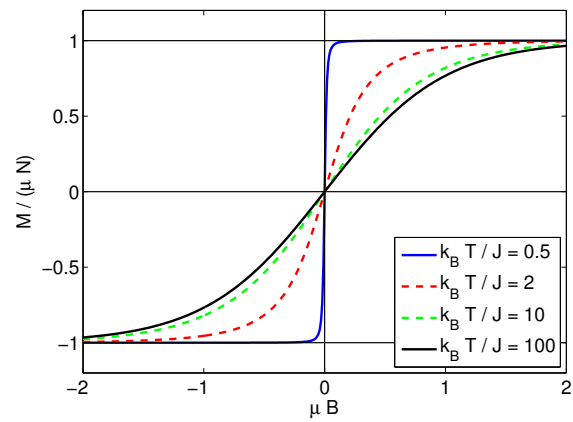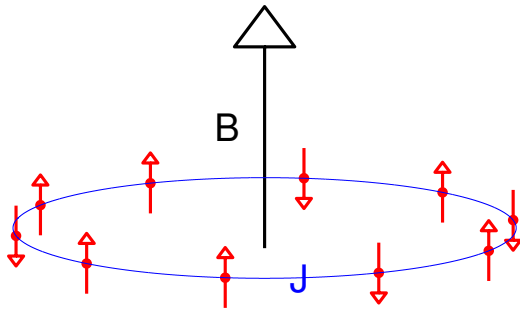# Statistical Mechanics

Univ. Prof. Dr. Wolfgang von der Linden   (Version of 16.12.2012)

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

December 14, 2017

Contents

Chapter 1

Introduction

When one examines the **behaviour** of a system of many particles, it is established, that it no longer depends on details and initial conditions. Usually a **thermodynamic** equilibrium, which is dependent only on few macroscopic variables – the so called **state variables** – is achieved after a very short time. The laws and phenomena of thermodynamics for macroscopic many particle systems are different from those at the atomic level. At all levels of scope there are organizing principles that are, for the most part, independant of microscopic properties. For example time reversal invariance no longer applies. The laws of thermodynamics can be derived from the microscopic equations of motion (classical resp. quantum mechanical). 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 the average quantities, for which the details of the individual particles are irrelevant. Phenomena of complex systems sometimes need only very little detail on a microscopic level. It would be similarly absurd for a doctor, in order to treat influenza, to solve the Schroedinger 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 behaviour, such as equilibria or irreversibility, evelolves from Newtonian equations of motion involving macroscopic parti-

cles, 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 to be in a cuboid volume of V, which we imagine to be divided into two sub-cubes of the volumes V_1 and V_2, by a vertical wall. The interface between those imagined sub-volumes shall be called A. Accordingly the expansion perpendicular to the wall is called L_1 resp. L_2. We define this direction to be the x-axis.

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. As we don't know where on the x-axis it is at any given moment, the probability that it will cross the wall A within the timeframe of dt is given by

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

As at the point in time t there are a total of N_1 atoms within the volume V_1 with an average velocity of v_x in x-direction. According to 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 current density ρ_1 in V_1. Over the course of the following considerations we will write this probability as

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

The same applies to V_2 of course. For the case of dt being infinitesimally small, there will be no cases of two atoms crossing A at the same time. Therefore within dt there exist 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 there are N_1 particles in the volume V_1.

We determine the sought-after 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) returns

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

We are only interested in the stationary distribution $P(\mathcal{N}_1^{(t \to \infty)} = m)$, the derivation of which can be found in Appendix (A.1) [Page 192]. The sought-after stationary distribution is

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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 allocated coincidentally, with apriori probabilities corresponding to the partial volumes.

From the known formula for the average number of particles in volume V_1 we get

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MEAN VALUES AND DENSITIES IN EQUILIBRIUM

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

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

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

</div>

Thus a homogeneous density distribution is achieved in equilibrium. In 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

$$dP = dt \; A \rho v_x = dt \; \frac{N v_x}{L_x} \; . \tag{1.2}$$

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

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RELATIVE UNCERTAINTY OF THE MEAN VALUE

$$\frac{\Delta N_1}{\langle N_1 \rangle} = \sqrt{\frac{q_2}{q_1 N}} = O(10^{-12}) \; ; \qquad \text{fÃ} \frac{1}{4} \text{r} \; 10^{24} \text{Atome} \; .$$

</div>

That means, the macroscopic system goes towards a stationary distribution for which the state variables **assume sharply peaked values**. The third and most valuable thing we have learned on the basis of this model, is the

fact that in equilibrium we have the state with the greatest probability, or at equal apriori probabilities 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 $N_1 = N/2$. This would be the average number of particles for a equal apriori probabilities $q_\alpha = 1/2$.

EQUILIBRIUM

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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 ($\Delta N_1 = r$). 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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THERMAL VELOCITY

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

For air molecules with $A \approx 29$ this is close to the speed of sound. Since we are only intersted in the magnitude, we consider the special case $V_1 = V_2$ and only take into account deviations, that are small enough for the probabilities for switching back and forth between the subsystems to be equal at all times. 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) . The changes from left to right and vice versa occur with the same probability ($P = 1/2$). The probability density for no event to occur is therefore $q = 1 - dP$.

Now let us calculate how many steps are needed 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 $0, 2, \ldots, 2r$. The starting point is r and it ends when the positions 0 or $2r$ are reached for the first time. A very thorough approach to the subject 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**.

Hereto we define the average runtime E_n, which indicates how long it takes on average until the walker reaches one of the two limits for the first time. There are two constraints

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

which apply, as in both cases the goal has already been reached and no further steps are necessary.

We look at 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 what the average runtime after the first step is. Furthermore, the time increment for the first step is added. This equation can be simplified to

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

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

That is the equation in which the **waiting times** have been eliminated, and a hopping process occurs within every timestep. This differential 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) [Page 7].

$$
\begin{aligned}
&a + b(n+1) - (n+1)^2 + a + b(n-1) - (n-1)^2 - 2\big(a + bn - n^2\big) \\
&= -(n+1)^2 - (n-1)^2 + 2n^2 \\
&= -\big(n^2 + 2n + 1 + n^2 - 2n + 1 - 2n^2\big) \\
&= -2 \ .
\end{aligned}
$$

To fulfill the boundary conditions of Equation (1.3) [Page 7] we still need

$$
\begin{aligned}
a + b \cdot 0 - 0^2 &= 0 \ ; &&\Rightarrow &a &= 0 \\
b \cdot 2r - (2r)^2 &= 0 \ ; &&\Rightarrow &b &= 2r \ .
\end{aligned}
$$

With that the sought number of steps is

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

A random walk takes an average of 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. We want to emphasise once again that we have neglected the density-dependant driving force towards equilibrium[1]. With these terms it would take even longer! Therefore we can conclude, that we will never observe such fluctuations. This is one of the reasons for the stability and universality of the thermal equilibrium.

Average time until a stationary distribution is reached

We have already shown that a macroscopic system will not leave the state of equilibrium and 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 furthest from equilibrium, i.e. all atoms are located in the sub-volume 1.
Similar to the previous consideration of fluctuations, we determine the average number of steps necessary to reach the state $N_1 = N/2$ for the first time when starting from the state $N_1 = 0$. We assume there is a total of N particles in the system.
We define the average runtime E_n, which indicates the time it takes on average for the distribution of $N_1 = n$ to reach the distribution of $N_1 = N/2$. However, here we have different boundary conditions

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

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 $\left(1 - \frac{n}{N}\right) \, dP$ one particle is added to N_1 and therefore the average runtime is now E_{n+1}.

---

[1] Changes of $\Delta N_1 = \pm 1$ were equally probable.

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 now reintroduce $D_n := dP\, E_n$ and therefore get

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

Again D_n is the average runtime for $dP = 1$ (or $r = 0$), i. e. each step is linked to a hopping process. The derivation for the result can be found in Appendix (A.2) [Page 195]. The solution to this problem is

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

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

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

AVERAGE 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 $L_x = 10cm$, then this time is

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

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

suitable model. In a volume of the size V there are N free classical non-interacting particles. The volume, as depicted in Figure 1.1, shall be imagined to be divided into two chambers V_u and V_l by a partition wall A. A micro-
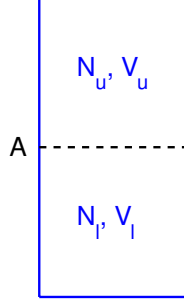
Figure 1.1: Schematic representation of the model system.

state consists of the exact location and velocity of the individual particles. At the beginning, the velocities are to be randomly distributed.[2] In addition the exact values of the initial conditions are unknown. Therefore, although the movement of the particles obeys the laws of Newtonian mechanics, the distribution of the particles on the elementary volumes is random: small, indiscernible changes in the 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 further simplify the model. The dynamics should lead to the particles being distributed stochastically to the M voxels – inside of which tere can only be one particle – at different times (therefore a kind of hard-core interaction). If a particle randomly moves through the volume V with constant speed, the apriori probability for the particle to be encountered in an elementary volume is proportional to its size. For simplicity's sake, all volumes are to be of the same size. A micro-state thus consists of the information, in which voxels the particles are located. We now assume that we are intersted in a macroscopic measurement parameter for our model, which only counts how many particles are located in the two chambers V_u and V_l, a distribution which comes about for reasons like differing electrical or magnetic fields. With this we have now defined our model.

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

1.2.1 Isolated chambers

At first we consider the two chambers V_u and V_l to be isolated from each other, i.e. the partition wall to be impenetrable. If N_ν particles are located within the volume V_ν with M_ν voxels ($\nu \in \{u, l\}$), then the number of micro-states that are compatible with this 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 this means that

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

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 (it is there given by h^3), so we can assume $M_\nu \gg N_\nu$ to be true. This further simplifies the result

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

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

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

The last term is proportional to N/M and therefore negligible compared to the other terms. The apriori 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 aposteriori individual probability for volume V_ν to be

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

From this follows that

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

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

$$N_\nu^0 := q_\nu^0 N \ . \tag{1.10}$$

The right sides of Equation (1.8) [Page 13] and Equation (1.9) [Page 13] respectively correspond to the relative entropy, which we have again expressed in the particle numbers.

1.2.2   Particle exchange between both parts

We now want to remove the partition 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 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 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 overall 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

$$\mathcal{S}_{12}(N_u, N_l) := \ln\left(L_{N_u|M_1}L_{N_l|M_2}\right) = \sum_{\nu\in\{u,l\}} \ln(L_{N_\nu|M_\nu}) = \sum_{\nu\in\{u,o\}} \mathcal{S}_\nu(N_\nu) \tag{1.11}$$

Since all involved numbers are of the scale of macroscopic values, we can use the stationary phase approximation, which is explained in Appendix (B) [Page 200]. 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 o fthe deviations from the maximum. First, we want to get the maximum as a function of N_u. As usual we determine the

maximum from the zero point of the derivation. Taking into account that $\frac{dN_l(N_u)}{dN_u} = -1$ we get

$$
\begin{aligned}
\frac{d\mathcal{S}(N_u, N_l(N_u))}{dN_u} &= \frac{\partial S_u, N_l(N_u))}{\partial N_u} - \frac{\partial S_l(N_u, N_l(N_u))}{\partial N_l} \\
&= -\ln\left(\frac{N_u}{N_u^0}\right) + \ln\left(\frac{N_l}{N_l^0}\right) \overset{!}{=} 0 \qquad (1.12) \\
\frac{N_u}{N_u^0} &= \frac{N_l}{N_l^0} = c \ .
\end{aligned}
$$

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

$$
\begin{aligned}
N_\nu &= c \cdot N_\nu^0 \\
N = \sum N_\nu &= c \sum N_\nu^0 = c \cdot N \\
\Rightarrow \quad c &= 1
\end{aligned}
$$

respectively

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

This means that in this case the equilibrium configuration corresponds to the case where th densities in both chambers are equal. At the same time we can discern 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 a quantity of equilibrium. It implies, that for a change of dN in the particle number, the entropy changes by $\tilde{\mu}dN$. This is identical on both sides. The quantity $\tilde{\mu}$ is proportional to the chemical potential. As a result, we obtain that equal densities are attained 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 point of the maximum. For this we use the first derivative from Equation (1.12) [Page 14]

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

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

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

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 execute the sum in the stationary phase approximation. To do this, we 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.

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

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

With this 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 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 the macroscopic model mesurement quantity, 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 size is determined with a relative accuracy 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.
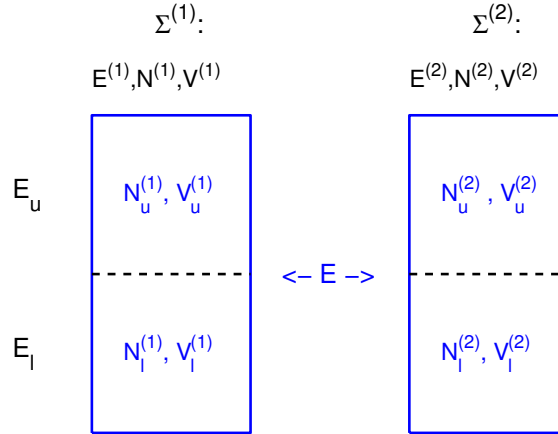
Figure 1.2: Schematic representation of the model system.

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

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

and contains a 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 apply to the energies $E^{(1)}$ and $E^{(2)}$ of the systems before establishing of thermal contact. These energies do not necessarily have to correspond to the maximum numbers of micro-states for the isolated systems, as we shall experimentally prepare the systems appropriately. Because both systems are isolated initially, they retain their energy.

Now we establish contact between the systems, so that 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

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

This energy exchange 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:

$$N^{(i)} = N_l^{(i)} + N_u^{(i)} \ ; \qquad\qquad \text{for } i = 1, 2 \ . \qquad (1.13)$$

However, the volumes of the chambers are fixed. For both systems $\Sigma^{(i)}$ the particle numbers of the sub-volumes now change from N_ν to the conditional particle numbers $N_{\nu|i}$. The total number of particles N of the single system now becomes the particle number N^i of the system i.

We are now intersted 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

$$\Gamma(N_u) = \sum_{N_u^{(1)}=0}^{N_u} \Gamma(N_u^{(1)}) \, \Gamma(N_u^{(2)}(N_u^{(1)})) \qquad (1.14)$$

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

With the stationary phase approximation we first simplify the summands in a similar way, as we have done before for a single system. For this we use Equation (1.11) [Page 13].

