}}{2\sqrt{3}} \left(\frac{m \omega k_B T_C}{2\pi \hbar \hbar \omega} \right)^{3/2} \zeta(3)$$

$$= \sqrt{\frac{\pi}{6}} \underbrace{\left(\frac{m k_B T_C}{2\pi \hbar^2} \right)^{3/2}}_{\lambda_{T_C}^{-3}} \zeta(3) \; .$$

TRANSITION TEMPERATURE FOR BEC IN A HARMONIC TRAP

$$\tilde{n} = \underbrace{\zeta(3) \sqrt{\frac{\pi}{6}}}_{=0.8698} \; \lambda_1^{-3} \; T_C^{3/2} \; ;$$

$$\lambda_1^{-3} = \left(\frac{k_B m}{2\pi \hbar^2} \right)^{3/2} \; .$$

We still have the same power law. Only the prefactor was canged.

7.2.9   Why does BEC only occur in quantum systems?

The reason for this is the indistinguishability of the particles. We shall once more consider the case of discrete single-particle energies ε_i for $i = 1, \ldots, L$. Each particle can occupy one of the single-particle energies ε_i. The total energy then is the sum over the occupied single-particle energies.

$$E = \sum_{\nu=1}^{N} \varepsilon_{i_\nu} \; ,$$

Here i_ν states, in which single-particle state the νth particle is. Alternatively we can also write the energy as

$$E(\{n_i\}) = \sum_{i=1}^{L} \varepsilon_i \, n_i \;,$$

With n_i stating the number of particles occupying the state i. These occupation numbers can assume the values $0, \ldots, \infty$. However, for the (micro-) canonical ensemble the condition for the number of particles has be fulfilled.

$$\sum_{i=1}^{L} n_i = N \;.$$

For every energy $E(\{n_i\})$ that is defined by the occupation numbers the

---

MULTIPICITY OF DISTINGUISHABLE PARTICLES

$$M(\{n_i\}) = \frac{N!}{\prod_i n_i!}$$

---

for different configurations $\{i_\nu\}$ contributes (multinomial coefficient). This means that the probability to find the particles with those occupation numbers together with the Boltzmann factor gives

$$P(\{n_i\}) = \frac{1}{Z} \frac{N!}{\prod_i n_i!} e^{-\beta E(\{n_i\})} \;.$$

In order to understand the main reason for or against BEC, we can simplify the Boltzmann factoer. We replace it with the step function: All energies below $k_B T$ occur with the same probability and the probability for those above is zero. Within the allowed range of energies there shall be L states, that all have the same probability $1/L$. The probability for a certain distribution of occupation numbers then can be simplified to

$$P(\{n_i\}) = \frac{N!}{\prod_i n_i!} L^{-N} \;.$$

We asume that the number of states within the range of energies $k_B T$ is smaller than the number of Bosons (only then BEC occurs). The most probable distribution of occupation numbers is the an equal distribution with

$$m := \frac{N}{L}$$

particles per single-particle level. We now calculate the ration between the
probability of the equal distribution to that of the distribution which occurs
for BEC, where all particles are in the lowest level.

$$q := \frac{P(\text{gleichverteilt})}{P(\text{alle in einer Zelle})} = \frac{\frac{N!}{(m!)^L} \, L^{-N}}{\frac{N!}{N!(0!)^{L-1}} \, L^{-N}} = \frac{N!}{(m!)^L} = \frac{N!}{((\frac{N}{L})!)^L}$$

$$\ln(q) \approx N \ln(N) - N - L \left(\frac{N}{L} \ln \left(\frac{N}{L} \right) - \frac{N}{L} \right)$$

$$= N \ln(N) - N - N \ln \left(\frac{N}{L} \right) + N$$

$$= N \ln(L) \; ;$$

$$q \approx e^{N \ln(L)} = L^N \gg 1 \; .$$

For indistinguishable particles, however, every distribution of occupation
numbers has the same apriori probability, as we already discussed. Thus
we have

$$q = 1 \; .$$

Therefore we can see that in the classical case of distinguishable particles
there is an extremely strong entropic force towards equal distribution. This
force cannot we overpowered by the Boltzmann factors. For indistinguishable
particles this part of the entropy term does not exist.

7.3   Black-body radiation

As a last application we shall discuss thermal radiation. An example for
thermal radiation is radiation produced by an ordinary heater or a campfire.
Aside from heat transport by convection, also thermal radiation exists. A
person in close proximity to the heat source feels the energy the fire radiates,
even when the surrounding air is very cold. Thermal radiation is produced,
when the thermal energy of the movement of charge carriers in the material
(electrons and protons) is converted into electromagnetic radiation. Sunlight
consists of electromagnetic radiation that is produced by the extremely hot
plasma of the sun. Obviously convection does not transport that energy to
earth.
*Definition from Wikipedia Black-body radiation is the thermal electromag-
netic radiation within or surrounding a body in thermodynamic equilibrium
with its environment, or emitted by a black body (an opaque and non-reflective
body). It has a specific spectrum and intensity that depends only on the body's
temperature, which is assumed for the sake of calculations and theory to be
uniform and constant*

7.3.1 Model system

As a model system we consider an empty box with walls that contain atoms, which are responsible for thermal energy (temperature) as well as for the processes of adsorption and the emission of photons. These photons move into the cavity of the box and form standing electromagnetic wave. We do not need to concern ourselves with the details of the processes in the walls. In this model the walls only represent a heat bath and a reservoire of photons. The number of photons in the entire coupled system is not conserved (same as for phonons, magnons and so on). When coupling a system to a heat bath, in general the free energy has to become minimal with respect to all parameters that are not fixed by the boundary conditions. Here, N is the variable of interest. Then we find

$$\left(\frac{\partial F(T,N,V)}{\partial N} \right) \bigg|_{T,V} = 0 \ .$$

On the other hand, the left side of this equation is the definition of the chemical potential. In the case where there is no conservation of particles, the following therefore applies

$$\mu = 0 \ ;$$
$$F = \Omega \ .$$

The photons in the cavity interact with the atoms in the walls, and photons are created and annihilated and their energy is exchanged. This leads to a thermal equilibrium, where the temperature is defined by the walls. Photons (electromagnetic waves, solutions of the free Maxwell equations) describe mass free excitations with linear dispersion

$$\varepsilon(\vec{k}) = \hbar\omega(\vec{k}) = \hbar c \ k \ ,$$

Here k is the absolute value of the wave vector $\vec{k}$. The cavity shall be – as it was in previous examples – a cuboid of the dimensions (L_x, L_y, L_z). We use *open boundary conditions*. I.e. the oscillations are expanded with respect to $\sin(k_\alpha x_\alpha)$. This leads to a quantisation of the components of the wave vector

$$k_\alpha = \frac{\pi}{L_\alpha} l_\alpha \ , \tag{7.50}$$

with $l_\alpha \in \mathcal{N}_0$. However, one has to consider:

There is no state with $\vec{k} = \vec{0}$, as it does not contain an oscillation quantum. Thus there is no condensation either.

The distribution function and the density of states for photons is is derived in equation (F.1) [Page 219] in Appendix (F.2) [Page 219].

We now have to consider that we not only have to sum over all k vectors but also two directions of polarisation. This yields an extra factor of 2.

DISTRIBUTION FUNCTION AND DENSITY OF STATES
(for photons in 3d)

$$\rho(\varepsilon) = C_{ph}\ \varepsilon^2\ ; \tag{7.51}$$

$$F_\rho(\varepsilon) = \frac{C_{ph}}{3}\ \varepsilon^3\ ; \tag{7.52}$$

$$C_{ph} = \frac{V}{\pi^2(\hbar c)^3}\ . \tag{7.53}$$

7.3.2   Grand canonical potential

Using equation (6.11) [Page 142] and equation (6.14) [Page 143], the grand canonical potential for **Bosons** can be calculated. It has to be taken into consideration that because of $\mu = 0$ the fugacity is $z = 1$.

$$\Omega(T, V) = -\int \frac{1}{e^{\beta\varepsilon} - 1}\ F_\rho(\varepsilon)\ d\varepsilon\ .$$

Therefore the grand canonical potential is

$$\Omega(T,V) \overset{(7.52)}{=} -\frac{V}{3\pi^2\ (\hbar c)^3}\ \int_0^\infty \frac{1}{e^{\beta\varepsilon} - 1}\varepsilon^4\ \frac{d\varepsilon}{\varepsilon}$$

$$\overset{(G.4)}{=} -\frac{V}{3\pi^2\ (\hbar c)^3}\ (k_B T)^4 \zeta(4)\Gamma(4)\ . \tag{7.54}$$

With $\zeta(4) = \pi^4/90$ and $\Gamma(4) = 6$ we finally get

$$\Omega(T,V) = -\frac{V\pi^2}{45}\frac{(k_B T)^4}{(\hbar c)^3}\ .$$

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GRAND CANONICAL POTENTIAL

$$\Omega(T,V) = -V\,\frac{\alpha}{3}\,T^4 \; ; \tag{7.55}$$

$$\alpha := \frac{\pi^2}{15}\frac{(k_B)^4}{(\hbar c)^3} \; ; \qquad \text{(Stefan-Boltzmann constant)} \tag{7.56}$$

$$\alpha = 1.3806485210^{-23}\frac{J}{m^2 K^4} \tag{7.57}$$

</div>

7.3.3   Radiation pressure

From equation (7.55) we can immediately read off the radiation pressure.