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

$$\overset{(1.11)}{=} \sum_{i} \sum_{\nu} \mathcal{S}_\nu^{(i)}(N_\nu^{(i)})$$

It is to be noted, that for the particle-number arguments, the constraints of Equation (1.13) [Page 17] have to be fulfilled. For the single summands we

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

now use Equation (1.9) [Page 13] and get

$$\mathcal{S} = \sum_i \underbrace{\left\{ -\sum_{\nu \in \{u,l\}} N_\nu^{(i)} \left[\ln\left(\frac{N_\nu^i}{N_\nu^{0(i)}}\right) - 1 \right] \right\}}_{\mathcal{S}_i} \tag{1.15}$$

$$= \mathcal{S}_1(N_u^{(1)}, N_l^{(1)}(N_u^{(1)})) + \mathcal{S}_2(N_u^{(2)}, N_l^{(2)}(N_u^{(2)})) \tag{1.16}$$

with: $\quad N_l^{(i)}(N_u^{(i)}) = N^{(i)} - N_u^i . \tag{1.17}$

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 those numbers of particles can be chosen freely, whereas all the others are dependent on this one through the constraints

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

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

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

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

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

Therefore $N_u^{(1)}$ is the only independant variable. We summarise the result

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<div align="center">

NUMBERS OF PARTICLES

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

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

dependant variable :

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

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

$$N_l^{(2)} = N^{(2)} - N_u + N_u^{(1)} \tag{1.18}$$

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

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

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

</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 point of the derivation of $\mathcal{S}$ with respect to $N_u^{(1)}$

$$\frac{d\mathcal{S}}{dN_u^{(1)}} = \frac{d\mathcal{S}^{(1)}}{dN_u^{(1)}} + \frac{d\mathcal{S}^{(2)}}{dN_u^{(1)}} = \frac{d\mathcal{S}^{(1)}}{dN_u^{(1)}} + \frac{d\mathcal{S}^{(2)}}{dN_u^{(2)}} \underbrace{\frac{dN_u^{(2)}}{dN_u^{(1)}}}_{-1} \tag{1.19}$$

$$= \frac{d\mathcal{S}^{(1)}}{dN_u^{(1)}} - \frac{d\mathcal{S}^{(2)}}{dN_u^{(2)}} \overset{!}{=} 0 \tag{1.20}$$

This gives us a new quantity of equilibrium, which assumes the same value in both systems. If we take into account that the energy in the system $\Sigma^{(i)}$ is given by $E^{(i)} = E_u N_u^{(i)}$, where E_u is the given energy unit, then in equilibrium (where the number of micro-states is maximal) the following applies:

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

THERMAL EQUILIBRIUM AND TEMPERATURE

$$\frac{dS^{(1)}}{dE^{(1)}} = \frac{dS^{(2)}}{dE^{(2)}} =: \frac{1}{k_B T} \qquad (1.21)$$

</div>

This formula also corresponds to the statistical definition of temperature. We further reshape the derivations in Equation (1.20) [Page 19]

$$\frac{dS^{(i)}}{dN_u^{(i)}} = \frac{dS^{(i)}(N_u^{(i)}, N_l^{(i)}(N_u^{(i)}))}{dN_u^{(i)}}$$

$$= \frac{\partial S^{(i)}}{\partial N_u^{(i)}} + \frac{\partial S^{(i)}}{\partial N_l^{(i)}} \underbrace{\frac{dN_l^{(i)}}{dN_u^{(i)}}}_{-1}$$

$$= \frac{\partial S^{(i)}}{\partial N_u^{(i)}} - \frac{\partial S^{(i)}}{\partial N_l^{(i)}}$$

$$\overset{(1.15)}{\Rightarrow} \qquad \frac{dS^{(i)}}{dN_u^{(i)}} = -\ln\left(\frac{N_u^{(i)}}{N_u^{0(i)}}\right) + \ln\left(\frac{N_l^{(i)}}{N_l^{0(i)}}\right). \qquad (1.22)$$

Barometric formula

We make sure that the temperature introduced in this way has the right properties. On the one hand, the following applies

$$\frac{E_u}{k_B T} = E_u \frac{dS^{(i)}}{dE^{(i)}} = \frac{dS^{(i)}(N_u^{(i)}, N_l^{(i)}(N_u^{(i)}))}{dN_u^{(i)}}$$

$$\overset{(1.22)}{=} -\ln\left(\frac{N_u^{(i)}}{N_u^{0(i)}}\right) + \ln\left(\frac{N_l^{(i)}}{N_l^{0(i)}}\right)$$

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

Therefore we have

$$\ln\left(\frac{N_u^{0(i)} N_l^{(i)}}{N_u^{(i)} N_l^{0(i)}}\right) = \frac{E_u}{k_B T} = \beta E_u. \qquad (1.23)$$

In this, we recognize the barometric formula. For the same apriori probability, 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 number gives

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

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

Direction of energy transfer

These model considerations also show in which direction energy flows during thermal contact. For this we consider an initial state, which is characterized by the occupation numbers $N_u^{*(i)}$ and $N_l^{*(i)}$. The temperatures of the two initially separate systems are defined in Equation (1.21) [Page 20].

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

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, then the left side is positive and the right side returns

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

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

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

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

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 only calculated the maximal contribution to the sum in Equation (1.14) [Page 17]. We now continue with the stationary phase approximation. To do this, we need the second derivative at the maximum. First, we further transform the first derivative which we calculated in Equation (1.19) [Page 19]

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

$$\overset{(1.22)}{=} -\left(\ln\left(\frac{N_u^{(1)}}{N_u^{0(1)}}\right) - \ln\left(\frac{N_l^{(1)}}{N_l^{0(1)}}\right) - \ln\left(\frac{N_u^{(2)}}{N_u^{0(2)}}\right) + \ln\left(\frac{N_l^{(2)}}{N_l^{0(2)}}\right) \right)$$

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

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

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

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 (1.18) [Page 19].

Now we can again transform the sum in Equation (1.14) [Page 17] into a gaussian integral and eventually we again 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 temperature definition

Based on this, 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 (1.18) [Page 19] we had found that

$$N_u^{(2)} = N_u - N_u^{(1)}$$
$$\frac{dN_u^{(2)}}{dN_u} = 1 - \frac{dN_u^{(1)}}{dN_u} \tag{1.24}$$

Dependency on N_u can be found 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. With this we have

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

$$= \underbrace{\frac{d\mathcal{S}^{(1)}(N_u^{(1)}, N_l^{(1)}(N_u^{(1)}))}{dN_u^{(1)}}}_{\frac{E_u}{k_B T^{(1)}}} \frac{dN_u^{(1)}}{dN_u} + \underbrace{\frac{d\mathcal{S}^{(2)}(N_u^{(2)}, N_l^{(2)}(N_u^{(2)}))}{dN_u^{(2)}}}_{\frac{E_u}{k_B T^{(2)}}} \underbrace{\frac{dN_u^{(2)}}{dN_u}}_{\overset{(1.24)}{=}1-\frac{dN_u^{(1)}}{dN_u}}$$

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

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 learned in probability theory? With p_l as the probability of the l-th microstate, the entropy we used in probability theory was

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

The principle of maximum entropy states, that this entropy is to be maximised strictly abiding by the constraints. 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

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

Entropy as a measure of uncertainty or disorder is fully defined except for a proportionality constant which has no influence on the maximum entropy. 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

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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. In doing so the previous value only contributes to the sum over positive values. Therefore also the number of micro-states and the entropy increase.

1.3   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 good – macroscopic measurement quantities[4] are time-independent. Furthermore, it can be determined that such measured quantities are dependent on very few state variables (such as temperature,

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[4]this of course implies spatial averaging

pressure, volume, density, ...) and are reversible. This means that no matter which values a state variable had beforehand, once these values are set, the measurement quantity always has the same value.
We will now try to understand this behaviour on a microscopic scale.

1.3.1   Hamiltonian equation of motion

For this we need to know some details of the Hamiltonian equations of motion. From analytical 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 space, the phase space for N particles is $2dN$-dimensional. The coordinates of a point in this phase space are defined in such a way that in a vector the d components of the first particle, then those of the second particle up to those of the N-th particle are given. Then the momentum-components are inserted

$$\pi = \left(x_1, x_2, \ldots, x_{\mathcal{N}}, p_1, p_2, \ldots, p_{\mathcal{N}} \right) \tag{1.25}$$

$$\mathcal{N} := N \cdot d \ . \tag{1.26}$$

The Hamilton equations then result in

$$\frac{dx_\nu}{dt} = \frac{\partial H}{\partial p_\nu} \tag{1.27}$$

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

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

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

Two important comments:

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

- Of course, at a later point in time the trajectory depends on its starting location. However, the rate of change $\frac{d\pi}{dt}$ does not depend on it, but only on the current position (like a markov process).

On the right side of (1.27) momentum and coordinate are reversed in the derivatives in contrast to the left side. Therefore we introduce a $2dN$-dimensional matrix T, which performs this swapping of ∇_π. This means we want to achieve

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

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

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

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

1.3.2 Time average

We now consider the movement of a point in phase space. At a starting time of $t = 0$, in phase space the system is at the point $\pi(t = 0)$. According to Hamilton's equations of motion, the point in phase space moves and at a point in time t it is located at $\pi(t)$. A measurement quantitiy F, which is not explicitly time-dependent then has the value $F(\pi(t))$ at time t. The fact that for macroscopic measurement quantities experimentally no time-dependency is observed means that averaging is always carried out over a finite volume in spatial space. Of course, if we look closely we wil see the individual atoms and their temporal behaviour. This averaging is already included in the macroscopic measurement quantity $F(\pi)$. Nevertheless, one would still not expect stationary behaviour. This can only be the case if one also averages over time. This means, that what one observes in "thermodynamic" experiments is a time average

$$\overline{F}^Z(t) := \frac{1}{t}\int_0^t F(\pi(t'))dt' = \frac{1}{t}\int_0^t F(\pi(t')) \underbrace{\left(\int \delta(\pi - \pi(t'))\, d^{2\mathcal{N}}\pi\right)}_{=1} dt'$$

$$= \int F(\pi) \underbrace{\left(\frac{1}{t}\int_0^t \delta(\pi - \pi(t'))\, dt'\right)}_{\rho^Z(\pi,t)} d^{2\mathcal{N}}\pi.$$

With this we have reshaped the time average into a common form for averages of functions over phase space.

<div style="text-align:center">TIME AVERAGE</div>

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

$$\rho^Z(\pi,t) := \left(\frac{1}{t}\int_0^t \delta(\pi - \pi(t'))\,dt'\right)$$

The thusly defined time average corresponds to the mean value of the function $F(\pi)$ with the probability density $\rho^Z(\pi,t)$, which determines how large the probability to find the trajectory within the volume $d\pi$ centered around the point π in phase space at the time t is. This probability density is synonymous with the average time that the phase space trajectory spends within the volume $d\pi$ at π altogether. The experimental observation that in thermal equilibrium the macroscopic measurement quantities are stationary means that $\rho^Z(\pi,t)$ is not dependant on t. This however, requires the measurement time to be sufficiently long.

1.3.3   Manifold average

There is another method for averaging, which is the so called manifold average. As one does not know the exact initial state, this situation can also be described by many points in phase space (ensemble). Those points all evolve over time according to Hamilton's equations of motion and are not correlated with each other. The trajectory for the n-th point of the ensemble shall be $\pi^n(t)$. The manifold-(ensemble)average therefore is

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

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

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

With this we have the solution for the manifold average.

MANIFOLD AVERAGE

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

This expression is formally equal to the time average. Only 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 the time t. For an infinite number of ensemble points we get something like a mass density, something that was introduced in fluid mechanics. For this density we can derive an equation of motion

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

$$= -\frac{1}{N} \sum_{n=1}^{N} \left(\nabla_\pi \delta(\pi - \pi^n(t)) \right) \, T \nabla_\pi H(\pi) \Big|_{\pi^n(t)} \; .$$

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

LIOUVILLE EQUATION

$$\frac{\partial}{\partial t} \rho^S(\pi, t) = -\left(\nabla_\pi \rho^S(\pi, t) \right) \dot{\pi}(\pi, t) \; . \qquad (1.29)$$

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

1.3.4   Derivation from prbability theory

1.3.5   Information-Theoretical approac

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 Hamilon'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.

Now we shall rewrite the notation to some extent. 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 can they originate from nothing and therefore the continuity equation has to apply here too. 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 (1.27) is – as was already discussed – only dependant on the respective point $\pi(t)$, but not on the starting point. Therefore we

have

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

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

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

This means that formally we have the same result as for the ensemble average in Equation (1.29) [Page 28].

This means that the approach via the artificial ensemble and the approach via probability theory are formally identical.

Therefore from now on we will only use the symbol ρ for density. Since $\rho\dot{\pi} = j$ is the current density, this is the continuity equation, albeit already in a specal form, since the derivative only affects the density and not the velocity field $u = \dot{\pi}(\pi',t)$. As the continuiety equation has to apply because of the conservation of trajectories, u obviously is divergence-free. We will show this now by using (1.27)

$$\nabla_{\pi} \ \dot{\pi}(\pi,t) = \nabla_{\pi} T \nabla_{\pi} H = 0 \ , \tag{1.30}$$

as $xTx = 0$ is valid for every vector. Therefore ρ is incompressible. This means in turn that the density along a trajectory does not change. For further verification we need the Eulerian-Cauchy equation

$$\frac{d}{dt}\rho(\pi(t),t) = \frac{\partial}{\partial t}\rho(\pi,t) + \nabla_{\pi}\rho(\pi,t)\dot{\pi} \overset{(1.29)}{=} 0 \ .$$

This implies that the density at the point in space, $\pi(t)$, which is assumed according to the equation of motion at time t, does not depend on time. In simple terms this means the following:

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

The density ρ is constant along a trajectory!

</div>

The continuity equation is a consequence of the preservation of the number of trajectories. However, the incompressibility additionally follows from Hamilton's equation of motion (see (1.30)).

1.3.6   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 strarting 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 of 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 norming constant will depend on the energy

$$\rho(\pi) = \frac{1}{Z(E)} \ , \qquad \text{for all } \pi \text{ on the hypersurface} \qquad (1.31)$$

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

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

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 a limit of E

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

1.3.7   Stationarity

We have already stated that with thermal equilibrium a stationary state, characterised by $\rho(\pi, t) = \rho(\pi)$, is reached.

In reversible processes one always observes the equilibrium to be reproducible and independent of the starting point. However, how can one understand on a microscopic level that this is the case? Here something comes into play, that is mostly caused by the large number of particles and not the dynamics. There are two reasons why and when the density becomes stationary. According to the above considerations, the density is $\rho_E(\pi) = 1/Z(E)$, for all

---

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

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 thus automatically constant on the energy-hypersurface. This automatically results in the stationarity of $\rho(\pi, t)$. For this purpose we rewrite Equation (1.29) to

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

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

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

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.

Chapter 2

Classical Statistical Physics

2.1   Introduction

2.1.1   What a thermodynamic system is

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

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

The whole is more than the sum of its parts!

Nevertheless, it will not be necessary to solve the coupled equations of motion of the individual copmonents, 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 transitions 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 by 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 movement 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 deriving with respect to E:

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

With the volume of the $3N$-dimensional hypersphere from Equation (C.2) [Page 202], which has the radius radius $\sqrt{2mE}$, we finally get

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

This result has some weaknesses, which can only be corrected by quantum mechanics. This includes the entropy of mixing, 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

$$
E_{\vec{l}} = \frac{1}{2m} \sum_{i=1}^{3} \left(\frac{2\pi \hbar l_i}{L_i}\right)^2 = \frac{1}{2m} \sum_{i=1}^{3} \left(\frac{h l_i}{L_i}\right)^2 \, ,
$$

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

$$
F_{\mathbf{1}}^{\mathrm{qm}}(E) = \sum_{\vec{l}} \theta(E - E_{\vec{l}}) \, \triangle^3 l
$$

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

$$F_1^{\mathrm{qm}}(E) = \frac{L_1 L_2 L_3}{h^3} \sum_{\vec{p}(\vec{l})} \theta(E - E_{\vec{n}}) \triangle^3 p$$

$$= \frac{V}{h^3} \sum_{\vec{p}(\vec{n})} \theta(E - E_{\vec{p}(\vec{n})}) \triangle^3 p .$$

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.

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

Initially, the number of microstates for N particles is $(F_1)^N$. If the particles are all of the same type, however, they are indistinguishable as quantum particles. Therefore, the result is as follows

$$F_N^{\mathrm{qm}}(E) = \frac{V^N}{h^N N!} \left(\int \theta(E - \frac{p^2}{2m}) \, d^3 p \right)^N .$$

We recognise a small but very important difference to the classical result. Due to quantisation and indistinguishability there is an additional prefactor $1/(h^N N!)$, which does not bring to bear in most cases, but is essential for the correct description of experiments in some situations. Without this prefactor the classical calculations yield the so-called Gibbs paradoxon, on which we will elaborate later on in Section (4.1.3) [Page 85].