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RADIATION PRESSURE

$$p = -\Omega/V = \frac{\alpha}{3}\,T^4 \; .$$

</div>

7.3.4   Entropy

Also the entropy can be derived from the grand canonical potential with ease.

$$S(T,V) = -\left(\frac{\partial\Omega}{\partial T}\right)\bigg|_V \; .$$

We obtain

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ENTROPY

$$S(T,V) = \frac{4\alpha}{3}VT^3$$

</div>

7.3.5 Spectral emissivity (Planck's law of radiation)

According to equation (6.12) [Page 142] the internal energy of an ideal quantum gas is

$$U = \langle H \rangle = \int \varepsilon \rho(\varepsilon) \langle n_\varepsilon \rangle_{T,\mu} \, d\varepsilon \; .$$

Therefore the amount of energy that is contained by the photons in the single-particle energy interval $(\varepsilon, \varepsilon + d\varepsilon)$ is equal to the integrand. The spectral emissivity is this average energy per unit of volume and thus

$$S(\varepsilon) = \frac{1}{V} \, \rho(\varepsilon) \, \varepsilon \, \langle n_\varepsilon \rangle_{T,\mu} \qquad (7.58)$$

The result can be understood easily. The oscillator-eigenmodes (photons) are characterised by $\vec{k}$. In thermal equilibrium there are $\langle n_{\varepsilon_{\vec{k}}} \rangle$ of those. The energy content of all photons in the cavity, that are of this wave number, therefore is $\varepsilon_{\vec{k}} \langle n_{\varepsilon_{\vec{k}}} \rangle$. This already explains the latter two factors of equation (7.58) [Page 188]. In the case of the spectral emissivity the analysis is not performed with respect to the wave vector $\vec{k}$, but with respect to the energy ε of the individual photons that leave the cavity through a small hole. The single-particle density of states $\rho(\varepsilon)$ states the number of $\vec{k}$-eigenmodes that contribute to the energy ε.

The factor 2 of the polarisation has to be added too.

Thus the spectral emissivity, i.e. the average energy per unit of volume that is emitted in form of quanta of energy ε, together with the density of states from equation (7.53) [Page 186] gives

---

PLANCK'S LAW OF RADIATION

$$S(\varepsilon, T)d\varepsilon = \frac{\varepsilon^3}{\pi^2 (\hbar c)^3} \frac{1}{e^{\beta \varepsilon} - 1} \, d\varepsilon \; ; \qquad (7.59)$$

$$S(\omega, T)d\omega = \frac{\hbar \omega^3}{\pi^2 \, c^3} \frac{1}{e^{\beta \hbar \omega} - 1} \, d\omega \; .$$

We will now consider the two limiting cases $\hbar\omega \gg k_B T$ and $\hbar\omega \ll k_B T$, which are of historical importance. For the first case we obtain

---

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WIEN APPROXIMATION

</div>

$$S(\omega, T)d\omega = \frac{\hbar\omega^3}{\pi^2\,c^3}\,e^{-\beta\hbar\omega}\,d\omega \; ; \qquad \text{for} \;\; \hbar\omega \gg k_B T \; .$$

---

and for the second case the

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CLASSICAL RAYLEIGHT-JEANS FORMULA

</div>

$$S(\omega, T)d\omega = \frac{\omega^2 k_B T}{\pi^2\,c^3} \; ; \qquad \text{for} \;\; \hbar\omega \ll k_B T \; .$$

7.3.6 Internal energy and average number of particles

Next we actually calculate the internal energy. For this we only have to integrate Planck's law equation (7.59) [Page 188] over ε.

$$U = \frac{V}{\pi^2(\hbar c)^3}\int_0^\infty \frac{1}{e^{\beta\varepsilon}-1}\,\varepsilon^4\,\frac{d\varepsilon}{\varepsilon}\;.$$

This is the same integral as for the grand canonical potential in equation (7.54) [Page 186]. The expression we have here differs only by a factor (-3). Therefore we have:

<div style="text-align: center;">

INTERNAL ENERGY

</div>

$$U = -3\Omega = V\alpha T^4 \; ; \qquad \text{(Stefan-Boltzmann law)} \; .$$

Average number of particles

Finally, the average number of particles (photons) is according to equation (6.13) [Page 142]

$$
\begin{aligned}
\langle N \rangle &= \int \frac{1}{e^{\beta \varepsilon} - 1} \, \rho(\varepsilon) d\varepsilon \\
&\overset{(G.4)}{=} C_{ph} \int \frac{1}{e^{\beta \varepsilon} - 1} \, \varepsilon^3 \frac{d\varepsilon}{\varepsilon} \\
&= C_{ph} \, (k_B T)^3 \, \zeta(3) \, \Gamma(3) \\
&\overset{(7.53)}{=} \frac{V \, 2}{\pi^2 (\hbar c)^3} \, (k_B T)^3 \, \zeta(3) \ .
\end{aligned}
$$

AVERAGE NUMBER OF PARTICLES
(*photons*)

$$
\langle N \rangle = V \, \frac{2 \, \zeta(3)}{\pi^2} \left(\frac{k_B T}{\hbar c} \right)^3 \ .
$$

Plugging in numerical values and $\zeta(3) = 1.20$ for room temperature we obtain

$$
\langle N \rangle \approx 5 \cdot 10^8 \ .
$$

within $1 cm^3$.

7.4 Work, heat and entropy

In the following, we deal with processes of an ideal gas for which we know that the energy in thermodynamic equilibrium and in d spatial dimensions is given by

$$E = \frac{d}{2}Nk_BT \ . \tag{7.60}$$

The following equation of state also applies:

$$pV = Nk_BT \ .$$

This equation does not immediately reveal how pressure and temperature behave when the system is compressed, i.e. the volume is decreased while the number of particles remains fixed, but not temperature. We will now derive this relationship.

7.4.1 Adiabatic Processes

We consider an ideal gas inside a cuboid box. One of the walls shall be a movable (piston) perpendicular to its plane. This direction is defined as the x direction. Now we move the piston with a very small but constant velocity u, which adiabatically decreases the volume of the box. We consider a particle that moves in the direction of the piston. The x component of its velocity is v_x. Now we switch to the reference frame that moves with the piston. There the velocity of the particle is

$$\tilde{v}_x = v_x + u \ .$$

After the collision with the wall, the particle has velocity

$$\tilde{v}_x' = -v_x - u \ .$$

If one transforms this velocity into the original reference frame, one obtains

$$v_x' = -v_x - 2u \ .$$

First we discuss the momentum transfer caused by the collision with the static piston

$$\Delta P_x = -2mv_x \ .$$

The number of particles that collide with the piston during the time dt is

$$dN = \rho A v_x dt \ ,$$

However, these are only the ones with a positive v_x and A is the surface area of the piston. The resulting average momentum transfer during the time dt of particles with velocity v_x yields a momentum transfer

$$dP_x = dN\Delta P_x = \rho A v_x dt \ (-2mv_x) = -2mA\rho \ dt \ v_x^2$$

Next we take the velocity distribution into account and determine the average momentum transfer

$$dP_x^{\mathrm{av}} = -2mA\rho \ dt \ \langle v_x^2 \rangle' \ .$$

One should note that in $\langle \cdot \rangle'$ only the part of the velocity distribution with $v_x > 0$ is used, hence $\langle v_x \rangle'$ is nonzero. We have $\langle v_x^2 \rangle' = \frac{1}{2}\langle v_x^2 \rangle$. Eventually, the the force transmitted to the wall due to these impacts is

$$F_x = \frac{dP_x^{\mathrm{av}}}{dt} = -mA\rho \ \langle v_x^2 \rangle \ .$$

According to Newton's law the force F_x that acts on the piston is also the force, which is transferred to the particles in the gas. The elastic collisions with the wall, therefore, create the pressure

$$p = \frac{|F_x|}{A} = m\rho\langle v_x^2 \rangle \ . \tag{7.61}$$

Furthermore, we have

$$m\rho\langle v_x^2 \rangle = 2\langle \big(N\frac{m}{2}v_x^2 \big) \rangle \frac{1}{V} = 2\frac{E_{kin,x}}{V} \ .$$

Now , for the ideal gas the kinetic energy per spatial direction, e.g. the x-direction, is given by

$$E_{kin,x} = \frac{1}{2}Nk_BT \ .$$

Then

$$m\rho\langle v_x^2 \rangle = 2\frac{E_{kin,x}}{V} = \frac{Nk_BT}{V}$$
$$\Rightarrow \quad pV = Nk_BT \ ,$$

So far we have merely derived the ideal gas law by another way. The result was obtained for the static piston. Now we will discuss the extra term we get by moving the piston adiabatically. As a consequence of the collision with the moving piston, the kinetic energy of a particle changes according to

$$\Delta E_{kin,x} = \frac{m}{2}\bigg(\big(-[v_x + 2u]\big)^2 - v_x^2 \bigg)$$
$$= 2mv_xu + O(u^2) \ .$$

Since the piston is moved adiabatically, we can neglect $O(u^2)$. Multiplying this equation by the number of particles hitting the wall in the time interval dt, we get

$$dE_{kin,x} = \rho A v_x dt \times (2mv_x u)$$
$$= 2m\rho v_x^2 \, A \, u \, dt$$

Now $udt = dx$ is the distance that the piston moves in dt, thereby decreasing the volume. Next we average again over the velocity and use equation (7.61) [Page 192]

$$p = m\rho \langle v_x^2 \rangle$$

and obtain

$$d\langle E_{kin,x} \rangle = -pdV$$

We have taken into account the sign that ensures the reduction of the volume. This is the microscopic derivation of the formula, which we had already derived macroscopically. The ideal gas has only kinetic energy. The change in energy of the ideal gas that is caused by the work of the piston is therefore

$$dE = -pdV = -dW \; .$$

This is the relation of energy, work and change of volume. The sign of the work dW was chosen as follows: When the system performs work (emits energy), we have $dW > 0$:

$$dW = pdV = \begin{cases} > 0 & \text{if } dV > 0 \\ < 0 & \text{if } dV < 0 \end{cases} \; .$$

Due to the work of the piston the energy changes. In the case of an ideal gas, the energy($E = \frac{d}{2} N k_B T$) only depends on T (since N is constant) and we have the relation

$$dE = \frac{3}{2} N k_B \, dT = -pdV \; .$$

Now we want to work out the relationship between T and V. For this purpose we replace p by $N k_B T / V$ and obtain

$$\frac{3}{2} N k_B \, dT = -\frac{N k_B T}{V} \, dV$$
$$\frac{dT}{T} = -\frac{2}{3} \frac{dV}{V}$$
$$\text{integration:} \quad \ln(T) = C + \ln\left(V^{-2/3}\right)$$
$$T \propto V^{-2/3} \; .$$

Applying that to a reference state (T_0, V_0) yields

TEMPERATURE VERSUS VOLUME
(*in adiabatic processes*)

$$\frac{T}{T_0} = \left(\frac{V}{V_0}\right)^{-2/3} .$$

Finally we will derive the relation between pressure and volume for adiabatic changes of the volume. For that purpose we use the ideal gas law and substitute temperature on the left hand side of the last equation by

$$T = \frac{pV}{Nk_B} .$$

Thus

$$\frac{T}{T_0} = \frac{p}{p_0}\frac{V}{V_0} = \left(\frac{V}{V_0}\right)^{-2/3}$$

PRESSURE VERSUS VOLUME
(*in adiabatic processes*)

$$\frac{p}{p_0} = \left(\frac{V}{V_0}\right)^{-5/3} \tag{7.62}$$

---

follows. This means $p \propto V^{-5/3}$.

7.4.2   Isothermal Processes

Next we consider a isothermal process, in which the temperature is kept constant. This is possible by the coupling to a heat bath. If temperature and particle number of the ideal gas do not change, then the energy Nk_BT

does not change, and we find from the equation of state

$$0 = d(Nk_BT) = d(pV) = pdV + Vdp$$
$$\Rightarrow \quad pdV = -Vdp$$
$$\frac{dV}{V} = -\frac{dp}{p} \; .$$

This gives

PRESSURE VERSUS VOLUME
(in isothermal processes)

$$\frac{p}{p_0} = \left(\frac{V}{V_0}\right)^{-1}$$

In this case, the change in pressure is smaller than in the case of he adiabatic compression.

The behaviour can be understood as follows: At first the particles gain kinetic energy because of the work of the piston, but then it is passed on to the heat bath. The increase in kinetic energy in the case of adiabatic compression leads to an additional contribution to the pressure.

In the isothermal process the additional kinetic energy is transmitted to the heat bath. Such a change in energy, which does not depend on work is called heat. Heat transport generally is the transport of energy due to temperature differences between different thermodynamic subsystems. The energy transferred in this way is called heat. One distinguishes between three types of transport:

1. heat transport (which has just been discussed).

2. Thermal radiation, which follows from radiation (see black-body radiation)

3. Convection. A circulating fluid (gas) transports energy from a warmer region to a colder one. There it loses kinetic energy and then returns to the warmer region.

Now we continue with the ideal gas. The (kinetic) energy of the system does not change if T is constant. Therefore

$$dE = dQ - dW \tag{7.63}$$

applies. Here dE is the change in the total energy of the system and dQ is the heat contribution. If dQ is positive, heat is emitted. Otherwise, heat is absorbed. Later we will define the term in more detail. dW is the work done by the system or performed on the system. For the isothermic case (T and $\Rightarrow E$ are constant) we have $dE = 0$ and therefore

$$dQ = dW \ .$$

When work is performed on the system, we have $dW < 0$ and therefore $dQ < 0$. This in turn means that the system emits heat. For the inverse case the volume of the system is allowed to expand. Then the system performs work and we have $dW > 0$. From this $dQ > 0$ follows and heat flows from the bath into the system. This is necessary to keep the temperature constant. Without the heat flow the temperature would decrease.

Now we shall discuss the adiabatic case. There we have $dQ = 0$ as the system is isolated. Then

$$dE = -dW = -pdV$$

applies. Finally, we bring equation (7.63) [Page 195] into the form

$$dQ = dE + dW \ .$$

Thus, we can understand the change in heat of the gas as the difference between the energy change in the system - defined by the energy - and the work done by the gas.

The heat transfer to the bath can also be understood as microscopic work of fluctuating forces. For this purpose, we can imagine the impenetrable walls of the container as a thin elastic film with uniform density. This wall is surrounded by particles that belong to the bath. When a particle of the system collides with this wall, it creates waves (phonons) that absorb and distribute the energy of the scattered particle. At some point in time, however, a particle of the bath will suitably collide with the wall and absorb the energy from the wave, causing the wave to lose energy and the bath particle to gain energy. Unlike the collision with the moving piston, these transfers of force are fluctuating and irreversable. On a microscopic level, we are only dealing with mechanical forces, but they fluctuate. Unlike the work of the piston, these forces can no longer be controlled. Heat is then the average work of these fluctuating forces.

7.4.3 Statistical treatment

The internal energy of a system (classical or quantum mechanical) is given by

$$E = U = \sum_n P_n E_n$$

Changes in the system can lead to changes of the internal energy.

$$dE = \underbrace{\sum_n P_n dE_n}_{=dE_1} + \underbrace{\sum_n dP_n E_n}_{=dE_2} \ .$$

This is not a decomposition according to the influences of dV and dT on E_n, but according to whether P_n changes or not. Otherwise, the change in E_n via $P_n = e^{-\beta E_n}/Z$ would also change P_n. I.e. if we change V and thus E_n, it is assumed in dE_1 that P_n nevertheless remains constant, e.g. due to a simultaneous change in temperature. For QM, this corresponds to the expression in the eigenbasis of $\hat{H}$. We continue to consider an ideal gas. The (eigen)energies then only change with the volume and we have

$$dE_1 = \sum_n P_n \frac{dE_n}{dV} dV$$

The change of the eigenvalues of $\hat{H}$ with changing volume is given by

$$dE_n = \frac{dE_n}{dV} dV = \underbrace{\frac{dE_n}{dV}}_{=K_n} A\,dx \ .$$

We assume that the system is in exactly this eigenstate. In order to change the volume, using the piston, the force K_n has to be applied. Conversely a particle in that eigenstate generates the pressure

$$-p_n = \frac{K_n}{A} = \frac{dE_n}{dV}$$

on the wall. For the states being occupied with a probability of P_n,

$$p = \sum_n P_n p_n$$

corresponds to the average pressure p. Therefore we have

$$dE_1 = \sum_n P_n dE_n \sum_n P_n(-p_n dV)$$
$$= -pdV = -dW \ .$$

Hence, dE_1 corresponds to the energy change do to mechanical work. Then, according to $dE = dQ - dW$ the other term dE_2 should describe the change in heat. Hence we have

$$dQ = \sum_n dP_n E_n \ .$$

This is at least consistent with the adiabatic processes. Adiabatic means that the changes are so slow that the system stays in the same state and therefore P_n does not change. We now consider the Gibbs entropy

$$S = -k_B \sum_n P_n \ln(P_n)$$

$$dS = -k_B \sum_n dP_n \ln(P_n) - k_B \sum_n P_n \frac{1}{P_n} dP_n$$

$$= -k_B \sum_n dP_n \ln(P_n) - k_B d\Big(\underbrace{\sum_n P_n}_{=1}\Big)$$

$$= -k_B \sum_n dP_n \ln(P_n) \ .$$

For the canonical ensemble we have

$$P_n = \frac{e^{-\beta E_n}}{Z}$$

$$\ln(P_n) = -\beta E_n - \ln(Z) \ .$$

Therefore we obtain

$$dS = -k_B \sum_n dP_n \big(-\beta E_n - \ln(Z)\big)$$

$$= \frac{1}{T} \sum_n dP_n E_n + k_B \ln(Z) \underbrace{\sum_n dP_n}_{=0}$$

$$TdS = \sum_n dP_n E_n = dE_2 = dQ \ .$$

With this we have derived the important and already often mentioned connection between entropy and heat:

$$dQ = TdS$$

or

$$dS = \frac{dQ}{T} \ .$$

These relations apply only to reversible changes of state. In general we have

$$dS \geq \frac{dQ}{T} \; .$$

Appendix A

Ehrenfest model

A.1 Stationary distribution

Here we will determine the stationary distribution of the Ehrenfest model, for which the following differential equation of differences applies

$$
\begin{aligned}
\frac{d}{dt} P(\mathcal{N}_1^{(t)} = m) = {} & P(\mathcal{N}_1^{(t)} = m) \left[(\lambda_2 - \lambda_1)m - \lambda_2 N \right] \\
& + P(\mathcal{N}_1^{(t)} = m + 1) \, \lambda_1(m + 1) \\
& + P(\mathcal{N}_1^{(t)} = m - 1) \, \lambda_2 [N - (m - 1)] \,.
\end{aligned} \tag{A.1}
$$

To that end we introduce the following generating functional:

$$
\Phi(x, t) = \sum_{m=0}^{N} P(\mathcal{N}_1^{(t)} = m) \, x^m \,.
$$

Next we will transform the differential equation of differences into a partial differential equation for $\Phi(x, t)$. To that end we multiply equation (A.1) [Page 200] with x^m and sum over m. By interchanging sum and derivative the left hand side of the equation yields

$$
\frac{d}{dt} \sum_{m=0}^{N} P(\mathcal{N}_1^{(t)} = m) x^m = \frac{\partial}{\partial t} \Phi(x, t) \,.
$$