It can be seen, that a quantum mechanical minimal correction is to use a different measure of integration instead of $d^{2\mathcal{N}} \pi$, namely

---

MEASURE IN PHASE SPACE FOR CLASSICAL PROBLEMS

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

Summarising the results we got so far:

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NUMBER OF MICROSTATES AND BOLTZMANN ENTROPY

$$Z(E, N, V, d) := \int \delta(H(\pi) - E) \, \mathcal{D}_\pi^\mathcal{N} = \frac{1}{h^\mathcal{N} N!} \int \delta(H(\pi) - E) \, d^{2\mathcal{N}} \pi$$

$$S^B(E, N, V) := k_B \ln\left[\text{Z(E, N, V)}\right] . \qquad (2.2)$$

</div>

These expressions are applicable to a system with only one type of particle, i.e. indistinguishable objects. For distinguishable particles the faculty $N!$ in the definition of the measure is missing.

2.2.2   Coupled subsystems

We shall abstractly consider two isolated systems, which we describe with the two state variables z_j. These state variables can be the energy, the particle number, the volume, etc.

As in the model example, we now connect the two isolated systems with the values of the state variables before the contact being $z_j^{(1/2)}$. Here the entire system shall still be insulated. 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. However the wall separating the subsystems can be moved while also energy can be exchanged. Only the individual number of particles remains fixed. We now break down the set of state variables in those that remain fixed – $\vec{f}$ – and those that are variable – $\vec{v}$. With this, before the contact there are the states $(\vec{f}^{(1)}, \vec{v}^{(1)})$ und $(\vec{f}^{(2)}, \vec{v}^{(2)})$ and after the contact the individual values $\vec{f}^{(1/2)}$ are preserved. The variable state variables will change, albeit subject to the following conditions

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

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 maximaml number of micro-states or the largest phase space volume (compatible with the specified macroscopic state variables). Otherwise the two systems should not interact and therefore the number of micro-states or phase space volumes is the same as the procuct 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 is obtained from partially deriving by the various $v_j^{(1)}$ while all other variables are fixed.

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

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

Dividing by Z yields

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

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

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

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

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.

DEFINITION OF TEMPERATURE

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

In terms of statistical physics, temperature thus corresponds to the relative change with energy, that occurs in the phase volume of a microcanonical unit.

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:

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

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

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.

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

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

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

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

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

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

Comparison with (*) yields

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

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

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

---

[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.

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

---

PRESSURE

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

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).

2.2.3 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 main 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

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

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

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

2.2.4 Second main 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 main 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 separate 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) 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 biggest 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 greater than the one belonging to the initial state. Therefore entropy
increases.

Direction of the energy flow

After having verified the validity of the second main 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 individu-
ally 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 thermody-
namic 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

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

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.

$$\Delta S = \left(\frac{\partial S^{(1)}}{\partial N_1} - \frac{\partial S^{(2)}}{\partial N_2} \right) (N_1^* - N_1^0)$$

$$= \left(\frac{\mu_1}{T} - \frac{\mu_2}{T} \right) \Delta N_1$$

$$= \left(\mu_1 - \mu_2 \right) \frac{\Delta N_1}{T}$$

$$\overset{!}{\geq} 0 \ .$$

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 partition wall between them so that the same pressure is applied on both sides. This is done in such a way that the volume increases in the subsystem in which the pressure was previously greater.

2.2.5 The first main law and the basic relations of thermodynamics

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:

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

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

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

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

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

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

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

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

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

$$
\text{FIRST LAW OF THERMODYNAMICS}
$$

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

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.

Implications from homogenity

The natural variables of entropy (E, N, V) are all extensive quantities. As a result of homogenity 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 side:

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

from the right 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 side is not dependent on λ, the same has to be true for the right side and therefore we can analyse it for $\lambda = 1$. For this we get

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

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. The approach for this is the following:

- Formulating the Hamilton function $H(\pi|\alpha)$, which may not only contain 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 (inner) 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.

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

Example: Ideal gas of classical particles

In Section (4.1.1) [Page 83] we consider an ideal gas of classical particles as an example.

2.2.6 The appeal of equilibrium and irreversibility

As was seen in the introductory example, a system converges to the state of equilibrium within a very short span of time. From there it does not emerge within a finite timeframe. Using the example of the model systems, it was shown 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 discepancy 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 measure of states, which lead to the system leaving equilibrium is zero in the thermodynamic limit.

2.3 Canonical ensemble

The microcanonical ensemble describes isolated systems. We shall thus change this idealised situation and now consider only a closed system, which can exchange energy with its environment. This system shall temporarily

be called **reference system**. The environment (**heat bath**) is significantly larger than the reference system. The whole system, consisting of heat bath and reference system, shall again be isolated. 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 heat bath's temperature. The statistical ensemble describing this situation is called **canonical ensemble**.

2.3.1 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. While doing so, the index R represents the reference system and B 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

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

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

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

The remaining integral is the area of the bath's hypersuface at the energy $E - H_R(\pi_1)$. 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 dependency of 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.

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

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

The first order term yields

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

whereby we have to be considered 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 in a way that in relation to this the second order term is a factor N_R/N_B smaller and can be neglected for $N_B \to \infty$.

Now, having derived the result, the indices can be omitted, as the bath as a temperature supply does not turn up anymore.

PROBABILITY DENSITY OF THE CANONICAL ENSEMBLE

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

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 90].

b) Free classical particle in an external potential

Considering 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 $\vec{p}$, in which the momentum coordinates of all particles are arranged in columns. The canonical partition function then is given by Die kanonische Zustandssumme ist dann

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

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

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

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

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

CANONICAL PARTITION FUNCTION FOR FREE CLASSICAL PARTICLES

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

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

2.3.2 Connection to thermodynamics

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

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

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

The microcanonical ensemble is defined by the variables $(E = U), N, V$. These are, as it is already known from thermodynamics, the **natural variables** of the **thermodynamic potential** $S = S(U, N, V)$. With this the energy $U(S, N, V)$ can be expressed as a function of S, N, V. Thus the internal energy is not a thermodynamical 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 within the canonical ensemble in stead of S. In order to transition from a function of the variables (S, N, V) to one of the variables (T, N, V) a Legendre transformation is needed. Here this leads to the **free energy**

FREE ENERGY

$$F(T, N, V) = U(T, V, N) - T \, S(T, V, N) \, . \tag{2.14}$$

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:

$$
\boxed{
\begin{array}{c}
\textsc{Free energy} \\
(\textit{Total differential}) \\
\hline
\\
dF(T, N, V) = -SdT - pdV + \mu dN \ . \qquad (2.15) \\
\\
\end{array}
}
$$

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

$$dF = -SdT - pdV \ . \qquad (2.16)$$

For the pressure the following relation is used

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

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

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 borders are plugged into the Hamilton function via a box shaped potential. Thus the integration borders are independent from V and it is possible to swap differential and integration

$$
\begin{aligned}
\frac{1}{\beta} \ln \left[Z(T, N, V) \right] &= \frac{1}{\beta Z} \int \frac{\partial}{\partial V} e^{-\beta H(\pi)} \ \mathcal{D}_\pi^\mathcal{N} \\
&= \frac{1}{\beta Z} \int e^{-\beta H(\pi)} \frac{\partial (-\beta H)}{\partial V} \ \mathcal{D}_\pi^\mathcal{N} \\
&= -\frac{1}{Z} \int e^{-\beta H(\pi)} \frac{\partial H}{\partial V} \ \mathcal{D}_\pi^\mathcal{N} = -\langle \frac{\partial H}{\partial V} \rangle = p \ .
\end{aligned}
$$

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

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

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

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

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

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

With this we have the sought after result

$$\boxed{\begin{array}{c}\text{FREE ENERGY}\\ \textit{(Partition function)}\\[1em] \hline \\ F(T, N, V) = -k_B T \ln[Z(T, N, V)]\\ Z(T, N, V) = e^{-\beta F}\ .\end{array}}$$

Since the free energy is a thermodynamical potential, from there, all independent variables can be determined by derivation. In principle, determinig the internal energy from F has already been done in Equation (2.13) [Page 54]. We get

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

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

Likewise the relation for pressure follows from Equation (2.17) [Page 55]

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

From Equation (2.15) [Page 55] we get the following for the entropy:

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

This is equivalent to the definition used in thermodynamcs. Later on it shall be shown, that the thus defined entropy is equivalent to the microcanonical definition.

Inferences 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:

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

b) from the right side:

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

Both sides together yield:

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

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

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

<div style="text-align:center">

FREE ENERGY
(*Alternative form*)

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

</div>

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

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

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

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

and, therefore, also the following is valid

HEAT CAPACITY II

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

From this **thermic stability** can be deduced that

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

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

Equation (2.19) [Page 58] can also be used to derive an interesting relation for the calculation of energy fluctuations

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

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
<div align="center">**Supplemental material**</div>

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

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

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

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

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

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

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

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

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

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

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

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

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

$$F = -k_BT\ln[Z]$$

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

$$= U - TS_{mkG} + O(\ln[N]) .$$

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

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

immediately yields the equivalence of the entropies, meaning

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

2.3.3 Virial theorem and equipartition theorem

We take a closer look at the thermodynamic expectation value

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

in the canonical ensemble. The microcanonical ensemble yields the same result. However, the calculation is far more extensive

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

Integration by parts finally yields

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

$$(2.22)$$

The first term in the integration by parts vanishes at the edges of the in-
tegration area. The edge for the momenta means $p \to \pm\infty$ and therefore
the cinetic energy is infinite. This prompts the Boltzmann factor to go to
zero. For the spatial part there are two possibilities. Either there is a finite
volume. However, the potential at the edge then has to be infinite. Or there
is an infinite volume. Here, the potential has to diverge too, as for example
for the harmonic oiscillator.
The result in Equation (2.22) [Page 63] is valid for any Hamiltonian function.
Now we shall consider the physical consequences. At first $\pi_i = p_l$ is the
canonical momentum for a generalised coordinate q_1. With this, according
to Hamilton's equations of motion we get the following

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

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

resp. $\sum_{l=1}^{\mathcal{N}} \langle p_l \dot{q}_l \rangle = 2\langle T \rangle = \mathcal{N} k_B T$.

This means that the average cinetic energy of each particle is

$$
\langle T \rangle = \frac{d}{2} k_B T \ .
$$

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

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

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

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

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

and therefore

$$
\langle T \rangle = \frac{\alpha}{2} \langle U \rangle \ .
$$

In the case of a quadratic potential the average cinetic 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

$$\langle T \rangle = \langle U \rangle = \frac{\mathcal{N} k_B T}{2}$$

$$\Rightarrow \quad \langle H \rangle = \mathcal{N} k_B T \; . \tag{2.23}$$

2.4 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 it is also difficult to keep the number of particles constant. In addition to that, it may change when changing other state variables. Therefore it is not a good state variable, something the chemical potential would be much better suited for. Thus we shall derive a thermodynamic potential whose natural variables are the temperature T, the 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 **heatbath** and a **particle reservoire**. From previous considerations we know that the system will attune to a common temperature and also a common chemical potential. Both state variables are determined by the heat bath, which shall be of infinite size. As the numbers of particles are not fixed, we have to expand phase space. To this end we define the **fock space**, which is a concatenation of phase spaces for different numbers of particles, beginning at zero particles and reaching up to infinite particles.

To further illustrate this we shall consider a simple example. For this we constrain the number of particles to 1 or 2 within a dimension $d = 1$ while only considering the spatial coordinate of the particles. For one particle we need a one dimensional 'phase space' and for two particles a two dimensional one. We assemble both of them to get a three dimensional coordinate system. The z-axis shall describe the phase space of a single particle system and the xy-plane the phase space for two particles. Legitimate points in this fock space are either located on the z-axis or in 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, where it also could have been defined as a part of π. If the reference system (R) is in the state $\pi_R^{N_R}$, then the number of particles in the bath has to be $N_B = N - N_R$ and it can be in any state $\pi_B^{N_B}$ with the particle number N_B. 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 through marginalisation leads to

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

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

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

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

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

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

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

However, now $T_B = T_R = T$ and $\mu_B = \mu_R = \mu$ apply again and the result therefore looks as follows:

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

It would now be possible to 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 $z := e^{\beta\mu}$.

This shows that the fact that total energy and total number of particles are conserved for the reference system means that temperature (average energy) and chemical potential (average number of particles) are determined by the bath.

2.4.1   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 we get

---

AVERAGE NUMBER OF PARTICLES

$$\langle N \rangle = \frac{\sum_N N z^N Z(T,N,V)}{\sum_N z^N Z(T,N,V)}$$

$$= \frac{1}{\beta} \left(\frac{\partial \ln[Z(T,\mu,V)]}{\partial\mu} \right)\bigg|_{T,V} . \tag{2.24}$$

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 then yields

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

Now the grand canonical partition function is dependent on the chemical potential only through the fugacity. Substituting μ by $\ln(z)/\beta$ in the partition function produces a funtion $Z(T, z, V)$ and with this also the following applies

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

Next we shall calculate the pressure within the framework of the grand canonical ensemble. Analogous to Equation (2.17) we get

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

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 for the derivation 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, has 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

$$\textsc{Grand canonical potential}$$

$$\Omega(T,\mu,V) = F(T,N,V) - \mu N$$
$$d\Omega = -SdT - pdV - Nd\mu$$
$$\left(\frac{\partial \Omega}{\partial T}\right)\bigg|_{V,\mu} = -S$$
$$\left(\frac{\partial \Omega}{\partial V}\right)\bigg|_{T,\mu} = -p \tag{2.28}$$
$$\left(\frac{\partial \Omega}{\partial \mu}\right)\bigg|_{V,T} = -\langle N \rangle \ .$$

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

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

The internal energy, the pressure and the average number of particles are then expressed according to Equation (2.27) [Page 67], (2.26) and (2.24) by the derivatives of $\ln(Z)$. With this we get

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

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*)

$$\Omega(T, \mu, V) = -k_B T \ln\left[Z(T, \mu, V)\right]$$
$$Z(T, \mu, V) = e^{-\beta\Omega(T,\mu,V)} \ .$$

Inferences from homogenity

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

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

The derivative of this equation with respect to λ is

left side: $$\frac{d}{d\lambda}\Omega(T, \lambda V, \mu) = \frac{\partial}{\partial V}\left(\Omega(T, V', \mu)\right)\Bigg|_{V'=\lambda V} V$$

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

both sides $$\frac{\partial}{\partial V'}\left(\Omega(T, V', \mu)\right)\Bigg|_{V'=\lambda V} V = \Omega(T, V, \mu) \ .$$

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

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

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) [Page 68]), 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.

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

The negative sign in the definition can be understood as being introduced as a consequence of the fact, that a reduction of volume should be accompanied by an increase in pressure. For this it is important to consider that the temperature is kept fixed, but not the chemical potential. Otherwise, because of

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

the following would have to apply:

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

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

$$\kappa_T \geq 0 \ .$$

In the frame of statistical mechanics the following relation can be deduced (see book of W. Nolting)

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

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

Fluctuation of the number of particles

In Equation (2.20) [Page 59] we had seen in the context of the canonical ensemble, that one can express energy fluctuations as the second derivative of the temperature (or β). Analogously the second derivative of the chemical potential can be considered for the fluctuation of the number of particles. Starting from Equation (2.28) [Page 68]

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

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 71] we get

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

As compressibility and temperature are intensive quantities we get

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

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 Section (4.1.5) [Page 95].