In the last step, we have taken into account that $\Phi(x, t)$ is a function of two variables and that, therefore, we have a partial derivative. If the same

operations are performed on the right side we obtain

$$\frac{\partial}{\partial t}\Phi(x,t) = (\lambda_2 - \lambda_1) \underbrace{\sum_{m=0}^{N} P(\mathcal{N}_1^{(t)} = m)\, x^m\, m}_{=x\frac{\partial}{\partial x}\Phi(x,t)} - \lambda_2 N \underbrace{\sum_{m=0}^{N} P(\mathcal{N}_1^{(t)} = m)\, x^m}_{=\Phi(x,t)}$$

$$+ \lambda_1 \sum_{m=0}^{N-1} P(\mathcal{N}_1^{(t)} = m+1)\, x^m\,(m+1) + \lambda_2 N \sum_{m=1}^{N} P(\mathcal{N}_1^{(t)} = m-1)\, x^m$$

$$- \lambda_2 \sum_{m=1}^{N} P(\mathcal{N}_1^{(t)} = m-1)\, x^m (m-1)\,.$$

Here we used the fact that we have $P(\mathcal{N}_1^{(t)} = -1) = P(\mathcal{N}_1^{(t)} = N+1) = 0$.
These equations are transformed again to

$$\frac{\partial}{\partial t}\Phi(x,t) = (\lambda_2 - \lambda_1)\, x\frac{\partial}{\partial x}\Phi(x,t) - \lambda_2 N\Phi(x,t)$$

$$+ \lambda_1 \sum_{n=1}^{N} P(\mathcal{N}_1^{(t)} = n)\, x^{n-1}\, n$$

$$+ \lambda_2 N \sum_{n=0}^{N-1} P(\mathcal{N}_1^{(t)} = n)\, x^{n+1} - \lambda_2 \sum_{n=0}^{N-1} P(\mathcal{N}_1^{(t)} = n)\, x^{n+1} n\,.$$

The sum in the third term can be started at $n = 0$ because of the factor n.
The sums in the last two terms both can be extended to $n = N$, because the
extra terms compensate each other. Then we find

$$\frac{\partial}{\partial t}\Phi(x,t) = (\lambda_2 - \lambda_1)\, x\frac{\partial}{\partial x}\Phi(x,t) - \lambda_2 N\Phi(x,t)$$

$$+ \lambda_1 \underbrace{\sum_{n=0}^{N} P(\mathcal{N}_1^{(t)} = n)\, x^{n-1}\, n}_{\frac{\partial}{\partial x}\Phi(x,t)}$$

$$+ \lambda_2 N \underbrace{\sum_{n=0}^{N} P(\mathcal{N}_1^{(t)} = n)\, x^{n+1}}_{=x\Phi(x,t)} - \lambda_2 \underbrace{\sum_{n=0}^{N} P(\mathcal{N}_1^{(t)} = n)\, x^{n+1} n}_{=x^2 \frac{\partial}{\partial x}\Phi(x,t)}\,;$$

$$\frac{\partial}{\partial t}\Phi(x,t) = (\lambda_2 - \lambda_1)\, x\frac{\partial}{\partial x}\Phi(x,t) - \lambda_2 N\Phi(x,t) + \lambda_1 \frac{\partial}{\partial x}\Phi(x,t) + \lambda_2 Nx\Phi(x,t) - \lambda_2 x^2 \frac{\partial}{\partial x}\Phi(x,t)$$

$$= \frac{\partial}{\partial x}\Phi(x,t)\Big((\lambda_2 - \lambda_1)\, x + \lambda_1 - \lambda_2 x^2\Big) + \Phi(x,t)\Big(-\lambda_2 N + \lambda_2 Nx\Big)$$

$$= -\lambda_2 \frac{\partial}{\partial x}\Phi(x,t)\Big(x^2 - (1 - \frac{\lambda_1}{\lambda_2})\, x - \frac{\lambda_1}{\lambda_2}\Big)\lambda_2 N\Phi(x,t)\Big(x - 1\Big)\,.$$

We now define $\tau = \lambda_2 t$ and $q = \frac{\lambda_1}{\lambda_2}$ and obtain

$$\frac{d}{d\tau}\Phi(x,\tau) = -\Phi'(x,\tau)\left(x^2 - (1-q)\,x - q\right) + N\Phi(x,\tau)\left(x - 1\right).$$

Furthermore

$$x^2 - (1-q)x - q = (x-1)(x+q)$$

$$\frac{d}{d\tau}\Phi(x,\tau) = \left(-(x+q)\,\Phi'(x,\tau) + N\Phi(x,\tau)\right)(x-1)$$

applies.

The stationary solution $\frac{\partial}{\partial t}\Phi(x,t) = 0$ therefore yields

$$\Phi'(x,\tau=\infty)\,(x+q) = N\Phi(x,\infty)$$

$$\Phi(x,\tau=\infty) = c(x+q)^N$$

Using the correct normalization, $\Phi(1,t) = 1$, we finally get

$$\Phi(x,\infty) = (1+q)^{-N}\,(x+q)^N$$

$$= \left(\frac{1}{1+q}x + \frac{q}{1+q}\right)^N = \left(\frac{1}{1+q}x + 1 - \frac{1}{1+q}\right)^N$$

$$= \left(\frac{1}{1+q}x + \frac{q}{1+q}\right)^N = \left(1 - \frac{1}{1+q} + \frac{1}{1+q}x\right)^N.$$

We recall the generating functional of the binomial distribution

$$P(n|N,q_1) \longrightarrow \quad \Phi_b(x) = (1 - q_1 + q_1 x)^N.$$

$$\Phi_b(x) = \sum_{n=0}^{N}\binom{N}{n}q_1^n(1-q_1)^{N-n}x^n$$

$$= \sum_{n=0}^{N}\binom{N}{n}(xq_1)^n(1-q_1)^{N-n}x^n$$

$$= \left(xq_1 + (1-q_1)\right)^N.$$

Obviously we have to identify $q_1 = \frac{1}{1+q} = \frac{\lambda_2}{\lambda_1+\lambda_2}$. With the definition $\lambda_\alpha = c/V_\alpha$ we obtain

$$q_1 = \frac{\frac{1}{V_2}}{\frac{1}{V_1}+\frac{1}{V_2}} = \frac{V_1}{V}$$

$$q_2 = \frac{V_2}{V},$$

and thus the stationary distribution reads

$$P(\mathcal{N}_1^{(t \to \infty)} = n) = \binom{N}{n} q_1^n q_2^{N-n} \ .$$

A.2 Mean time reach equilibrium

Here we will solve equation (1.5) [Page 13] in order to determine the mean time for a system to reach equilibrium in the Ehrenfest model. The equation to solve is

$$D_n = \frac{n}{N} D_{n-1} + (1 - \frac{n}{N}) D_{n+1} + 1 \ .$$

We assume that N is even and instead use $N = 2\tilde{N}$.

$$D_n = D_{n+1} - \frac{n}{2\tilde{N}} \left(D_{n+1} - D_{n-1} \right) + 1 \ . \tag{A.2}$$

The series expansion of $D_{n\pm 1} = D_n \pm D_n' + \frac{1}{2} D_n''$ around n yields

$$D_n = \underbrace{D_n + D_n' + \frac{1}{2} D_n''}_{=D_{n+1}} - \frac{n}{\tilde{N}} D_n' + 1$$

$$0 = D_n'' + 2(1 - \frac{n}{\tilde{N}}) D_n' + 2 \ . \tag{A.3}$$

The series expansion is useful if $n \gg 1$ and D_n is smooth, because than a chance $n \pm 1$ actually corresponds to to a relative change of $\pm 1/n$. With $G := D'$ we have to solve the linear inhomogeneous first order differntial equation

$$G_n' + 2(1 - \frac{n}{\tilde{N}}) G_n = -2 \tag{A.4}$$

We first consider the homogeneous differential equation

$$G' = -2(1 - \frac{n}{\tilde{N}}) G$$

$$\frac{dG}{G} = 2 \frac{n - \tilde{N}}{\tilde{N}} \, dn$$

$$\ln(G) = c + \frac{(n - \tilde{N})^2}{\tilde{N}}$$

$$G = g e^{\frac{(n - \tilde{N})^2}{\tilde{N}}} \ .$$

For the inhomogenous differential equation we let g be dependent on n and obtain

$$G' = G\frac{2(n - \tilde{N})}{\tilde{N}} + g'e^{\frac{(n-\tilde{N})^2}{\tilde{N}}}$$

$$G' + \frac{2(\tilde{N} - n)}{\tilde{N}}G = -2 \qquad \Rightarrow \quad g' = -2e^{-\frac{(\tilde{N}-n)^2}{\tilde{N}}}$$

$$g = a - 2\int_{-\infty}^{n} e^{-\frac{(\tilde{N}-t)^2}{\tilde{N}}} \, dt \; .$$

With the substitution

$$\frac{(\tilde{N} - t)^2}{\tilde{N}} =: z^2 \; ;$$

$$\tilde{N} - t = \sqrt{\tilde{N}}z \; ;$$

$$dt = -\sqrt{\tilde{N}}dz$$

we get

$$g = a + 2\sqrt{\tilde{N}} \int_{-\infty}^{\frac{\tilde{N}-n}{\sqrt{\tilde{N}}}} e^{-z^2} \, dz = \tilde{a} + 2\sqrt{\tilde{N}} \int_{0}^{\frac{\tilde{N}-n}{\sqrt{\tilde{N}}}} e^{-z^2} \, dz$$

$$= \tilde{a} + \sqrt{\tilde{N}\pi} \, \Phi\left(\frac{N-n}{\sqrt{\tilde{N}}}\right) \; .$$

Thus

$$D'_n = G_n = \left(\tilde{a} + \sqrt{\tilde{N}\pi} \, \Phi\left(\frac{\tilde{N}-n}{\sqrt{\tilde{N}}}\right)\right)e^{\frac{(\tilde{N}-n)^2}{\tilde{N}}}$$

is valid for the output variable. Actually we are interested in $n = 0$. From equation (A.2) we obtain

$$D_0 = D_1 + 1$$
$$D_1 - D_0 = -1$$
$$D'_0 = -1 \; .$$

With this initial condition we determine the parameter $\tilde{a}$

$$D'_0 = \left(\tilde{a} + \sqrt{\tilde{N}\pi} \, \Phi(\sqrt{\tilde{N}})\right)e^{\tilde{N}} = -1$$

$$\tilde{a} = -\sqrt{\tilde{N}\pi} \, \Phi(\sqrt{\tilde{N}}) - e^{-\tilde{N}} \; .$$

Thus the differential equation becomes

$$D'_n = -\left[e^{\frac{(\tilde{N}-n)^2}{\tilde{N}} - \tilde{N}} + \sqrt{\tilde{N}\pi}\left(\Phi(\sqrt{\tilde{N}}) - \Phi(\frac{\tilde{N}-n}{\sqrt{\tilde{N}}}) \right) e^{\frac{(\tilde{N}-n)^2}{\tilde{N}}} \right]$$

$$D_n = C + \int_0^n D'_z dz$$

$$D_{\tilde{N}} = 0 \;\Rightarrow\; \quad C = -\int_0^{\tilde{N}} D'_z dz$$

$$D_n = -\int_n^{\tilde{N}} D'_z dz \;.$$

Hence the desired mean runtime is

$$D_0 = \int_0^{\tilde{N}} \left(e^{\frac{(\tilde{N}-t)^2}{\tilde{N}} - \tilde{N}} + \sqrt{\tilde{N}\pi}\left(\Phi(\sqrt{\tilde{N}}) - \Phi(\frac{\tilde{N}-t}{\sqrt{\tilde{N}}}) \right) e^{\frac{(\tilde{N}-t)^2}{\tilde{N}}} \right) dt \;.$$

Again, we use the substitution

$$\frac{(\tilde{N}-t)^2}{\tilde{N}} = z^2 \;; \quad \tilde{N} - t = \sqrt{\tilde{N}}z \;; \quad dt = -\sqrt{\tilde{N}}dz$$

and get

$$D_0 = \sqrt{\tilde{N}} \int_0^{\sqrt{\tilde{N}}} \left(e^{z^2 - \tilde{N}} + \sqrt{\tilde{N}\pi}\left(\Phi(\sqrt{\tilde{N}}) - \Phi(z) \right) e^{z^2} \right) dz \;.$$

When substituting $z = t\sqrt{\tilde{N}}$, the first summand yields

$$D_0^{(1)} = \sqrt{\tilde{N}} \int_0^{\sqrt{\tilde{N}}} e^{z^2 - \tilde{N}} dn = \tilde{N} \int_0^1 e^{-\tilde{N}(1-t^2)} dt$$

$$= \sqrt{\tilde{N}} DawsonF(\sqrt{\tilde{N}}) \overset{\tilde{N} \to \infty}{\longrightarrow} \frac{1}{2} \;.$$

The other summands are

$$D_0^{(2)} = \tilde{N}\sqrt{\pi} \int_0^{\sqrt{\tilde{N}}} e^{z^2} \left(\Phi(\sqrt{\tilde{N}}) - \Phi(z) \right) dz$$

$$= \tilde{N}\sqrt{\pi} \int_0^{\sqrt{\tilde{N}}} e^{z^2} \left(\left(\Phi(\sqrt{\tilde{N}}) - 1 \right) - \left(\Phi(z) - 1 \right) \right) dz$$

$$= -2\tilde{N} \int_0^{\sqrt{\tilde{N}}} e^{z^2} \left(\int_{\sqrt{\tilde{N}}}^\infty e^{-x^2} dx - \int_z^\infty e^{-x^2} dx \right) dz$$

$$= -2\tilde{N} \int_0^{\sqrt{\tilde{N}}} e^{z^2} \left(\int_0^\infty e^{-(t+\sqrt{\tilde{N}})^2} dt - \int_0^\infty e^{-(t+z)^2} dt \right) dz \;. \qquad \text{(A.5)}$$

The first term yields

$$T_1 := -2\tilde{N} \int_0^{\sqrt{\tilde{N}}} e^{z^2} \int_0^\infty e^{-(t+\sqrt{\tilde{N}})^2} dt dz = -2\tilde{N} \left(\int_0^{\sqrt{\tilde{N}}} e^{z^2-\tilde{N}} dz \right) \left(\int_0^\infty e^{-t^2-2t\sqrt{\tilde{N}}} dt \right)$$

$$= -2\tilde{N} \left(\sqrt{\tilde{N}} \int_0^1 e^{-\tilde{N}(1-x^2)} dx \right) \left(\int_0^\infty e^{-t^2-2t\sqrt{\tilde{N}}} dt \right)$$

$$= -2 \left(\tilde{N} \int_0^1 e^{-\tilde{N}(1-x^2)} dx \right) \left(\sqrt{\tilde{N}} \int_0^\infty e^{-t^2-2t\sqrt{\tilde{N}}} dt \right)$$

$$= -2 \underbrace{\left(\sqrt{\tilde{N}} Dawson(\sqrt{\tilde{N}}) \right)}_{\to 1/2} \underbrace{\left(e^{\tilde{N}} \sqrt{\tilde{N}} \frac{\sqrt{\pi}}{2}(1-\Phi(\sqrt{\tilde{N}})) \right)}_{\to 1/2} \overset{\tilde{N}\to\infty}{\longrightarrow} -\frac{1}{2}$$

The second term in equation (A.5) [Page 205] yields

$$T_2 := 2\tilde{N} \int_0^{\sqrt{\tilde{N}}} e^{z^2} \int_0^\infty e^{-(t+z)^2} dt dz = 2\tilde{N} \int_0^{\sqrt{\tilde{N}}} \int_0^\infty e^{-t^2-2tz} dt dz$$

$$= 2\tilde{N} \int_0^\infty dt\, e^{-t^2} \int_0^{\sqrt{\tilde{N}}} e^{-2tz} dz = 2\tilde{N} \int_0^\infty dt\, e^{-t^2} \frac{1-e^{-2t\sqrt{\tilde{N}}}}{2t}$$

$$= \tilde{N} \int_0^\infty e^{-\frac{t^2}{\tilde{N}}} \frac{1-e^{-2t}}{t} dt \ .$$

We split the integral in two parts in order to get the divergence under control.

$$T_2 = \tilde{N} \left(\int_0^\xi e^{-\frac{t^2}{\tilde{N}}} \frac{1-e^{-2t}}{t} dt + \int_\xi^\infty e^{-\frac{t^2}{\tilde{N}}} \frac{1-e^{-2t}}{t} dt \right) \ .$$

Now we define $1 \ll \xi \ll \sqrt{\tilde{N}}$ in order to get $t^2/\tilde{N} \ll 1$ in the first integral. The first integral thus gives

$$\int_0^\xi e^{-\frac{t^2}{\tilde{N}}} \frac{1-e^{-2t}}{t} dt = \int_0^\xi \frac{1-e^{-2t}}{t} dt$$

$$= \gamma + \ln(2\xi) + \underbrace{\Gamma(0, 2\xi)}_{\ll 1 \text{ (da } \xi \gg 1)} \ .$$

Here $\gamma = 0.5771$ is the Euler constant and $\Gamma(\nu, x)$ is the incomplete gamma

function. The second integral respectively yields

$$\int_{\xi}^{\infty} e^{-\frac{t^2}{\tilde{N}}} \frac{1}{t}\, dt = \frac{1}{2} \int_{\frac{\xi^2}{\tilde{N}}}^{\infty} \frac{e^{-z}}{z}\, dz$$

$$= \frac{1}{2}\Gamma(0, \frac{\xi^2}{\tilde{N}})$$

$$= -\frac{1}{2}(\gamma + \ln(\xi^2/\tilde{N}))$$

$$= -\frac{\gamma}{2} - \ln(\xi) + \frac{1}{2}\ln(\tilde{N}) \ .$$

With that we have

$$T_2 = \tilde{N}\left(\frac{\gamma}{2} + \ln(2) + \frac{1}{2}\ln(\tilde{N}) \right)$$

and the final result is

$$D_0 = D_0^1 + T_1 + T_2$$

$$= \frac{1}{2} - \frac{1}{2} + \tilde{N}\left(\frac{\gamma}{2} + \ln(2) + \frac{1}{2}\ln(\tilde{N}) \right)$$

$$= \tilde{N}\left(\frac{\gamma}{2} + \ln(2) + \frac{1}{2}\ln(\tilde{N}) \right)$$

$$= \frac{N}{2}\left(\frac{\gamma}{2} + \ln(2) + \frac{1}{2}\ln(\frac{N}{2}) \right)$$

$$= \frac{N}{4}\left(\underbrace{\gamma + \ln(2)}_{1.27} + \ln(N) \right) \ .$$

As N is macroscopic we finally get the simple result

$$D_0 = \frac{N}{4}\ln(N) \ .$$

The $N\ln(N)$ behaviour can be attained with a very simple and descriptive estimation. The average number of steps that are needed to get from $N_1 = 0$ to $N_1 = \tilde{N}$ with t rw-steps shall be $n(t)$. The rate of change approximately corresponds to the drift velocity, namely $P_r - P_l = (1 - \frac{n}{2\tilde{N}}) - \frac{n}{2\tilde{N}} = 1 - \frac{n}{\tilde{N}}$. Therefore we have

$$\dot{n} = 1 - \frac{n}{\tilde{N}}$$

$$\frac{dn}{1 - \frac{n}{\tilde{N}}} = dt$$

$$n(t = 0) = 0$$

$$t = -\tilde{N}\ln(1 - \frac{n}{\tilde{N}}) = \tilde{N}(\ln(\tilde{N}) - \ln(\tilde{N} - n)) \ .$$

The time until we reach $n = \tilde{N} - 1$ therefore is $t = \tilde{N} \ln(\tilde{N})$.