Chapter 3

Approach by 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'**

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

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 additionally the constraints that energy, volume and particle number are predefined apply. This defines the

---

[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.

statistical population. Within this statistical population maximising the entropy yields a constant probability density of

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

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

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 36]. The value of the Gibbs entropy at the point of the MaxEnt solution for $p(\pi)$ then yields

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

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

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

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.

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.

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

<small>EXTREMAL CONDITION FOR THE MICROCANONICAL ENSEMBLE</small>

$$\text{Entropy is maximal for fixed } N, V. \qquad (3.1)$$

3.3   Canonical ensemble

In the case of the canonical ensemble not only the energy, but also the temperature (and therefore the average energy) is present.

$$\frac{1}{T} := \left(\frac{\partial S(E, N, V)}{\partial E} \right) \bigg|_{V,N} = k_B \left(\frac{\partial \ln \left[Z(E, N, V) \right]}{\partial E} \right) \bigg|_{V,N}.$$

This means that we have a new 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, we get

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

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

with Z defining the norming factor as

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

With this the entropy at the position of the MaxEnt solution (Boltzmann entropy) 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

$$\frac{1}{T} = \frac{\partial S^*}{\partial \overline{E}} = k_B \lambda_1$$

$$\Rightarrow \quad \lambda_1 = \beta \ .$$

Therefore we have the relation

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

$$U(T, N, V) = S \, T + F \ .$$

Here we used the denotion 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 (2.3) [Page 50]. The Gibbs/Bayes approach is therefore more powerful than the Boltzmann approach.

3.3.1   Extremal conditions

Here we have maximised the functional

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

with regard to the possible probability density with consideration to the normalisation. This maximisation is valid for all values of λ_1 and therefore especially for $\lambda_1 = 1/T$. With this

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

becomes maximal for a 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

The free energy is minimal for fixed N, V. (3.2)

3.4   Grand canonical ensemble

If the particle number also stays variable and μ gives the average particle number, then the entropy has to 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

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

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

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 .

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

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

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

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. (3.3)

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

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 BOLTZMANN H-FUNCTION

$$H := -k_B \int p_g(\pi)\ln\left[\frac{p_g(\pi)}{p(\pi)}\right] \mathcal{D}_\pi^{\mathcal{N}}$$
$$= \left\langle \ln\left[\frac{p_g(\pi)}{p(\pi)}\right] \right\rangle_g .$$

</div>

It can be easily shown that $H \leq 0$ for arbitrary probability densities p_g and p. First we prove that

$$\ln(x) \leq x - 1 ; \qquad \forall x \geq 0 . \tag{3.4}$$

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 (3.4) is proven.
Now we shall use this inequation 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

One can easily deduce what happens if energy and volume are free and only temperature and pressure, and therefore the average energy and the average 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

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

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

$$S^* = k_B\lambda_1\langle H\rangle + k_B\lambda_2\langle V\rangle + k_B\ln{[Z]}$$

bzw. $$TS^* = k_BT\lambda_1\,U + k_BT\lambda_2\,\langle V\rangle + k_BT\ln{[Z]}$$

$$-k_BT\ln{[Z]} = k_BT\lambda_1\,U + k_BT\lambda_2\,\langle V\rangle - TS^*\,.$$

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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FREE GIBBS ENTHALPY

$$G(T, N, p) = -k_BT\ln{[Z]}$$
$$Z(T, N, p) = e^{-\beta G}$$
$$p(\pi|T, N, p) = \frac{1}{Z(T, N, p)}\,e^{-\beta(H(\pi)+pV)}$$
$$Z(T, N, p) := \int e^{-\beta(H(\pi)+pV)}\,\mathcal{D}_\pi^N\,.$$

</div>

From this it can be easily derived that

$$\left(\frac{\partial\ln{[Z(T, N, p)]}}{\partial T}\right)\bigg|_{N,p} = -\beta\langle H\rangle$$
$$\left(\frac{\partial\ln{[Z(T, N, p)]}}{\partial p}\right)\bigg|_{T,N} = -\beta\langle V\rangle$$

and therefore because of $G = -k_BT\ln{[Z]}$ the following applies:

$$\left(\frac{\partial G(Z(T, N, p))}{\partial p}\right)\bigg|_{T,N} = k_BT\beta\langle V\rangle = \langle V\rangle\,.$$

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 55] 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

$$G = \mu \ N$$

applies as well as $\qquad G = F + pV = U - TS + pV \ .$

Chapter 4

Implementation

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 hypersurface in phase space. This quantity (density) however, is easier to calculate by derivation of the associated distribution function, namely the phase space volume $\Gamma_N^{kl}(E)$.

$$\Gamma_N^{\text{kl}}(E) := \int \theta(E - H(\pi))\, \mathcal{D}_\pi^{\mathcal{N}}$$

$$= \frac{1}{h^{\mathcal{N}} N!} \int \theta(E - \frac{p_{ges}^2}{2m}) d^{\mathcal{N}} x\, d^{\mathcal{N}} p$$

$$= \frac{V_{\mathcal{N}}}{h^{\mathcal{N}} N!}\, V^N\, (\sqrt{2mE})\;.$$

With the volume of the $\mathcal{N} = 3N$-dimensional hypersphere of radius $\sqrt{2mE}$ from Equation (C.2) [Page 202] we eventually get

$$\Gamma_N^{\text{kl}}(E) = \frac{V^N}{h^{\mathcal{N}} N!}\, (2mE)^{\frac{\mathcal{N}}{2}}\, \frac{\pi^{\frac{\mathcal{N}}{2}}}{\Gamma(\frac{\mathcal{N}}{2} + 1)} \tag{4.1}$$

$$= \frac{V^N}{N!} \left(\frac{2\pi m E}{h^2} \right)^{\mathcal{N}/2} \frac{1}{\Gamma(\frac{\mathcal{N}}{2} + 1)}\;. \tag{4.2}$$

Entropy

Now we shall 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 $Z(E, N, V)$.

$$S = k_B \ln(\Gamma_N^{\text{kl}}(E))$$

$$= k_B \left\{ N\ln \left[V\left(\frac{2\pi mE}{h^2}\right)^{\frac{d}{2}} \right] - \ln(N!) - \ln \left[\Gamma(\frac{\mathcal{N}}{2} + 1) \right] \right\}$$

$$\ln(N!) + \ln \left[\Gamma(\frac{\mathcal{N}}{2} + 1) \right] = N\ln(N) - N + \frac{\mathcal{N}}{2}\ln(\frac{\mathcal{N}}{2}) - \frac{dN}{2}$$

$$= N \left\{ \ln(N) + \ln \left[(\frac{\mathcal{N}}{2})^{\frac{d}{2}} \right] - \frac{d+2}{2} \right\} .$$

For the entropy this gives

$$S = k_B N \left\{ \ln \left[V\left(\frac{2\pi mE}{h^2}\right)^{\frac{d}{2}} \right] - \ln(N) - \ln \left[(\frac{\mathcal{N}}{2})^{\frac{d}{2}} \right] + \frac{d+2}{2} \right\}$$

$$= k_B N \left\{ \ln \left[\frac{V}{N}\left(\frac{4\pi mE}{\mathcal{N}h^2}\right)^{\frac{d}{2}} \right] + \frac{d+2}{2} \right\} .$$

Entropy of the free classical 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 be seen explicitly. Equally easy to see is that the entropy is a homogenous function in the extensive quantities. **This would not be the case without the quantum mechanical correction.**
Actually, the entropy is to be derived 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 83] $\Gamma = cE^{\frac{N}{2}}$ pertains and therefore we get

$$\tilde{S} = k_B \ln\left[Z(E, N, V)\right] = k_B \ln\left[\frac{\partial \Gamma_N(E)}{\partial E}\right]$$

$$= k_B \ln\left[\Gamma \frac{\mathcal{N}}{2E}\right]$$

$$= S + k_B \ln\left[\frac{\mathcal{N}}{2E}\right]$$

$$\tilde{S} = S + O(1) \ .$$

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 40] 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

$$\frac{1}{T} = \frac{dk_B N}{2E}$$

$$T = \frac{2E}{dk_B N}$$

$$\text{bzw.} \quad E = \frac{d}{2} N k_B T \tag{4.4}$$

4.1.3   Gibbs paradoxon

We shall consider the following situation: At first we have two separate chambers with the volumes V_i and numbers of particles N_i. The two chambers

are separated by a mobile wall, which ensures equal pressurein both chambers. Additionally the chambers are to be in thermal contact to also ensure equal temperature. Now we shall remove the separating wall. The particles are to be ideal indistinguishable particles. Because of the particular starting conditions neither temperature nor pressure change when removing the wall. From the thermic equation of state, Equation (4.10) [Page 90], we can derive that the densities of particles in both chambers

$$n_i := \frac{N_i}{V_i} = \frac{kT}{p} = n$$

do not change with the removal of the separating wall either. Because of Equation (4.11) [Page 90] the same is true for the energy per particle $\tilde{E} := E/N$.

Now we shall calculate the entropy before the removal of the partitioning wall. According to Equation (4.3b) [Page 84] in chamber i it 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

$$S^{\text{vorher}} = \sum_{i=1}^{2} S(E_i, V_i, N_i) = k_B N \left(\ln \left[\frac{1}{n} \left(\frac{4\pi m \tilde{E}}{dh^2} \right)^{d/2} \right] + \frac{d+2}{2} \right) . \quad (4.5)$$

The total number of particles for this is of course $N = N_1 + N_2$. After the coupling Equation (4.3b) [Page 84] still pertains, however, now with the total number of particles. With this we realise that we have

$$S^{\text{vorher}} = S^{\text{nachher}}, \quad (4.6)$$

as it should be for identical particles. It is also possible to consider the experiment for indistinguishable particles by introducing the partition wall after mixing. With this the entropy should not change, as the state is the same before and afterwards.

We would have gotten a wrong result, had we not introduced the correction term $1/N!$ in phase space. This can be understood easily: The correction term causes an additive change in entropy

$$\Delta S(E, V, N) = -k_B \ln(N!) = -k_B \left(N \ln(N) - N \right) .$$

Therefore, from this we get a change of the total system

$$\Delta S^{\text{vorher}} = \sum_{i=1}^{2} \Delta S(E_i, V_i, N_i) = -k_B \sum_{i=1}^{2} \ln(N_i!) = -k_B \ln(N_1! N_2!)$$

After removing the partition wall, because of the correction term the change in entropy has the following form

$$\Delta S^{\text{nachher}} = -k_B \ln(N!) \; .$$

Thus the correction terms differ as such:

$$\Delta S^{\text{nachher}} - \Delta S^{\text{vorher}} = -k_B \ln\left(\frac{N!}{N_1! N_2!}\right) = k_B \ln\binom{N}{N_1} \qquad (4.7)$$

Before it was realised, that identical quantum particles ares strictrly indistinguishable the correction term had not been used, resulting in different entropies. This is called the Gibbs paradoxon.

Mixing entropy This is a wholly different case for nonidentical particles, though. Assuming that the particles in chamber one were coloured red and the ones in chamber two were coloured blue before the removal of the partition wall, the new (colour-)state is of course different. The same is true for the entropy, which is the logarithm of the number of microstates.
Of course, at first the particles in the two chambers are still indistinguishable and Equation (4.8) [Page 87] pertains. After the mixing the two entropies are still additive. However, the volumes change with the removal of the wall and therefore the densities change. The energy per particles still stays the same, as we are still dealing with noninteracting particles. Therefore we have:

$$S^{\text{nachher}} = \sum_{i=1}^{2} S(E_i = N_i \tilde{E}, V, N_i) = k_B \sum_{i=1}^{2} N_i \left(\ln\left[\frac{V}{N_i}\left(\frac{4\pi m \tilde{E}}{dh^2}\right)^{\frac{d}{2}} \right] + \frac{d+2}{2} \right) ,$$

$$(4.8)$$

With this the difference in entropy is

$$\Delta S^{\text{Mischung}} := S^{\text{nachher}} - S^{\text{vorher}} = -k_B \sum_{i=1}^{2} N_i \ln(N_i) + k_B N \ln(N)$$

This corresponds to the stirling approximation of the negative correction in Equation (4.7) [Page 87]. In other words: Without the correction term $1/N!$ we would get the correct result for this, as in that case the particles would be distinguishable. This difference in entropy is called *mixing entropy*. According to Equation (4.7) [Page 87] we therefore get

$$\Delta S^{\text{Mischung}} := -k_B \ln\binom{N}{N_1} \; .$$

This difference in entropy is a result of the particles being distinguishable in their colour. For Equation (4.6) [Page 86] indistiunguishable particles yield $\Delta S = 0$. The entropy-difference can be understood easily: The **microstates** of the system are fixed by the number $N_{f,i}$, which indicates the numbers of particles N_1 and N_2 in both chambers and also is characterised by

$$N_{f=1,i=1} = N_1 \ , \qquad\qquad \Rightarrow N_{f=2,i=1} = 0 \ ,$$
$$N_{f=1,i=2} = 0 \ , \qquad\qquad \Rightarrow N_{f=2,i=2} = N_1$$

Concerning the degree of freedom, these are the natural variables. For this *macrostate* there exists only one *microstate* $(F = 1)$ and the entropy for the degree of freedom in respect to colour is

$$S_{\text{Farbe}}^{\text{vorher}} = -k_B \ln(F) = 0 \ .$$

After removing the partition wall, the macrostate is characterised only by the numbers of particles N_1 and N_2. Although the missing wall would allow other numbers of particles, those are already given by $N_i = n \ V_i$ without colour distinction in the thermic equilibrium. And as we have seen above, those numbers do not change with the removal of the partition wall. This means that even though the particles move between the chambers, they do this in a way so that the average particle number remains unchanged.

Therefore, after the removal of the partition, the **macrostate** is given by the number of particles in the two chambers, N_1 and N_2, and characterised by $N_r(N_b)$, which is the number of red (blue) particles. However, the distribution of the colours on the cambers is not fixed. From this we get the number of microstates. We get this number as follows: For arranging the particles in a row there are $F' = \binom{N}{N_r}$ different colour sequences. The first N_1 particles are put into chamber 1 for each sequence. With this F simultaneously is the number of microstates. Because of the initial situation also $N_r = N_1$ is valid and therefore we get

$$S_{\text{Farbe}}^{\text{nachher}} = -k_B \ln(F') = -k_B \ln \binom{N}{N_1} \ .$$

With this ΔS is explained.

Internal energy

Now we shall resolve Equation (4.3a) [Page 84] for 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 with this get the internal energy as a function of 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-dependency of the internal energy

$$U = cV^{-\frac{2}{d}} \; .$$

From this we calculate the pressure

$$p = - \left(\frac{\partial U}{\partial V}\right)\bigg|_{S,N} = -c(-\frac{2}{d}) \; V^{-\frac{2}{3}-1} = U\left(\frac{2}{dV}\right) \; .$$

With that we get

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

PRESSURE OF THE IDEAL GAS
(*microcanonical ensemble, classical*)
[*Caloric state equation*]

$$pV = \frac{2}{d} \, U \; . \tag{4.9}$$

</div>

State equations

Alternatively, via Equation (2.4) [Page 43] together with Equation (4.3a) [Page 84]

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

we get the

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

THERMIC STATE EQUATION OF THE IDEAL GAS
(*microcanonical ensemble, classical*)

$$pV = Nk_BT \ . \tag{4.10}$$

</div>

Interestingly, the state equation is independent of the spatial dimension d.