Appendix B

Stationary phase approximation for $\Gamma(x)$

$$\Gamma(x) = \int_0^\infty e^{-t} t^{x-1} dt$$

$$= \int_0^\infty e^{-t+(x-1)\ln(t)} dt \ .$$

We expand the argument Φ of the exponential function around its maximum.

$$\Phi = -t + (x-1)\ln(t)$$

$$\frac{d\Phi}{dt} = -1 + \frac{x-1}{t} = 0 \ ; \Rightarrow t^* = x - 1$$

$$\Phi(t^*) = -t^* + (x-1)\ln(t^*) = (x-1)\ln(x-1) - (x-1)$$

$$\left.\frac{d^2\Phi}{dt^2}\right|_{t^*} = -\frac{x-1}{(t^*)^2} = -\frac{1}{x-1}$$

$$e^\Phi \approx e^{\Phi^*} e^{-\frac{1}{2(x-1)}(t-t^*)^2}$$

$$\Gamma(x) \approx e^{\Phi^*} \int_0^\infty e^{-\frac{1}{2(x-1)}(t-t^*)^2} dt$$

$$\approx (x-1)^{(x-1)} e^{-x+1} \sqrt{2\pi(x-1)}$$

$$\approx (x-1)^{(x-1/2)} e^{-(x+1)} \sqrt{2\pi}$$

$$N! = \Gamma(N+1) \approx N^{(N+1/2)} e^{-N} \sqrt{2\pi} \ .$$

Appendix C

Volume of a d-dimensional sphere

The volume of a d-dimensional sphere of radius R is obtained from

$$V_d(R) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \theta(x^2 \le R^2) d^d x = \Omega_d \int_0^R r^d \frac{dr}{r}$$
$$= \Omega_d \frac{R^d}{d} \ .$$

The d-dimensional solid angle Ω_d is calculated using the d-dimensional Gauss integral. On the one hand we have

$$I_d := \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\vec{x}^2} d^d x = \left(\int_{-\infty}^{\infty} e^{-x^2} dx \right)^d = \pi^{d/2} \ .$$

On the other hand it is also possible to calculate the integral using spherical coordinates.

$$I_d = \Omega_d \int_0^{\infty} e^{-r^2} r^d \frac{dr}{r}$$

Substituting $r = \sqrt{t}$ yields

$$= \frac{1}{2} \; \Omega_d \; \underbrace{\int_0^\infty e^{-t} \; t^{d/2} \; \frac{dt}{t}}_{\Gamma(\frac{d}{2})}$$

$$= \frac{\Gamma(\frac{d}{2})}{2} \; \Omega_d$$

$$\Omega_d = \frac{2 \; \pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2})}$$

$$V_d(R) = R^d \; \frac{2\pi^{\frac{d}{2}}}{d \; \Gamma(\frac{d}{2})} = R^d \; \frac{\pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2} + 1)}$$

Therefore the results are

VOLUME AND SOLID ANGLE OF A d-DIMENSIONAL SPHERE

$$\Omega_d = \frac{2 \; \pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2})} \; ; \tag{C.1}$$

$$V_d(R) = R^d \; \frac{\pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2} + 1)} \; ; \tag{C.2}$$

$$= R^d \; \frac{\pi^{\frac{d}{2}}}{(\frac{d}{2})!} \; ; \qquad \text{(for even } d) \; . \tag{C.3}$$

Appendix D

Consequences of noncommuting operators for derivatives of partition functions

Partition functions are often used as generating functionals for the calculation of expectation values. Here we will show that this also works for noncommuting operators.

We consider the universal case of a partition function of the form

$$F(\lambda) := \operatorname{tr}\left\{ e^{\alpha(\hat{A}+\lambda\hat{B})}\right\} .$$

For this we want to calculate the derivation with respect to λ. As the operators generally do not commute, the exponential function cannot be factoriesed. On the contrary, we have

$$e^{\alpha(\hat{A}+\lambda\hat{B})} = e^{\alpha\hat{A}}e^{\alpha\lambda\hat{B}} + O(\alpha^2\lambda[\hat{A},\hat{B}]) . \tag{D.1}$$

However, the factorisation is needed in order to be able to calculate the derivative. Because of equation (D.1) ,

$$e^{\alpha(\hat{A}+\lambda\hat{B})} = \lim_{M\to\infty}\left(e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}}\right)^M ;$$
$$\epsilon := \frac{\alpha}{M} .$$

applies. Therefore, for the partition function we have

$$F(\lambda) = \lim_{M\to\infty}\operatorname{tr}\left\{ \left(e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}}\right)^M\right\} = \lim_{M\to\infty}\operatorname{tr}\left\{ \prod_{k=1}^{M} e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}}\right\} .$$

When we take the derivative with respect to λ, as a result of the product rule we have to take the derivative of the factors individually. With the definition $\prod_{k=1}^{0} = 1$ we can perform the derivation as follows:

$$\frac{d}{d\lambda}F(\lambda) = \lim_{M\to\infty} \sum_{l=1}^{M} \text{tr} \left\{ \left[\prod_{k=1}^{l-1} e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}} \right] \left[\frac{d}{d\lambda}e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}} \right] \left[\prod_{k=l+1}^{M} e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}} \right] \right\}$$

$$= \lim_{M\to\infty} \sum_{l=1}^{M} \text{tr} \left\{ \left[\prod_{k=1}^{l-1} e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}} \right] \left[e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}}\epsilon\hat{B} \right] \left[\prod_{k=l+1}^{M} e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}} \right] \right\}$$

$$= \epsilon \lim_{M\to\infty} \sum_{l=1}^{M} \text{tr} \left\{ \prod_{k=1}^{l} e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}} \left[\hat{B} \right] \prod_{k=l+1}^{M} e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}} \right\} .$$

Because the trace is invariant to cyclical permutation of the factors we get

$$\frac{d}{d\lambda}F(\lambda) = \epsilon \lim_{M\to\infty} \sum_{l=1}^{M} \text{tr} \left\{ \hat{B} \left(e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}} \right)^{M} \right\}$$

$$= \epsilon \underbrace{\sum_{l=1}^{M}}_{=\frac{\alpha}{M}\ M=\alpha} \text{tr} \left\{ \hat{B}e^{\alpha(\hat{A}+\lambda\hat{B})} \right\} .$$

Thus we confirmed, what we already suspected: We may indeed use the derivative, even though the operators that are involved do not commute.

DERIVATIVE OF THE PARTITION FUNCTION

$$\frac{d}{d\lambda}F(\lambda) = \alpha \text{tr} \left\{ \hat{B}e^{\alpha(\hat{A}+\lambda\hat{B})} \right\} .$$

For the second derivative with respect to λ this is not possible as easily anymore. There one gets time dependent correlation factors.

Appendix E

Conversion of sums into integrals

Here a different reasoning for the conversion of sums into integrals shall be presented. The sums shall be d-dimensional sums over k-points of a cubic lattice with

$$\left(\vec{k}_{\vec{l}}\right)_{\alpha} = \frac{2\pi l_{\alpha}}{L}$$

$$S = \sum_{\vec{l}} f(\vec{k}_{\vec{l}}) \; .$$

We shall generalise this sum in the following form:

$$S = \underbrace{\sum_{l_1=N_{1,a}}^{N_{1,b}} \cdots \sum_{l_d=N_{d,a}}^{N_{d,b}}}_{:=\sum_{\vec{l}}} f(\vec{x}_{\vec{l}}) \; ;$$

$$\vec{x}_{\vec{l}} := (\delta_1 l_1, \ldots, \delta_d l_d)^T \; ;$$

$$\delta_i \ll 1 \; .$$

The vectros $\vec{x}_{\vec{l}}$ that are summed over, cover a hypercube. The ith edge of the cuboid extends from $\delta_i N_{i,a}$ to $\delta_i N_{i,b}$. Instead we now consider an integral over a hypercube with slightly modified edges. The ith edge shall now extend from $\delta_i(N_{i,a} - 1/2)$ to $\delta_i(N_{i,b} + 1/2)$. This cube is built from unit cells of the size

$$\Delta V := \prod_{i=1}^{d} \delta_i \; .$$

The integral shall be

$$I := \frac{1}{\Delta V} \int_{\delta_1(N_{1,a}-1/2)}^{\delta_1(N_{1,b}+1/2)} \cdots \int_{\delta_d(N_{d,a}-1/2)}^{\delta_d(N_{d,b}+1/2)} f(\vec{x}) \, d^d x \ .$$

We now divide the volume of integration into partial volumes of the size ΔV whose centres actually are the points $\vec{x}_{\vec{l}}$, therefore being

$$I = \frac{1}{\Delta V} \sum_{\vec{l}} \int_{-\delta_1/2}^{\delta_1/2} \cdots \int_{-\delta_d/2}^{\delta_d/2} f(\vec{x}_l + \vec{x}) \, d^d x \ .$$

Next we expand the integrand around $\vec{x}_{\vec{l}}$ up to the second order. The contrbution of the first order vanishes, because integrals of the type

$$\int_{-\delta/2}^{+\delta/2} x \, dx = 0$$

are featured. The series expansion then yields

$$I = \frac{1}{\Delta V} \sum_{\vec{l}} f(\vec{x}_l) \overbrace{\int_{-\delta_1/2}^{\delta_1/2} \cdots \int_{-\delta_d/2}^{\delta_d/2} d^d x}^{\Delta V}$$
$$+ \frac{1}{2\Delta V} \sum_{\vec{l}} \sum_{i,j} \frac{\partial^2 f(\vec{x})}{\partial x_i \partial x_j}\bigg|_{\vec{x}=\vec{x}_l} \underbrace{\int_{-\delta_1/2}^{\delta_1/2} \cdots \int_{-\delta_d/2}^{\delta_d/2} x_i x_j \, d^d x}_{\delta_{ij} \cdot J} \ .$$