Internal energy

Equation (4.10) [Page 90] together with Equation (4.9) [Page 89] yields

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

INTERNAL ENERGY
(*microcanonical ensemble, classical*)

$$U = \frac{d}{2} \ Nk_BT \ . \tag{4.11}$$

</div>

4.1.4 Canonical ensemble

Partition function

Now we shall consider the same model 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

$$
\begin{aligned}
Z(T, V, N) &= \frac{V^N}{h^{\mathcal{N}} N!} \, \Omega_{\mathcal{N}} \left(\frac{2m}{\beta}\right)^{\mathcal{N}/2} \frac{1}{2} \int_0^\infty e^{-x} x^{\mathcal{N}/2} \frac{dx}{x} \\
&= \frac{V^N}{h^{\mathcal{N}} N!} \frac{2\pi^{\mathcal{N}/2}}{\Gamma(\mathcal{N}/2)} \left(\frac{2m}{\beta}\right)^{\mathcal{N}/2} \frac{1}{2} \Gamma(\mathcal{N}/2) \\
&= \frac{V^N}{N!} \left(\frac{2\pi m}{h^2 \beta}\right)^{\mathcal{N}/2} = \frac{V^N}{N!} \, \lambda_T^{-dN} \ .
\end{aligned}
$$

With this we have already calculated the key quantity, the partition function.

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

CANONICAL PARTITION FUNCTION OF THE IDEAL GAS
(classical)

$$
Z(T, N, V) = \frac{V^N}{N!} \, \lambda_T^{-dN} \tag{4.12}
$$

$$
\lambda_T := \frac{h}{\sqrt{2\pi m k_B T}} \quad \text{(thermic de Broglie wavelength) .} \tag{4.13}
$$

</div>

Here we introduced the definition of the thermic de Broglie wavelength, which will be, among other things, relevant for Bose-condensation.

Free energy

Next we calculate the free energy

$$
F(T, N, V) = -k_B T \ln(Z) = -k_B T \left[N \ln\left(V \lambda_T^{-d}\right) - N \ln(N) + N \right] \ .
$$

With this we get the

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

FREE ENERGY OF AN IDEAL GAS
(classical)

$$
F(T, N, V) = -N \, k_B T \left[\ln\left(\frac{V}{N} \lambda_T^{-d}\right) + 1 \right] \ .
$$

</div>

The free energy is extensive and is of the correct homogenity.

Entropy

The entropy that can be derived from this yields

$$
\begin{aligned}
S &= - \left. \left(\frac{\partial F(T, N, V)}{\partial T} \right) \right|_{N,V} \\
&= N \, k_B \left[\ln \left(\frac{V}{N} \lambda^{-d} \right) + 1 \right] + N \, k_B T \, \frac{d}{dT} \ln(T^{d/2}) \\
&= N \, k_B \left[\ln \left(\frac{V}{N} \lambda^{-d} \right) + 1 \right] + \frac{d}{2} N \, k_B \frac{T}{T} \ .
\end{aligned}
$$

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

ENTROPY OF AN IDEAL GAS
(*canonical ensemble, classical*)

$$
S(T, N, V) = N \, k_B \left[\ln \left(\frac{V}{N} \lambda_T^{-d} \right) + \frac{d+2}{2} \right] \ . \tag{4.14}
$$

</div>

This corresponds to the result, which we got for the microcanonical ensemble in Equation (4.3a) [Page 84] when one considers that there, because of Equation (4.4) [Page 85], $\tilde{E}$ 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 55]

$$
\begin{aligned}
\mu &= \left(\frac{\partial F(T,N,V)}{\partial N} \right) \bigg|_{T,V} \\
&= -k_B T \left(\frac{\partial}{\partial N} \right) \bigg|_{T,V} \left(N \left[\ln \left(\frac{V}{N} \lambda_T^{-d} \right) + 1 \right] \right) \\
&= -k_B T \left\{ \ln \left(\frac{V}{N} \lambda_T^{-d} \right) + 1 + N \underbrace{ \left(\frac{\partial}{\partial N} \right) \bigg|_{T,V} \ln \left(\frac{V}{N} \lambda_T^{-d} \right) }_{=-1/N} \right\} \\
&= -k_B T \left\{ \ln \left(\frac{V}{N} \lambda_T^{-d} \right) \right\}
\end{aligned}
$$

CHEMICAL POTENTIAL OF THE IDEAL GAS
(kanonical ensemble, classical)

$$
\begin{aligned}
\mu &= -k_B T \, \ln \left(\frac{V}{N} \lambda_T^{-d} \right) \\
&= \frac{F}{N} + k_B T \ .
\end{aligned}
$$

Internal energy

Now we shall calculate the internal energy

$$
\begin{aligned}
U &= F(T,V,N) + TS(T,V,N) \\
&= -N \, k_B T \left[\ln \left(\frac{V}{N} \lambda_T^{-d} \right) + 1 \right] + N \, k_B T \left[\ln \left(\frac{V}{N} \lambda_T^{-d} \right) + \frac{d+2}{2} \right] \\
&= \frac{3}{2} N k_B T \ .
\end{aligned}
$$

> 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 (4.11) [Page 90]. With this, for the entropy we can replace the temperature with the energy $E = U$ and then also get the Sackur-Tetrode result from Equation (4.3a) [Page 84]. 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 predefined. 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 derivation of the internal energy with respect to β.

$$-\frac{\partial}{\partial \beta} \frac{\text{tr}\left\{\text{H}e^{-\beta \text{H}}\right\}}{\text{tr}\left\{e^{-\beta \text{H}}\right\}} = \frac{\text{tr}\left\{\text{H}^2 e^{-\beta \text{H}}\right\}}{\text{tr}\left\{e^{-\beta \text{H}}\right\}} + \frac{\text{tr}\left\{\text{H}e^{-\beta \text{H}}\right\}}{(\text{tr}\left\{e^{-\beta \text{H}}\right\})^2}\left(\frac{\partial}{\partial \beta}\text{tr}\left\{e^{-\beta \text{H}}\right\}\right)$$

$$= \langle H^2 \rangle - \langle H \rangle^2$$

$$\Rightarrow \qquad \sigma_E^2 := \langle (\Delta H)^2 \rangle = -\left(\frac{\partial U(T, N, V)}{\partial \beta}\right)\Bigg|_{N,V}$$

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 vanisehes 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 aquired 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

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

$$= k_B T V \lambda_T^{-d} \; \underbrace{\frac{\partial z}{\partial \mu}}_{z\beta} = V z \lambda_T^{-d} \; .$$

Pressure

From the universally valid formula $\Omega = -pV$ we conveniently get the pressure

$$
\begin{array}{c}
\text{PRESSURE OF THE IDEAL GAS} \\
\textit{(grand canonical ensemble, classical)} \\
\hline
\\
p = k_B T z\, \lambda_T^{-d} \,. \qquad\qquad (4.17)
\end{array}
$$

With this the average number of particles can also be expressed by

$$
\langle N \rangle = V p \beta
$$

This in turn corresponds to the state equation of the microcanonical ensemble in Equation (4.9) [Page 89]. With this it is proven that the average number of particles of the grand canonical ensemble corresponds to the fixed number of particles of the microcanonical ensemble. Likewise, the following has to be true:

$$
pV = -V \left(\frac{\partial F(T, N, V)}{\partial V} \right) \bigg|_{T,N} = V\, N k_B T \left(\frac{\partial}{\partial V} \ln(V) \right) = N k_B T
$$

$$
\Rightarrow \qquad \langle N \rangle = V p \beta = N \,.
$$

This means that the average number of particles for the grand canonical ensemble has to correspond to the fixed number of particles for the canonical ensemble.

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.

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

$$= k_B T \frac{1}{Z(T,\mu,V)} \left(\frac{\partial Z(T,\mu,V)}{\partial \mu}\right)\Big|_{T,V}$$

$$= k_B T \frac{1}{Z(T,\mu,V)} \sum_{N=0}^{\infty} Z(T,N,V)\frac{\partial}{\partial \mu}z^N$$

$$= k_B T \frac{1}{Z(T,\mu,V)} \sum_{N=0}^{\infty} Z(T,N,V)\, N z^N \beta$$

$$= \sum_{N=0}^{\infty} N \underbrace{\frac{Z(T,N,V)}{Z(T,\mu,V)}\, z^N}_{=P_N}$$

$$P_N \stackrel{(4.12)}{=} \frac{1}{Z(T,\mu,V)}\frac{\left(V\lambda_T^{-d}z\right)^N}{N!} \ .$$

Together with Equation (4.15) we get the Poisson distribution

---

DISTRIBUTION OF NUMBERS OF PARTICLES IN THE IDEAL GAS
(*grand canonical ensemble, classical*)

$$P_N = e^{-\eta}\frac{\eta^N}{N!}$$

$$\eta := \langle N \rangle = V\lambda_T^{-d}z \ .$$

With this also the relative uncertainty of the particle number is proportional to $1/\sqrt{N}$.

Determination of the chemical potential

Lastly we want to determine the chemical potential.

$$\langle N \rangle \stackrel{(4.17)}{=} zV\lambda_T^{-d} \ ,$$

$$\Rightarrow \quad e^{\beta\mu} = z = \frac{\langle N \rangle}{V}\lambda_T^d \ .$$

4.1.6 Velocity distribution

We will calculate the velocity distribution of an ideal classical gas for three dimensions. This means that the particles do not feel any interaction. 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.

$$p(\pi|N,V,T) = \frac{1}{Z} e^{-\beta H(\pi)} = \prod_{i=1}^{N} p_0(\vec{p}_i^{\,2}) \;,$$

$$p_0(\vec{p}) := \left(\frac{1}{2\pi m k_B T}\right)^{3/2} e^{-\frac{\vec{p}_i^{\,2}}{2m k_B T}} \;.$$

We now pick a random particle and determine the probability density of its momentum $p(\vec{p})$. Using marginalisation we introduce the index of the particle, that it was chosen randomly and also which momentum the particle has. As the particles are independent and identical this is also the marginal probability density of the first particle

$$p(\vec{p}) = p_0(\vec{p}) \;.$$

Here the spatial coordinate was marginalised too. By considering that here $\vec{p} = m\vec{v}$ applies and also transforming to spherical coordinates we get

$$p(\vec{v})d^3v = p_0(m\vec{v})d^3p = p_0(m\vec{v})m^3d^3v$$

$$= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\frac{m\,\vec{v}^2}{2k_B T}} \; d^3v$$

$$= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\frac{m\,v^2}{2k_B T}} \; v^2 \; \sin(\theta) \; dv d\theta d\phi \;.$$

With this we have the

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 portion.

$$p(v) = \int p(v, \theta, \phi) d\theta d\phi$$

$$= \frac{1}{z'} \, v^2 \, e^{-\frac{m}{2k_B T} v^2}$$

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

$$z' = \left(\frac{2k_B T}{m}\right)^{3/2} \frac{1}{2} \int_0^\infty e^{-x} x^{3/2} \frac{dx}{x}$$

$$= \left(\frac{2k_B T}{m}\right)^{3/2} \frac{1}{2} \Gamma(3/2)$$

$$= \left(\frac{2k_B T}{m}\right)^{3/2} \frac{\sqrt{\pi}}{4} = \left(\frac{2k_B T \pi}{m}\right)^{3/2} \frac{1}{4\pi} \ .$$

With this we have the

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MAXWELL VELOCITY DISTRIBUTION

$$p(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \, e^{-\frac{m}{2k_B T} v^2} \ . \qquad (4.19)$$

</div>

In addition we calculate the lower moments for this

$$\langle v^n \rangle = \frac{\int_0^\infty v^{2+n} e^{-\alpha v^2} dv}{\int_0^\infty v^2 e^{-\alpha v^2} dv}$$

$$\alpha := \frac{m}{2k_B T} \ .$$

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

$$I_m = \frac{1}{2}\alpha^{-\frac{m}{2}} \int_0^\infty x^{\frac{m}{2}} e^{-x} \frac{dx}{x} = \frac{1}{2}\alpha^{-\frac{m}{2}} \Gamma(\frac{m}{2})$$

$$\int_0^\infty v^{3+n} e^{-\alpha v^2} \frac{dv}{v} = \frac{1}{2} (\alpha)^{-\frac{n+3}{2}} \int_0^\infty x^{\frac{n+3}{2}} e^{-x} \frac{dx}{x}$$
$$= \frac{1}{2} \alpha^{-\frac{n+3}{2}} \Gamma(\frac{n+3}{2})$$

$$\boxed{\int_0^\infty v^{3+m} e^{-\alpha v^2} \frac{dv}{v} = \frac{1}{2} \alpha^{-\frac{m+3}{2}} \Gamma(\frac{m+3}{2})} \qquad (4.20)$$

Thus we have

$$\langle v^n \rangle = \frac{\alpha^{-\frac{n+3}{2}}\Gamma(\frac{n+3}{2})}{\alpha^{-\frac{3}{2}}\Gamma(\frac{3}{2})} = \alpha^{-\frac{n}{2}} \frac{\Gamma(\frac{n+1}{2}+1)}{\frac{1}{2}\sqrt{\pi}} = \left(\frac{2k_BT}{m}\right)^{\frac{n}{2}} \frac{n+1}{\sqrt{\pi}} \Gamma(\frac{n+1}{2})$$

and in particular

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Moments of the Maxwell distribution

$$\langle v \rangle = \left(\frac{2k_BT}{m}\right)^{\frac{1}{2}} \frac{2}{\sqrt{\pi}} \Gamma(1) = 4\left(\frac{k_BT}{2\pi m}\right)^{\frac{1}{2}} \qquad (4.21a)$$
$$\langle v^2 \rangle = \frac{2k_BT}{m} \frac{3}{\sqrt{\pi}} \Gamma(\frac{3}{2}) = \frac{3k_BT}{m} . \qquad (4.21b)$$

</div>

From the last equation follows

$$\frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}k_BT ,$$

which corresponds to the previous calculations.

4.1.7   Effusion

We now want to consider what happens, if there is an infinitesimally small hole in the partition wall.
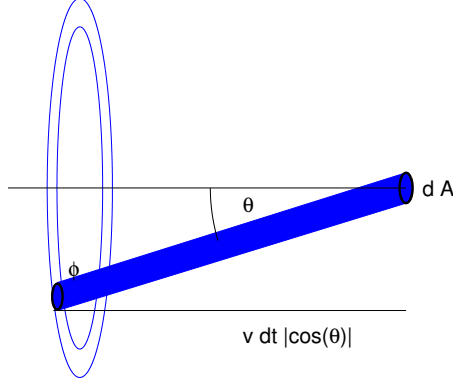

Figure 4.1:   All particles within the blue cylinder, whose velocity vector is infinitesimally close to (v, θ, ϕ) will reach the infinitesimal opening dA within the time dt.