The integral J yields

$$\int_{-\delta_1/2}^{\delta_1/2} \cdots \int_{-\delta_d/2}^{\delta_d/2} x_i^2 \, d^d x = \left(\prod_{n \neq i} \delta_n\right) \int_{-\delta_i/2}^{+\delta_i/2} x_i^2 dx_i = \prod_{l \neq i} \delta_l \cdot \frac{2 \, (\delta_i/2)^3}{3} = \Delta V \frac{\delta_i^2}{12}$$

$$I = \sum_{\vec{l}} f(\vec{x}_l) + \frac{1}{24} \sum_{\vec{l}} \left(\sum_{i=1}^{d} \delta_i^2 \frac{\partial^2 f(\vec{x})}{\partial x_i^2}\bigg|_{\vec{x}=\vec{x}_{\vec{l}}}\right) \ .$$

The sum over the second derivatives can also be approximated with a similar integral. For small quantities we define

$$\delta_i = c_i \cdot \delta \ ,$$

with $c_i = O(1)$ and $\delta \ll 1$. With this we see that the relative uncertainty of the summation furmula is of the order $O(\delta^2)$, given that the second derivative does not diverge. Thus we have

---

SUMMATION FORMULA

$$\sum_{\vec{l}} f(\vec{x}_l) = \frac{1}{\Delta V} \int_{\delta_1(N_{1,a}-1/2)}^{\delta_1(N_{1,b}+1/2)} \cdots \int_{\delta_d(N_{d,a}-1/2)}^{\delta_d(N_{d,b}+1/2)} f(\vec{x}) d^d x \cdot \left(1 + O(\delta^2)\right).$$

(E.1)

Discrete values with $l_i \in \mathbb{Z}$:

If the edges of the hypercube of the discrete values l_i extend from $-\infty$ to $+\infty$, then the integral extends over all of $\mathbb{R}^d$ and therefore

---

SUMMATION FORMULA IN $\mathbb{Z}^d$

$$\sum_{\vec{l}} f(\vec{x}_l) = \frac{1}{\Delta V} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} f(\vec{x}) d^d x \cdot \left(1 + O(\delta^2)\right).$$

(E.2)

Discrete values with $l_i \in \mathbb{N}_0$:

If the edges of the hypercube of the discrete values l_i extend from 0 to $+\infty$, then the integral for the coordinate i actually extends from $-\delta_i/2$ to ∞. However, if a relative uncertainty of the order $O(\delta)$ is acceptable, the integration interval $(0, \infty)$ can be chosen too, as we have

$$\int_{-\delta/2}^{\infty} f(x)dx = \int_{-\delta/2}^{0} f(x)dx + \int_{0}^{\infty} f(x)dx$$
$$= f(0)\frac{\delta}{2} + \int_{0}^{\infty} f(x)dx + O(\delta^2).$$

Therefore, the first term leads to an approximation of the order $O(\delta)$. With that accuracy the summation formula then is

---

<div align="center">

SUMMATION FORMULA IN $\mathbb{N}_0^d$

</div>

$$\sum_{\vec{l}} f(\vec{x}_l) = \frac{1}{\Delta V} \int_0^\infty \cdots \int_0^\infty f(\vec{x}) d^d x \cdot \left(1 + O(\delta)\right) . \qquad \text{(E.3)}$$

One gets the same result for the discrete values starting with $l_i = 1$.

Appendix F

Densities of state

F.1   Quadratic dispersion

Here we will determine the density of states for free, non-relativistic particles in d dimensions. The easiest way to do this is via distribution funcions. Including spin degeneracy M_S, the distribution functions are

$$
\begin{aligned}
F_d(E) &:= M_S \sum_{\vec{l}} \theta \left[\frac{\hbar^2 \vec{k}^2(\vec{l})}{2m} < E \right] \\
&= M_S \frac{V}{(2\pi)^d} \sum_{\vec{l}} \theta \left[\frac{\hbar^2 \vec{k}^2(\vec{l})}{2m} < E \right] \triangle^d k \\
&= \frac{M_S V}{(2\pi)^d} \int \theta \left[\vec{k}^2 < \frac{2mE}{\hbar^2} \right] d^d k \\
&= \frac{M_S V}{(2\pi)^d} V_d \left(R = \sqrt{2mE/\hbar^2} \right) \\
&= \frac{M_S V}{(2\pi)^d} \frac{(2mE)^{\frac{d}{2}}}{\hbar^d} \frac{\pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2} + 1)} \\
&= M_S V \left(\frac{2\pi m}{h^2} \right)^{\frac{d}{2}} \frac{2}{d\, \Gamma(\frac{d}{2})} E^{\frac{d}{2}} \ .
\end{aligned}
$$

We get the density of states by differentiating w.r.t. E.

$$
\begin{aligned}
\rho(E) = \frac{d}{dE} F_d(E) &= M_S V \left(\frac{2\pi m}{h^2} \right)^{\frac{d}{2}} \frac{2}{d\, \Gamma(\frac{d}{2})} \frac{d}{2} E^{\frac{d}{2} - 1} \\
&= M_S V \left(\frac{2\pi m}{h^2} \right)^{\frac{d}{2}} \frac{1}{\Gamma(\frac{d}{2})} E^{\frac{d}{2} - 1} \ .
\end{aligned}
$$

F.2 Linear dispersion

Now we will limit the number of dimensions to three. The dispersion relation then is

$$\varepsilon(\vec{k}) = \hbar c \, |\vec{k}|$$

and the allowed k-values are

$$(\vec{k_{\vec{l}}})_i := \frac{\pi}{L_i} l_i \; ; \quad l_i \geq 0 \; .$$

Thus, the distribution function becomes

$$F(\varepsilon) := \frac{V}{\pi^3} \sum_{\substack{\vec{l} \\ l_i \geq 0}} \theta \left[\hbar c k(\vec{l}) < \varepsilon \right] \triangle^3 k$$

$$= \frac{V}{\pi^3} \frac{4\pi}{8} \int_0^\infty \theta \left[\varepsilon - \hbar c k \right] \; k^2 \; dk \; .$$

The factor $4\pi/8$ is caused by the integration of angles when considering that the integraion comprises only of the first octant. The distribution function then is

$$F(\varepsilon) = \frac{V}{2\pi^2} \int_0^{\frac{\varepsilon}{\hbar c}} k^2 \; dk = \frac{V}{2\pi^2 \, 3} \left(\frac{\varepsilon}{\hbar c} \right)^3 = \frac{V \, \varepsilon^3}{6\pi^2 \, \hbar^3 \, c^3} \; .$$

From the derivation we get the density of states as

$$\rho(\varepsilon) = \frac{dF(\varepsilon)}{d\varepsilon} = \frac{3V \, \varepsilon^2}{6\pi^2 \, \hbar^3 \, c^3} \; .$$

Summarising the results we get

$$\boxed{\begin{array}{c} \textsc{Distribution function} \\ \textit{(for linear dispersion (3d))} \\ \hline \\ \rho(\varepsilon) = C_{ph} \, \varepsilon^2 \; ; \\ F(\varepsilon) = \frac{C_{ph}}{3} \, \varepsilon^3 \; ; \\ C_{ph} := \frac{V}{2\pi^2 \, \hbar^3 \, c^3} \; . \end{array}} \qquad \text{(F.1)}$$

Appendix G

Quantum mechanical gamma function

G.1 Recursion formula for the quantum mechanical gamma function

For the quantum mechanical gamma function

$$g_l^{(\sigma)}(z) = \frac{1}{\Gamma(l)} \int_0^\infty \frac{z}{e^t - \sigma z} t^{l-1} \, dt$$

we shall derive a useful recursion function for $l > 1$.

$$\frac{d}{dz} g_l^{(\sigma)}(z) = \frac{1}{\Gamma(l)} \int_0^\infty \frac{e^t - \sigma z + \sigma z}{(e^t - \sigma z)^2} t^{l-1} \, dt = \frac{1}{\Gamma(l)} \int_0^\infty \frac{e^t}{(e^t - \sigma z)^2} t^{l-1} \, dt$$

$$= -\frac{1}{\Gamma(l)} \int_0^\infty t^{l-1} \frac{d}{dt} \frac{1}{e^t - \sigma z} dt$$

$$\overset{\text{part.Int.}}{=} -\frac{1}{\Gamma(l)} \underbrace{t^{l-1} \frac{1}{e^t - \sigma z}\Big|_0^\infty}_{0} + \frac{(l-1)}{\Gamma(l)} \int_0^\infty t^{l-2} \frac{1}{e^t - \sigma z} dt$$

$$= \frac{1}{\Gamma(l-1)} \int_0^\infty t^{l-2} \frac{1}{e^t - \sigma z} dt = \frac{1}{z} g_{l-1}^{\sigma}(z) \; M.$$

G.2 Series expansion for the quantum mechanical gamma function

We shall perform a series expansion in z around $z = 0$ for $z \ll 1$.

$$
g_l^\sigma(z) = \frac{1}{\Gamma(l)} \int_0^\infty t^{l-1} \frac{z}{e^t - \sigma z} dt = \frac{z}{\Gamma(l)} \int_0^\infty e^{-t} t^{l-1} \frac{1}{1 - \sigma z e^{-t}} dt
$$

$$
= \frac{z}{\Gamma(l)} \int_0^\infty e^{-t} t^{l-1} \left(\sum_{n=0}^\infty \left[\sigma z e^{-t} \right]^n \right) dt
$$

$$
= \frac{1}{\Gamma(l)} \sum_{n=0}^\infty z^{n+1} \sigma^n \int_0^\infty e^{-(n+1)t} t^{l-1} dt
$$

$$
= \frac{\sigma}{\Gamma(l)} \sum_{m=1}^\infty [z\sigma]^m \int_0^\infty e^{-mt} t^{l-1} dt
$$

$$
= \frac{\sigma}{\cancel{\Gamma(l)}} \sum_{m=1}^\infty \frac{[z\sigma]^m}{m^l} \underbrace{\int_0^\infty e^{-x} x^{l-1} dx}_{=\cancel{\Gamma(l)}} \ .
$$

The result is

<div style="text-align:center">

SERIES EXPANSION OF $g_l^\sigma(z)$

(in z around $z = 0$)

</div>

$$
g_l^\sigma(z) = \sigma \sum_{m=1}^\infty \frac{[z\sigma]^m}{m^l} \tag{G.1a}
$$

$$
= z + \sigma \frac{z^2}{2^l} + \ldots \tag{G.1b}
$$

G.3 Bosonic gamma function

In the case of Bosons ($\sigma = +1$), the series expansion from equation (G.1) [Page 221] can be condensed to

$$
g_l^{+1}(z) = \sum_{m=1}^\infty \frac{[z]^m}{m^l} \ . \tag{G.2}
$$

There are the following denotions for the result:

POLYLOGARITHM
(de Jonquière function)

$$g_l^{+1}(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^l} \; . \qquad\qquad \text{(G.3)}$$

Especially for $z = 1$ we get

BOSONIC GAMMA FUNCTION

$$g_l^{+1}(1) = \sum_{n=1}^{\infty} \frac{1}{n^l} = \; \zeta(n) \; . \qquad\qquad \text{(G.4)}$$

Here $\zeta(l)$ is the Riemann ζ-function. Some values of the ζ-function that we will need, are

---

SPECIAL VALUES OF THE RIEMANN ζ-FUNCTION

$$\zeta(1) = \infty \qquad\qquad \text{(G.5a)}$$
$$\zeta(2) = 1.645 \qquad\qquad \text{(G.5b)}$$
$$\zeta(3) = 1.202 \qquad\qquad \text{(G.5c)}$$
$$\zeta(1/2) = \infty \qquad\qquad \text{(G.5d)}$$
$$\zeta(3/2) = 2.612 \qquad\qquad \text{(G.5e)}$$
$$\zeta(5/2) = 1.3415 \; . \qquad\qquad \text{(G.5f)}$$

Appendix H

Bosonic correction

H.1 Contribution of higher states to the condensate

We consider the contribution of the excited state $\varepsilon_{\vec{k}_{\vec{l}}}$ to the density.

$$\langle n_{\varepsilon_{\vec{k}_{\vec{l}}}} \rangle := \frac{1}{V} \frac{1}{e^{\beta(\varepsilon_{\vec{k}_{\vec{l}}} - \mu)} - 1} \ .$$

The factor of the spin degeneracy was suppressed, as it does not influence the main statement. These contributions are only then relevant for Bose condensation, when the exponential function goes to one in the thermodynamic limit. As we already know, the single-particle energies are greater than or equal to zero. The chemical potential approaches zero from the negative side. This means that only energies close to the ground state can contribute to the condensate, if they contribute at all.

It is also important to state that for the transition into the thermodynamic limt the limit $V \to \infty$ has to be performed before $T \to 0$ can be considered. If one does not do that, the finite-size gaps yield wrong results!

For arbitrarily small but fixed T, all energies close to the ground state $\beta\varepsilon_{\vec{k}_{\vec{l}}}$ go to zero in the thermodynamic limit, because the energies of the excited state of free particles in a cuboid of the edge dimensions $L_\alpha := c_\alpha L$ is given by

$$\varepsilon_{\vec{k}_{\vec{l}}} = \frac{2(\pi\hbar)^2}{mL^2} \sum_{\alpha=1}^{3} \frac{l_\alpha^2}{c_\alpha^2} = C\, L^{-2} \ . \, ,$$

The energies close to the ground state are characterised by the fixed finite values l_α[1]. This also means that C remains finite in the thermodynamic

---

[1] In principle, these finite values l_α can be arbitrarily big, they just are not allowed to grow with L.

limit. Then all those energies are proportional to L^{-2}, respectively to $V^{-2/3}$. Thus we can once again use a series expansion, because the single-particle energies as well as μ go to zero.

We determine the Bose occupation numbers of the ground state energy ($\varepsilon_0 = 0$) and one other arbitrary energy $\varepsilon_{\vec{k}_{\vec{l}}}$ close to the ground state. For this we utilise the fact that we have $-\beta\mu = \left(V(\tilde{n} - \tilde{n}_C)\right)^{-1}$. Thus we get

$$\langle n_{\varepsilon_0} \rangle = \frac{1}{e^{-\beta\mu} - 1} = \frac{1}{(-\beta\mu)\left[1 + O(|\beta\mu|)\right]} = V(\tilde{n} - \tilde{n}_C)\left[1 + O(\tfrac{1}{V})\right] \; ;$$

$$\langle n_{\varepsilon_{\vec{k}_{\vec{l}}}} \rangle = \frac{1}{e^{\beta(\varepsilon_{\vec{k}_{\vec{l}}} - \mu)} - 1} = \frac{1}{\beta(\varepsilon_{\vec{k}_{\vec{l}}} - \mu)}\left[1 + O(\tfrac{1}{V})\right] \; ;$$

$$\frac{\langle n_{\varepsilon_0} \rangle}{\langle n_{\varepsilon_{\vec{k}_{\vec{l}}}} \rangle} = \frac{\varepsilon_{\vec{k}_{\vec{l}}} - \mu}{-\mu}\left[1 + O(\tfrac{1}{V})\right] = \left[\frac{\varepsilon_{\vec{k}_{\vec{l}}}}{-\mu} + 1\right]\left[1 + O(\tfrac{1}{V})\right] = \left[\frac{\beta\varepsilon_{\vec{k}_{\vec{l}}}}{-\beta\mu} + 1\right]\left[1 + O(\tfrac{1}{V})\right]$$

$$= \left[\beta\varepsilon_{\vec{k}_{\vec{l}}}\big(V(\tilde{n} - \tilde{n}_C)\big) + 1\right]\left[1 + O(\tfrac{1}{V})\right]$$

Therefore, from this follows

$$\frac{\langle n_{\varepsilon_0} \rangle}{\langle n_{\varepsilon_{\vec{k}_{\vec{l}}}} \rangle} = \beta C \, \frac{1}{L^2} \, (\tilde{n} - \tilde{n}_C)V + O(V^0)$$

$$= \beta C \, (\tilde{n} - n_C)V^{1/3} + O(V^0) \; ;$$

$$\frac{\langle n_{\varepsilon_0} \rangle}{\langle n_{\varepsilon_{\vec{k}_{\vec{l}}}} \rangle} \propto V^{-1/3} + O(V^0) \; .$$

Because in the thermodynamic limit we have $\langle n_{\varepsilon_0} \rangle \to V(\tilde{n} - \tilde{n}_C)$ in the leading order

$$\frac{\langle n_{\varepsilon_0} \rangle}{V} = \frac{1}{\tilde{n} - \tilde{n}_C} \; ;$$

$$\frac{\langle n_{\varepsilon_{\vec{k}_{\vec{l}}}} \rangle}{V} = V^{-2/3}\frac{1}{\tilde{n} - \tilde{n}_C}$$

applies. I.e. only the occupatio of the ground state is macroscopic ($\propto N$ or $\propto V$). The other energies do not contribute to the condensate.

Appendix I

Compendium

I.1 Thermodynamic potentials

Table I.1: Thermodynamic potentials

Quantity	Name	Derivative	
$U(S, V, N)$	(Internal) Energie	dU	$= TdS - pdV + \mu dN$
$S(E, V, N$	Entropy	dS	$= \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$
$F(T, N, V) = U - TS$	Free Energie	dF	$= -SdT - pdV + \mu dN$
$\Omega(T, \mu, V) = U - TS - \mu N$	Grand c. Potential	$d\Omega$	$= -SdT - pdV - Nd\mu$
$G(T, N, p) = U - TS + pV$	Free Enthalpie	dG	$= -SdT + Vdp + \mu dN$
$H(S, N, p) = U + pV$	Enthalpy	dH	$= TdS + Vdp + \mu dN$

From the homogenity of the potentials for the extensive quantities follows

$$U(S, N, V) = TS + \mu N - pV \; ;$$
$$S(U, V, N) = \frac{U}{T} - \frac{\mu N}{T} + \frac{pV}{T} \; ;$$
$$F(T, N, V) = \mu N - pV \; ;$$
$$\Omega(T, \mu, N) = -pV \; ;$$
$$(= F - \mu N \; ;$$
$$= U - TS - \mu N) \; ;$$
$$G(T, N, p) = \mu N \; ;$$
$$H(S, N, p) = TS + \mu N \; .$$

On the right side of the equations that are a result of homogenity, there are only the extensive natural variables togther with the respective conjugated intensive quantities.

Attention: Only when it is known how a thermodynamic potential depends on its natural variables one can calculate all the thermodynamic quantities of the system. The relation $\Omega = -pV$ for the potential for example is not sufficient, as the naqtural varaiables of Ω are not p, V but T, μ, V.

I.2   Useful natural constants

Electron charge	e	$= 1.602176487 \cdot 10^{-19}$	C
Avogadro constant	N_A	$= 6.02214179 \cdot 10^{23}$	
Boltzmann constant	k_B	$= 1.3806504 \cdot 10^{-23}$	J/K
	k_B	$= 8.617343 \cdot 10^{-5}$	eV/K
Planck constant	$\hbar$	$= 1.054571628 \cdot 10^{-34}$	Js
Elektron mass	m_e	$= 9.10938215 \cdot 10^{-31}$	kg
Proton mass	m_p	$= 1.672621637 \cdot 10^{-27}$	kg
Atomic unit of mass	m_a	$= 1.660538782 \cdot 10^{-27}$	kg

Appendix J

List of literature

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