For this we consider the geometry seen 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 opening with a velocity of (v, θ, ϕ) in $(dv, d\theta, d\phi)$ in the timeframe of dt, it has to have been in the cylindrical volume, seen in the figure, just before that. 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 opening. 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 99] and Equation (4.18) [Page 98] 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 opening or away from it. We define the numer of particles to be positive for a particle moving towards the opening and negative for the inverse case. For the thusly defined number of particles, which we shall 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 opening 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 opening 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 of 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 effusion rates

DENSITY OF EFFUSION RATES

$$\frac{d^3 \tilde{N}(v|B)}{dt \; dA \; dv} = \frac{1}{4} \; \rho \; v \; p(v) \; . \tag{4.24}$$

At the same time this is also the velocity distribution of the particles that move through the opening, respectively those that are observed directly behind the opening. Because of the additional factor v the corresponding probability density is

$$p_{\text{effusion}}(v) = \frac{1}{z}\, v^3 e^{-\frac{m}{2kT}v^2}$$

$$z = \int_0^\infty v^3 e^{-\alpha v^2} dv = \frac{1}{2}\int_0^\infty v^2 e^{-\alpha v^2} d(v^2)$$

$$= \frac{1}{2}\int_0^\infty x e^{-\alpha x} dx$$

$$= \frac{1}{2}\left(-\frac{\partial}{\partial \alpha}\right)\int_0^\infty e^{-\alpha x} dx = \frac{1}{2}\left(-\frac{\partial}{\partial \alpha}\right)\frac{1}{\alpha} = \frac{1}{2\alpha^2}$$

$$z = \frac{1}{2\alpha^2} = \frac{1}{2}\left(\frac{2kT}{m}\right)^2.$$

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VELOCITY DISTRIBUTION FOR EFFUSION

$$p_{\text{effusion}}(v) = \frac{m^2}{2(kT)^2}\, v^3 e^{-\frac{m}{2kT}v^2}$$

</div>

Outflow velocity

From this we get the average outflow velocity

$$\langle v \rangle_{\text{effusion}} = \frac{\int_0^\infty v^4 e^{-\alpha v^2} dv}{\int_0^\infty v^3 e^{-\alpha v^2} dv}$$

$$\overset{(4.20)}{=} \frac{\alpha^{-\frac{5}{2}}\Gamma\left(\frac{5}{2}\right)}{\alpha^{-\frac{4}{2}}\Gamma\left(\frac{4}{2}\right)} = \alpha^{-\frac{1}{2}}\,\frac{3\sqrt{\pi}}{4}$$

$$= \frac{3\sqrt{\pi}}{4}\left(\frac{2k_B T}{m}\right)^{\frac{1}{2}}.$$

Interestingly this is dependent on $1/\sqrt{m}$. This dependenc is called $Graham's\,law$. This is used technically, for example for uranium enrichment.

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 velocity). For this we only have to integrate the density of the rate of effusion in Equation (4.24) [Page 102] over all velocities, which yields

$$\frac{d^2 \tilde{N}(A)}{dAdt} = \frac{1}{4} \, \rho \, \langle v \rangle$$

In doing so, $\langle v \rangle$ is the average of the absolute value of the velocity of the fluid when flowing out. In hindsight the structure of the result is trivial, as on the left side there is the number of particles per unit of time and area and therefore the current density. The product of velocity and particle density is a current density too. However, here the average absolute value is part of the velocity. Therefore, not all particles whose average velocity has this absolute, move through the opening. Obviously effectively only $1/4$ of those do that. This factor is a result of the integration over the angles.

As was already mentioned, $\langle v \rangle$ is the average of the Maxwell distribution from Equation (4.19) [Page 99]. This was stated in Equation (4.21) [Page 100]. Hence the average number of particles leaving the box per unit of time and area is

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RATE OF EFFUSION

$$\frac{d^2 \tilde{N}(A)}{dAdt} = \rho \left(\frac{k_B T}{2\pi m} \right)^{\frac{1}{2}} . \tag{4.25}$$

</div>

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

$$\Delta \vec{p} = -2p_x \vec{e}_x . \tag{*}$$

Per collision with 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 102] 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 100], getting $\langle v^2 \rangle = \frac{3}{m} k_B T$ as the result. With this we now get the thermic equation of state:

$$
\begin{aligned}
p &= \rho k_B T = \frac{N}{V} k_B T \\
pV &= N k_B T .
\end{aligned}
$$

4.2   Bohr Van-Leeuwen theorem

We will now discuss non-interacting charged particles in a 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 is dependent on the locations of the particles. The dependence on the magnetic field originates from the vector potential $\vec{A}$. The canonical partition function is

$$Z(T, N, V, B) = \frac{1}{h^N N!} \int d^N x \; e^{-\beta V(\mathbf{x})} \underbrace{\int d^N p \; e^{-\beta \sum_{i=1}^{N} \frac{1}{2m} \left(\vec{p}_i - \frac{q_i}{c} \vec{A}(\vec{x}_i) \right)^2}}_{:=I_p} .$$

With the substitution

$$\vec{p}_i - \frac{q_i}{c} \vec{A}(\vec{x}_i) := \vec{z}_i$$

the integral over the momenta

$$I_p = \int d^N z \; e^{-\beta \sum_{i=1}^{N} \frac{1}{2m} \vec{z}_i^{\,2}}$$

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.

4.3   Solid spheres

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) [Page 91].

$$Z_p(T, N, V) = \frac{1}{N!} \, \lambda_T^{-\mathcal{N}} \ .$$

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.

$$Z_x = \sum_P \int_\sigma^{L-\sigma} \ldots \int_\sigma^{L-\sigma} \Theta(x) O(Px) d^N x$$

$$\overset{y=Px}{=} \sum_P \int_\sigma^{L-\sigma} \ldots \int_\sigma^{L-\sigma} \Theta(P^{-1}y) O(y) d^N P^{-1} y$$

$d^N x$ 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:

$$Z_x = \sum_P \int_\sigma^{L-\sigma} \ldots \int_\sigma^{L-\sigma} \Theta(y) O(y) d^N y$$

$$= N! \int_\sigma^{L-\sigma} dy_1 \int_{y_1+2\sigma}^{L-\sigma} dy_2 \ldots \int_{y_{N-1}+2\sigma}^{L-\sigma} dy_N .$$

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
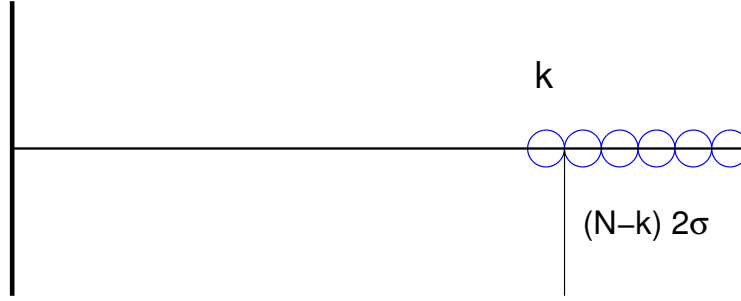
Figure 4.2: On the right side of the sphere k there are $N - k$ spheres that when lined up have a length of $(N - k)2\sigma$.

get

$$x_k \leq L - (2\sigma(N - k) + \sigma) = L - 2N\sigma + \sigma(2k - 1) .$$

Therefore we can further simplify Z_x to

$$Z_x = N! \int_\sigma^{L-2\sigma N+\sigma(2-1)} dy_1 \ldots \int_{y_{k-1}+2\sigma}^{L-2\sigma N+\sigma(2k-1)} dy_k \ldots \int_{y_{N-1}+2\sigma}^{L-2\sigma N+\sigma(2N-1)} dy_N .$$

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: $0 \leq x_1 \leq x_2 \leq \ldots \leq L - 2\sigma N$. 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

$$Z_x = (L - NL_0)^N := V_{\text{eff}}^N .$$

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,

$$F = -Nk_B T \left[\ln \left[\frac{V_{\text{eff}}}{N} \lambda_T^{-3} \right] + 1 \right] .$$

From this the pressure is calculated as follows:

$$\begin{aligned}
p &= - \left(\frac{\partial F(T, N, V)}{\partial V} \right) \bigg|_{T,N} \\
&= Nk_B T \left(\frac{\partial \ln(V_{\text{eff}})}{\partial V} \right) \bigg|_{T,N} = Nk_B T \frac{1}{V_{\text{eff}}} \frac{\partial V_{\text{eff}}}{\partial V} \\
&= \frac{Nk_B T}{V_{\text{eff}}} , \\
pV_{\text{eff}} &= NK_B T .
\end{aligned}$$

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

$$p_{\text{eff}} V_{\text{eff}} = Nk_B T . \tag{4.26}$$

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.
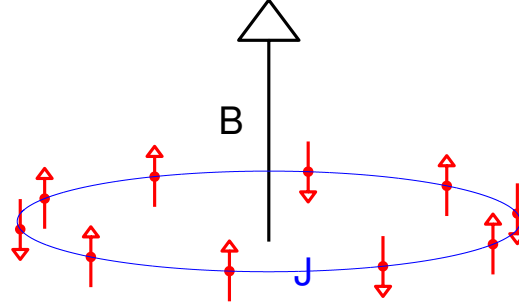
Figure 4.3: *Arrangement of the Ising spins as a chain with periodical boundary conditions*

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 function:

$$H = -J \sum_{\langle i,j \rangle} s_i s_j - \mu B \sum_i s_i \ ,$$

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): $s_{i+N} = s_i \ .$

---

[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

$$M_{s,s'} = \begin{array}{c|cc} & +1 & -1 \\ \hline +1 & e^{j+b} & e^{-j} \\ -1 & e^{-j} & e^{j-b} \end{array}$$

we have:

$$Z(T, N, B) = \sum_{\{s_i\}=\pm 1} \prod_{i=1}^{N} M_{s_i, s_{i+1}} \ .$$

At first we consider the case of $N = 2$, for which the partition function is

$$Z(T, N = 2, B) = \sum_{s_1 = \pm 1} \sum_{s_2 = \pm 1} M_{s_1, s_2} \ M_{s_2, s_1} = \sum_{s_1} \left(M^2 \right)_{s_1, s_1} = \mathrm{tr} \left\{ M^2 \right\}$$

Now the generalisation obviously is

$$Z(T, N, B) = \mathrm{tr} \left\{ M^N \right\} \ .$$

The transfer matrix is real and symmetrical. 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). With this we get

$$Z(T, N, B) = \mathrm{tr} \left\{ M^N \right\} = \mathrm{tr} \left\{ (UDU^\dagger)^N \right\} = \mathrm{tr} \left\{ UD^N U^\dagger \right\} = \mathrm{tr} \left\{ D^N \right\}$$
$$= d_1^N + d_2^N \ .$$

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

$$F(T, N, B) = -k_B T \ln [Z(\mathrm{T, V})] = -k_B T N \ln(d_1) - k_B T \ln \left[1 + \underbrace{\left(\frac{d_2}{d_1} \right)^N}_{\to 0} \right]$$

$$= -N k_B T \ln(d_1) .$$

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:

$$M = \frac{1}{\beta} \left(\frac{\partial \ln(Z)}{\partial B} \right) \Bigg|_{T,N} = - \left(\frac{\partial F}{\partial B} \right) \Bigg|_{T,N}$$

$$= -\mu \beta \left(\frac{\partial F}{\partial b} \right) \Bigg|_{T,N}$$

$$= -\mu \beta (-k_B T N) \left(\frac{\partial \ln(d_1)}{\partial b} \right) \Bigg|_{T,N}$$

$$= N\mu \frac{\frac{\partial d_1}{\partial b}}{d_1} = N\mu \frac{\sinh(b) + \frac{\sinh(b)\cosh(b)}{\sqrt{\sinh^2(b) + e^{-4j}}}}{\cosh(b) + \sqrt{\sinh^2(b) + e^{-4j}}}$$

$$= N\mu \sinh(b) \frac{1 + \frac{\cosh(b)}{\sqrt{\sinh^2(b) + e^{-4j}}}}{\cosh(b) + \sqrt{\sinh^2(b) + e^{-4j}}}$$

$$= N\mu \frac{\sinh(b)}{\sqrt{\sinh^2(b) + e^{-4j}}} \frac{\sqrt{\sinh^2(b) + e^{-4j}} + \cosh(b)}{\cosh(b) + \sqrt{\sinh^2(b) + e^{-4j}}} .$$

MAGNETISATION OF THE 1D ISING MODEL

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

Paramagnet

Without interaction of the magnetic moments with each other – $J = 0$ – 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.

Boundary crossings

There is a dependence on the order of the boundary crossings. If we at first choose $B = 0$, we get a vanishing magnetisation for all temperatures $T > 0$:

$$M(T, N, B = 0) = 0$$

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 phase transition at $T = 0$

Magnetisation curve

We choose the interaction coupling J as a 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 $\tilde{B}$.
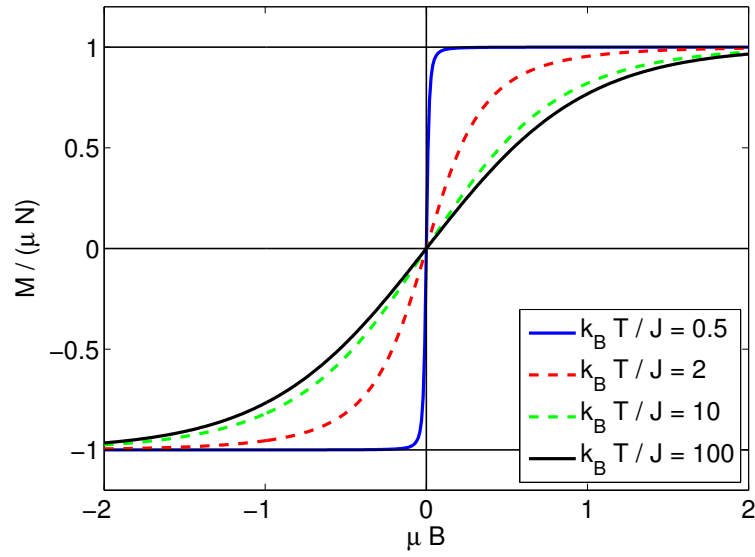
Figure 4.4: Magnetisation curve of the 1d Ising model.

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 that
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 for both 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 momentum are altogether senseless in the quantum mechanical dimen-
sion, or that it is impossible to measure these quantities without disturbing
the system. With this, of course, the concept of phase space is now obsolete.
However, even when constraining to a dynamic variable, e.g. to the spatial
coordinate of the particles, on a quantum level one has to give up deter-
minism. Normally one cannot predict the outcome of an experiment with
absolute certainty, one can only describe the state by means of probability
amplitudes. However, one can calculate the temporal bahaviour of those. For
this the whole system, including the spectator (measurement devices), is an
integral part. It still goes on: The many particle state cannot be described by
the spatial coordinates of the single particles anymore. Interacting particles
loose their identity and form a collective probability density, which 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 here we already deal only with probabilites we assumed that we can
determine the starting vector of the many particles system and are able to

make definitive predictions for the state vector at a later point in time. This is possible when there are only few particles to consider. This corresponds to the situation in analytical mechanics where we can make exact presets for the starting conditions. As in classical statistical mechanics, in quantum statistics the situation changes drastically too, if a macroscopic number of particles are involved. Within a state vector we are now unable to prepare the system unambiguously. In classical statistical mechanics we stated that the probability density $p(\pi)$ for the system to be at the phase space point π. The quantum mechanical equivalent to phases space points are the pure states corresponding to the eigenvectors $|\psi_i\rangle$ of the Hamilton operator. In quantum mechanics all information of a state is described by a density operator with the following characteristics:

- $\hat{\rho}$ is Hermitian:

  - $\hat{\rho}^\dagger = \hat{\rho} \Rightarrow$
  - real eigenvalues p_i
  - complete set of orthonormal eigenvectors

- Eigenvalues are probabilities:

  - $0 \le p_i \le 1$
  - $\sum_i p_i = 1$
  - $\Rightarrow \operatorname{tr}\{\hat{\rho}\} = 1$

- 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 c_i.

THERMODYNAMIC EXPECTATION VALUES
(of an observable O)

$$\langle O \rangle = \operatorname{tr}\left\{\hat{\rho}\,\hat{O}\right\}.$$

Until now everything concerns only the description of a quantum state at a fixed time, e.g. preparation. At a later time the density operator is a consequence of the Schroedinger equation

---

TIME EVOLUTION OF THE DENSITY OPERATOR

$$i\hbar\frac{\partial\hat{\rho}(t)}{\partial t} = [\hat{H}, \hat{\rho}(t)] \, ,$$

---

with $\hat{H}$ as the Hamiltonian of the system.

$$\hat{\rho}_i = |\psi_i\rangle\langle\psi_i| \, .$$

Instead of the eigenbasis of $\hat{H}$ also every other orthonoermal basis can be used to define the density operator. The probabilities then have an accordingly modified meaning.

The probability densities $p(\pi)$ now transition into the probabilities p_i with which those states are present or enter into the density operator

---

QUANTUM STATISTICAL DENSITY OPERATOR

$$\hat{\rho} = \sum p_i \, |\psi_i\rangle\langle\psi_i| \, .$$

For those probabilities we use 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

Using the maximum entropy formalism again, we get the probabilites p_i for the different ensembles. This simple use of MaxEnt yields the probabilities that define the density operators. The results are the following:

DENSITY OPERATOR FOR THE MICROCANONICAL ENSEMBLE

$$\hat{\rho}_E^{mkG} = \frac{1}{Z(E, N, V)} \begin{cases} \delta_{E,\hat{H}} \; ; & \text{discrete spectrum} \\ \delta(E - \hat{H}) \; ; & \text{continuous spectrum} \end{cases}$$

$$Z(E, N, V) = \begin{cases} \text{tr} \left\{ \delta_{E,\hat{H}} \right\} \; ; & \text{discrete spectrum} \\ \text{tr} \left\{ \delta(E - \hat{H}) \right\} \; ; & \text{continuous spectrum} \end{cases}$$

$$S(E, N, V) = -k_B \text{tr} \left\{ \hat{\rho} \ln(\hat{\rho}) \right\} = k_B \ln \left[Z(E, N, V) \right] .$$

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DENSITY OPERATOR FOR THE CANONICAL ENSEMBLE

$$\hat{\rho}_T^{kG} = \frac{1}{Z(T,N,V)} \, e^{-\beta \hat{H}} \; ;$$

$$Z(T,N,V) = \mathrm{tr}\left\{ \mathrm{e}^{-\beta \hat{H}} \right\} \; ;$$

$$F(T,N,V) = -k_B T \ln\left[Z(T,N,V) \right] .$$

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DENSITY OPERATOR FOR THE GRAND CANONICAL ENSEMBLE

$$\hat{\rho}_T^{gkG} = \frac{1}{Z(T,\mu)} \, e^{-\beta(\hat{H} - \mu \hat{N})} \; ;$$

$$Z(T,\mu,V) = \mathrm{tr}\left\{ \mathrm{e}^{-\beta(\hat{H} - \mu \hat{N})} \right\} \; ;$$

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

</div>

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. Because of equivalency this is enough to calculate the entropy of an ensemble. For simlicity's sake we choose the microcanonical ensemble. Here the entropy is

$$\begin{aligned}
S(E,N,V) &= -k_B \mathrm{tr}\left\{ \hat{\rho}_E^{mkG} \ln\left[\hat{\rho}_E^{mkG} \right] \right\} \\
&= k_B \ln\left[Z(E,N,V \right] = k_B \ln\left[\mathrm{tr}\left\{ \delta_{E,\hat{H}} \right\} \right] \\
&= k_B \ln\left[\Gamma(E,N,V) \right] ,
\end{aligned}$$

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. Also for $T \to 0$ the entropy is given by

$$S \xrightarrow[T \to 0]{} k_B \ln\left[\Gamma(E_0) \right] .$$

Therefore, for $T \to 0$ the entropy is given by the degeneracy of the ground state. Of course there are system with a undegenerated ground state. For those systems entropy is zero. However, should the ground state be degenerate, as a rule this is caused by symmetries, which are negated by small external disturbances. The split-up, however, can be very small, so that in order to observe $S \to 0$ in experiment, one has to use very low temperatures. The third law of thermodynamics is also called **Nernst-Planck-Theorem**. H. Nernst had – on the foundation of examinations of numerous chemical reactions – formulated the thesis 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 of 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 zero point of the energy. The quantum numbers can – same as for an onedimensional oscillator – assume the 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 microscopical 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 certainly are not. Thus, the task is to distribute M objects over $\mathcal{N}$ 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 macroscopic ($\mathcal{N} \gg 1$). Therefore we can substitute $\mathcal{N} - 1$ by $\mathcal{N}$ and use the Stirling formula to calculate the entropy. We assume that $M \gg 1$.

$$S(E_M, N) = k_B \ln(\Gamma_M) = k_B \left(\ln\left[(\mathcal{N} - 1 + M)!\right] - \ln\left[(\mathcal{N} - 1)!\right] - \ln\left[M!\right] \right)$$

$$\approx k_B \left((\mathcal{N} + M)\ln\left[\mathcal{N} + M\right] + \mathcal{N} + M - \mathcal{N}\ln\left[\mathcal{N}\right] - \mathcal{N} - M \ln M - M \right)$$

$$= k_B \left((\mathcal{N} + M)\ln\left[\mathcal{N} + M\right] - \mathcal{N}\ln\left[\mathcal{N}\right] - M\ln\left[M\right] \right)$$

$$= k_B \left((\mathcal{N} + M)\left(\ln(\mathcal{N}) + \ln\left[1 + \frac{M}{\mathcal{N}}\right] \right) - \mathcal{N}\ln(\mathcal{N}) - M\ln(M) \right)$$

$$= k_B \left(\overbrace{\mathcal{N}\ln(\mathcal{N})}^{(1)} + M\ln(\mathcal{N}) + (\mathcal{N} + M)\ln\left[1 + \frac{M}{\mathcal{N}}\right] - \overbrace{\mathcal{N}\ln(\mathcal{N})}^{(1)} - M\ln\left[M\right] \right)$$

$$= k_B \left(M\ln(\mathcal{N}) + (\mathcal{N} + M)\ln\left[1 + \frac{M}{\mathcal{N}}\right] - M\ln\left[M\right] \right) .$$

Therefore, the expression for entropy is

$$S(E_M, N) = k_B \mathcal{N} \left((1 + \frac{M}{\mathcal{N}})\ln\left[1 + \frac{M}{\mathcal{N}}\right] - \frac{M}{\mathcal{N}}\ln\left[\frac{M}{\mathcal{N}}\right] \right) . \qquad (5.2)$$

This means that entropy is extensive!

Temperature

Temperature in the microcanonical ensemble yields

$$
\begin{aligned}
\frac{1}{T} &= \left(\frac{\partial S}{\partial E}\right)\bigg|_{\mathcal{N}} = \frac{1}{\hbar\omega}\left(\frac{\partial S}{\partial M}\right)\bigg|_{\mathcal{N}} \\
&= \frac{k_B}{\hbar\omega}\left(1 + \ln\left[1 + \frac{M}{\mathcal{N}}\right] - 1 - \ln\left[\frac{M}{\mathcal{N}}\right]\right) \\
&= \frac{k_B}{\hbar\omega}\ln\left[1 + \frac{\mathcal{N}}{M}\right].
\end{aligned}
$$

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TEMPERATURE
(*Einstein solid*)

$$
\beta = \frac{1}{\hbar\omega}\ln\left[1 + \frac{\mathcal{N}}{M}\right]; \tag{5.3}
$$

$$
T(E_M, N) = \frac{\hbar\omega}{k_B}\left(\ln\left[1 + \frac{\mathcal{N}}{M}\right]\right)^{-1}. \tag{5.4}
$$

</div>

Internal energy

At first we solve Equation (5.3) for M

$$
\begin{aligned}
\beta\hbar\omega &= \ln\left[1 + \frac{\mathcal{N}}{M}\right] \\
\frac{\mathcal{N}}{M} &= e^{\beta\hbar\omega} - 1 \\
M &= \frac{\mathcal{N}}{e^{\beta\hbar\omega} - 1}.
\end{aligned}
$$

With this the internal energy is

INTERNAL ENERGY
(*Einstein solid*)

$$E_M(T) = \frac{\mathcal{N}\hbar\omega}{e^{\beta\hbar\omega} - 1} \ .$$

(5.5)

With this we see that energy is extensive, as it is supposed to be. Now we can convert entropy from $S(M, \mathcal{N})$ to $S(T, \mathcal{N})$ by substituting $M/\mathcal{N}$ by $1/(e^\gamma - 1)$ with $\gamma = \beta\hbar\omega$. Starting from Equation (5.2)

$$
\begin{aligned}
S(T, N) &= k_B\mathcal{N}\left((1 + \frac{M}{\mathcal{N}})\ln\left[1 + \frac{M}{\mathcal{N}}\right] - \frac{M}{\mathcal{N}}\ln\left[\frac{M}{\mathcal{N}}\right]\right) \\
&= k_B\mathcal{N}\left((1 + \frac{1}{e^\gamma - 1})\ln\left[1 + \frac{1}{e^\gamma - 1}\right] + \frac{1}{e^\gamma - 1}\ln\left[e^\gamma - 1\right]\right) \\
&= k_B\mathcal{N}\left(\frac{e^\gamma}{e^\gamma - 1}\ln\left[\frac{e^\gamma}{e^\gamma - 1}\right] + \frac{1}{e^\gamma - 1}\ln\left[e^\gamma - 1\right]\right) \\
&= k_B\mathcal{N}\left(\frac{e^\gamma}{e^\gamma - 1}\ln\left[e^\gamma\right] - \frac{e^\gamma - 1}{e^\gamma - 1}\ln\left[e^\gamma - 1\right]\right) \\
&= k_B\mathcal{N}\left(\frac{\gamma e^\gamma}{e^\gamma - 1} - \ln\left[e^\gamma - 1\right]\right) \\
&= k_B\mathcal{N}\left(\frac{\gamma e^\gamma}{e^\gamma - 1} - \ln\left[e^\gamma(1 - e^{-\gamma})\right]\right) \\
&= k_B\mathcal{N}\left(\frac{\gamma e^\gamma}{e^\gamma - 1} - \gamma - \ln\left[1 - e^{-\gamma}\right]\right) \\
&= k_B\mathcal{N}\left(\frac{\gamma}{e^\gamma - 1} - \ln\left[1 - e^{-\gamma}\right]\right) .
\end{aligned}
$$

With this we have the entropy as a function of natural variables.

ENTROPY
(*Einstein Solid*)

$$S(T, \mathcal{N}) = k_B\mathcal{N}\left(-\ln\left[1 - e^{-\beta\hbar\omega}\right] + \frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1}\right) \ .$$

(5.6)

5.4.3   Canonical ensemble

As a general rule it is easier to use the canonical or grand canonical ensemble, as we will see shortly, using the example 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 number of quanta n_i can freely assume any value between zero and infinite for each oscillator.

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)

$$Z(T,\mathcal{N}) = \left(\frac{1}{1-e^{-\beta \hbar \omega}}\right)^{\mathcal{N}}.$$

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

From this 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) , which we calculated for the framework of the microcanonical ensemble. For $T \to 0$, and thus $\beta \to \infty$, the entropy becomes zero. This is in accordance 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 also is in accordance with the result for the microcanonical ensemble. This corresponds to the earlier result in Equation (5.5) .
According to the equipartition theorem (Equation (2.23)), however, the internal energy should be $U = \mathcal{N}k_BT$. We see, that the equipartition theorem is not valid for harmonic oscillators. It only is valid in the classical limit for $\hbar\omega \ll k_BT$.

Heat capacity

Next we calculate the heat capacity

$$
\begin{aligned}
C_V &= \left(\frac{\partial U(T,\mathcal{N})}{\partial T}\right)\bigg|_{\mathcal{N}} = \left(\frac{\partial U(T,\mathcal{N})}{\partial\beta}\right)\bigg|_{\mathcal{N}}\left(-\frac{1}{k_BT^2}\right) \\
&= \mathcal{N}k_B\beta^2\hbar\omega\,\frac{\hbar\omega e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}.
\end{aligned}
$$

HEAT CAPACITY
(*Einstein solid*)

$$C_V = \mathcal{N} k_B (\beta\hbar\omega)^2 \, \frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2} \; .$$

For low tempertatures $\beta\hbar\omega \gg 1$ the heat capacity approaches zero in exponentially, as there is a minimum excitation energy. For very high temperatures $\beta\hbar\omega \ll 1$ the heat capacity behaves as follows:

$$C_V \xrightarrow[T\to\infty]{} \mathcal{N} k_B (\beta\hbar\omega)^2 \frac{1 - \beta\hbar\omega}{(1 - 1 + \beta\hbar\omega)^2} = \mathcal{N} k_B (\beta\hbar\omega)^2 \frac{1}{(\beta\hbar\omega)^2} = \mathcal{N} k_B \; .$$

The heat capacity per degree of freedom then goes to k_B. 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 a result of the centers of mass of the oscillators not performing any translational movement.

Chapter 6

Interaction-free quantum systems
of identical particles

For interaction-free quantum systems of identical particles 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 then is the sum over all particles

$$E_N(\{i_\nu\}) = \sum_{\nu=1}^{N} \varepsilon_{i_\nu} \; .$$

In the case of identical distinguishable particles the canonical ensemble is especially suitable. In that case we only have to, as was already hinted at in the example in Table (6.1), state 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
⋮	⋮	⋮	⋮	⋮	⋮
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

---

CANONICAL PARTITION FUNCTION
(for identical distinguishable particles)

$$Z(T, N, V) = \sum_{i_1=1}^{L} \cdots \sum_{i_N=1}^{L} e^{-\beta \sum_{\nu=1}^{N} \varepsilon_{i_\nu}}$$

$$= \prod_{\nu=1}^{N} \sum_{i_\nu} e^{-\beta \varepsilon_{i_\nu}} = \left(\sum_{i} e^{-\beta \varepsilon_i} \right)^N$$

$$= Z^N(T, N = 1, V) \; .$$

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)

$$M(m|N) = \binom{N}{m} . \tag{6.1}$$

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 $M(m|N)$ from Equation (6.1) [Page 130] becomes

---

MULTIPLICITY OF OCCUPATION NUMBERS
(for indistinguishable particles)

$$M(m|L) = 1 . \tag{6.2}$$

6.2.1 Second quantisation

A partition function goes 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].

6.2.2 Partition function of the grand canonical ensemble

In order to calculate the partition function in this description, one only has to sum over all possible configurations of occupation numbers $\{n_i\}$.

$$Z(T, \mu, V) = \mathrm{tr}\left\{e^{-\beta(\hat{H} - \mu\hat{N})}\right\} = \sum_{\{n_i\}} e^{-\beta \sum_i (\varepsilon_i - \mu) n_i} = \sum_{\{n_i\}} \prod_{i=1}^{L} e^{-\beta (\varepsilon_i - \mu) n_i}$$

$$= \prod_{i=1}^{L} \underbrace{\left(\sum_n e^{-\beta(\varepsilon_i - \mu)n} \right)}_{:=Z_{\varepsilon_i}} = \prod_{i=1}^{L} Z_{\varepsilon_i} . \tag{6.3}$$

6.2.3 Grand canonical potential

First we determine the grand canonical potential.

$$\Omega(T, \mu, V) = -k_B T \ln\left[Z(T, \mu, V)\right]$$
$$= -k_B T \sum_i \ln\left[Z_{\varepsilon_i}\right] .$$

For the calculation of 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.
With this we get

$$Z_\varepsilon(T, \mu) = 1 + e^{-\beta(\varepsilon - \mu)} ; \qquad \text{(Fermions)}$$
$$Z_\varepsilon(T, \mu) = (1 - e^{-\beta(\varepsilon - \mu)})^{-1} ; \qquad \text{(Bosons)}$$
$$\Rightarrow \quad \ln\left[Z_\varepsilon(T, \mu)\right] = -\sigma \ln\left[1 - \sigma z e^{-\beta\varepsilon}\right] . \tag{6.4}$$

---

[1] As all ensembles are equivalent one can choose the mathematically most convenien one.

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 signe σ corresponds to the sign that appears when exchanging two particles

---
GRAND CANONICAL POTENTIAL

$$\Omega(T, \mu, V) = k_B T \, \sigma \sum_i \ln\left[1 - \sigma z e^{-\beta\varepsilon_i}\right] . \tag{6.7}$$

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:

$$U = \langle H \rangle_{T,\mu} = \frac{1}{Z(T, \mu, V)} \, \text{tr}\left\{\hat{H} e^{-\beta\hat{H} + \beta\mu\hat{N}}\right\} ,$$

We also find the following thermodynamical relation to be validated:

$$U = -\left(\frac{\partial \ln(Z(T, \mu, V))}{\partial\beta}\right)\bigg|_{\mu, N} + \mu\langle\hat{N}\rangle$$

The additional term comes from the factor β in front of the number of particles. In order to avoid this term, while deriving for β the fugacity z can be kept fixed. The 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 obvious at all that the derivations that were just used yield the correct results at all, as in the exponent of the density operator not only numbers are present. The proof that the approach is still correct for permuted operators can be found in Appendix (D) [Page 203]. For the second derivative with respect to λ, however, this is usually not so easy anymore. There, one gets the time dependent correlation function.

We shall now continue with the calculation of the internal energy

$$
U = -\left(\frac{\partial \ln(Z)}{\partial \beta}\right)\bigg|_{z,V} \overset{(6.3)}{=} -\sum_i \left(\frac{\partial \ln(Z_i)}{\partial \beta}\right)\bigg|_{z,V}
$$

$$
= -\sum_{i=1}^{L} \frac{\left(\frac{\partial Z_i}{\partial \beta}\right)\bigg|_{z,V}}{Z_i} = \sum_{i=1}^{L} \varepsilon_i \underbrace{\sum_n n \frac{e^{-\beta(\varepsilon_i-\mu)n}}{Z_i}}_{\langle n_{\varepsilon_i}\rangle_{T,\mu}}
$$

$$
= \sum_{i=1}^{L} \varepsilon_i \, \langle n_{\varepsilon_i}\rangle_{T,\mu} \; .
$$

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 NUMBERL
> *(via partition function)*
> _____
>
> $$\langle N \rangle_{T,\mu} = \frac{1}{Z(T,\mu,V)} \ \mathrm{tr} \left\{ \hat{N} \mathrm{e}^{-\beta\hat{H}+\beta\mu\hat{N}} \right\}$$
> $$= \frac{1}{\beta} \left(\frac{\partial \ln(Z(T,\mu,V))}{\partial \mu} \right) \bigg|_{T,N} .$$

Analogous to the derivation of the internal energy here we get

$$\ln(Z) = \sum_i \ln(Z(\varepsilon_i)) \qquad \Rightarrow$$

$$\langle N \rangle = \sum_{i=1}^{L} \frac{1}{\beta} \left(\frac{\partial \ln(Z(\varepsilon_i))}{\partial \mu} \right) \bigg|_{T,N}$$

$$= \sum_{i=1}^{L} \underbrace{\frac{1}{\beta} \left(\frac{\partial \ln(Z(\varepsilon_i))}{\partial \mu} \right) \bigg|_{T,N}}_{=\langle n_{\varepsilon_i} \rangle_{T,\mu}} .$$

This corresponds to Equation (6.9) [Page 133].

> AVERAGE PARTICLE NUMBER
> _____
>
> $$\langle N \rangle = \sum_{i=1}^{L} \langle n_{\varepsilon_i} \rangle_{T,\mu} . \qquad (6.10)$$

6.3 Density of states

The sum over i for d-dimensional problems leads to d-dimensional sums or integrals[2]. However, it is easy to see that all summands in Ω, U and $\langle N \rangle$ are

_____

[2]In Appendix (E) [Page 205] an alternative derivation of the transition from sum to intgral can be found.

dependent on 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

$$\rho(\varepsilon) = \sum_i \delta(\varepsilon - E_i) \ .$$

With this the grand canonical potential can be expressed as

$$\Omega(T, \mu, V) = k_B T \sigma \int \ln \left[1 - \sigma z \mathrm{e}^{-\beta\varepsilon} \right] \rho(\varepsilon) d\varepsilon \ .$$

The logarithm is rather obstructive for the purpose of integrating. Thus we use integration by parts in order to get the derivative of the logarithm and the antiderivative of the partition function (distribution function):

$$\Omega(T, \mu, V) = -k_B T \sigma \int \left(\frac{\partial}{\partial \varepsilon} \ln \left[1 - \sigma z \mathrm{e}^{-\beta\varepsilon} \right] \right) \Bigg|_{T,z} F_\rho(\varepsilon) d\varepsilon$$

$$= -k_B T \sigma \int \frac{(-\sigma z)(-\beta)\mathrm{e}^{-\beta\varepsilon}}{1 - \sigma z \mathrm{e}^{-\beta\varepsilon}} F_\rho(\varepsilon) d\varepsilon$$

$$= -\int \frac{z}{\mathrm{e}^{\beta\varepsilon} - \sigma z} F_\rho(\varepsilon) d\varepsilon$$

$$= -\int \langle n_\varepsilon \rangle_{T,\mu}\, F_\rho(\varepsilon)\, d\varepsilon \ .$$

Thus, Ω, U and $\langle N \rangle$ can be expressed by similar one dimensional integrals.

GRAND CANONICAL VARIABLES

$$\Omega(T, \mu, V) = - \int \langle n_\varepsilon \rangle_{T,\mu} \, F_\rho(\varepsilon) \, d\varepsilon \; ; \tag{6.11}$$

$$U = \int \varepsilon \, \langle n_\varepsilon \rangle_{T,\mu} \, \rho(\varepsilon) d\varepsilon \; ; \tag{6.12}$$

$$\langle N \rangle = \int \langle n_\varepsilon \rangle_{T,\mu} \, \rho(\varepsilon) d\varepsilon \; . \tag{6.13}$$

Here it shall be pointet out that the introduction of the density of states may be exact, but caution is called for if the rest of the integrand diverges. Then, one has to take into account that the density of states is in reality a delta functional. The thermodynamic limit has to be executed with great care. This we will discuss in the context of the Bose gas.

6.4 Average occupation number of single particle states

A key role for non-interacting systems is the average occupation number of the single particle niveaus, which was defined in Equation (6.4) [Page 131] and Equation (6.9) [Page 133]

$$\langle n_\varepsilon \rangle_{T,\mu} = \sum_n n \frac{e^{-\beta(\varepsilon-\mu)n}}{Z_\varepsilon(T,\mu)} \; ;$$

$$Z_\varepsilon(T,\mu) = \sum_n e^{-\beta(\varepsilon-\mu)n} \; ; \Rightarrow$$

$$\langle n_\varepsilon \rangle_{T,\mu} = \frac{1}{\beta} \left(\frac{\partial \ln(Z_\varepsilon(T,\mu))}{\partial \mu} \right) \Bigg|_{T,V} \; .$$

From Equation (6.4) [Page 131] then follows

<div style="text-align:center">

FERMI AND BOSE DISTRIBUTION

</div>

$$\langle n_\varepsilon \rangle_{T\mu} = \frac{z}{e^{\beta\varepsilon} - \sigma z} = \frac{1}{e^{\beta(\varepsilon-\mu)} - \sigma} \; ; \qquad (6.14)$$

$$\text{with } \sigma = \begin{cases} -1 & \text{Fermions} \\ +1 & \text{Bosons} \end{cases}$$

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

---

<div style="text-align:center">

FERMI-DIRAC DISTRIBUTION

</div>

$$f_D(\varepsilon, T) := \langle n(\varepsilon_\nu) \rangle_T = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1} \; ; \qquad 0 \le f_D(\varepsilon) \le 1^{(*)}$$

$$f_D(\varepsilon, T) \xrightarrow[T\to 0]{} \Theta(\varepsilon < \mu) \; ;$$

$$f_D(\varepsilon = \mu, T) = \frac{1}{2} \; .$$

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 deviations 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 for $|\varepsilon - \mu| = k_B T$ the deviation from the limit value (1 or 0) is already only a eth. Thus the deviation of the step function is constrained
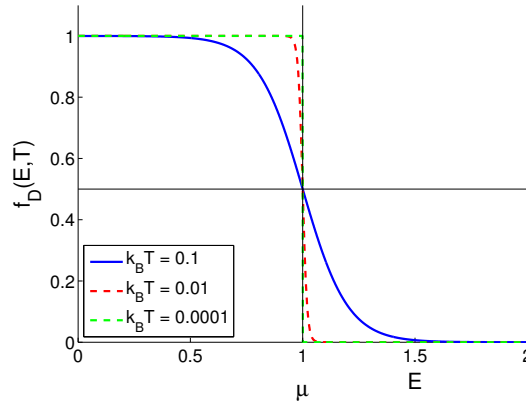
to the area $k_B T$ around the Fermi level.

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 in a way, so that $\varepsilon_0 = 0$. With this convention $\mu < 0$ has to be valid. As the cemical potential has to be chosen in a way, so that the result is a predefined average particle number, μ will adjust itself the right way for self consistent calculations.

Chapter 7

Implementation

7.1 The ideal quantum gas

The ideal quantum gas is the simplest quantum mechanical many-particle system. Nevertheless, it already exhibits interesting thermodynamic properties. It consists of non-interacting Fermions or Bosons. The particles are confined to a cuboid and are not influenced by any 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 state that considers degeneration

$$M_S := 2S + 1 .$$

The derivation of the density of states can be found in . The result is

SINGLE-PARTICLE DENSITY OF STATES
(*free, non-relativistic particles*)

$$\rho(\varepsilon) = C_d \, \varepsilon^{\frac{d}{2}-1} \; ; \tag{7.1}$$

$$F_{\rho_d} = C_d \, \frac{2}{d} \, \varepsilon^{\frac{d}{2}} \; ; \tag{7.2}$$

$$C_d = M_S V \left(\frac{2\pi m}{h^2} \right)^{\frac{d}{2}} \frac{1}{\Gamma(\frac{d}{2})} \; . \tag{7.3}$$

7.1.2 Grand canonical potential

With this we are now able to use Equation (6.11) [Page 136] and Equation (6.14) [Page 137] to calculate the grand canonical potential.

$$\Omega(T, \mu, V) = - \int \langle n_\varepsilon \rangle_{T,\mu} \, F_\rho(\varepsilon) \, d\varepsilon = -\frac{2C_d}{d} \int \frac{z}{e^{\beta\varepsilon} - \sigma z} \, \varepsilon^{\frac{d}{2}} \, d\varepsilon \; . \tag{7.4}$$

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 is going to show up on multiple occasions. Because of its similarity to the gamma fuction we shall call it *quantum mechanical gamma function* and formulate it as follows

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QUANTUM MECHANICAL GAMMA FUNCTION
(and recursion formula)

$$g_l^{(\sigma)}(z) := \frac{1}{\Gamma(l)} \int \frac{z}{e^t - \sigma z} \, t^l \, \frac{dt}{t} \; ; \qquad (7.5)$$

$$z \frac{dg_l^\sigma(z)}{dz} = g_{l-1}^\sigma(z) \; ; \qquad (l > 1) \; . \qquad (7.6)$$

The recursion formula is derived in Appendix (G.1) [Page 211]. 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)

$$\beta \, \Omega(T, \mu, V) = -M_S V \, \lambda_T^{-d} \, g_{\frac{d}{2}+1}^\sigma(z) \; ; \qquad (7.7)$$

$$\lambda_T := \sqrt{\frac{2\pi\beta\hbar^2}{m}} \; . \qquad \text{(thermic de Broglie wavelength)} \qquad (7.8)$$

Again we used the thermic de Broglie wavelength.

7.1.3 Pressure

From $\Omega = -pV$ we directly get

PRESSURE
(bosonic correction term is not yet introduced)

$$\beta p = M_S \lambda_T^{-d} g_{\frac{d}{2}+1}^\sigma(z) \; . \qquad (7.9)$$

7.1.4 Average number of particles

In order to calculate the average number of particles, Equation (6.13) [Page 136] 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

$$\langle N \rangle = C_d \, (k_B T)^{\frac{d}{2}} \underbrace{\int \frac{z}{e^t - \sigma z} \, t^{\frac{d}{2}} \, \frac{dt}{t}}_{:=\Gamma(\frac{d}{2}) \, g^\sigma_{\frac{d}{2}}(z)}$$

$$\overset{(7.3)}{=} M_S V \left(\frac{2\pi m}{h^2} \right)^{\frac{d}{2}} \frac{1}{\Gamma(\frac{d}{2})} \, (k_B T)^{\frac{d}{2}} \Gamma(\frac{d}{2}) \, g^\sigma_{\frac{d}{2}}(z)$$

$$n := \frac{\langle N \rangle_{T,\mu}}{V} = M_S \left(\frac{2\pi m}{\beta h^2} \right)^{\frac{d}{2}} g^\sigma_{\frac{d}{2}}(z) \ .$$

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 thermic equation of state for the ideal quantum gas.

THERMIC EQUATION OF STATE
(*bosonic correction term is not yet introduced*)

$$\beta p = M_S \; \lambda_T^{-d} g_{\frac{d}{2}+1}^{\sigma}(z(n,T)) \; .$$

(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 expansion of Equation (G.1) [Page 212], 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 142]

$$n = M_S \lambda_T^{-d} g_{d/2}^{\sigma}(z) = M_S \lambda_T^{-d} z \qquad \Rightarrow$$
$$z = \frac{n \lambda_T^d}{M_S} \; .$$

This result is plugged into the expression for pressure (Equation (7.11) [Page 143])

$$\beta p = M_S \lambda_T^{-d} g_{\frac{d}{2}+1}^{\sigma}(z) = M_S \lambda_T^{-d} z = n \; ;$$
$$\Rightarrow \qquad pV = N k_B T \; .$$

This is the known result for classical free particles. Classically there is no differentiation 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 single-particle levels we get

$$\langle n_k \rangle = \frac{z}{e^{\beta E(k')} - \sigma z} = z e^{-\beta E(k)} \; \frac{1}{1 - \sigma z e^{-\beta E(k)}} \xrightarrow[z \ll 1]{} e^{-\beta(E(k)-\mu)} + O(z^2) \; .$$

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. Bosonic systems exhibit interesting macroscopic quantum phenomena, which are a result of the occupation number of a single state being able to grow indefinitely. 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, at first we shall consider the occupation numbers of the ground state as well as the first excited staate at $T \to 0$. The Bose-Einstein distribution has the form

$$f_B(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} - 1} .$$

Therfore, 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 case that the thermodynamic limit yields $\mu \to 0$, 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 once again consider the initial expression for the number of particles in Equation (6.10) [Page 134]. 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 214]. Therefore, we can again convert the remaining sum into an integral of 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 it contributes only insignificantly. Especially this is the reason for this term not to be considered correctly for the conversion into an integral and the usage of the continuous density of states without the extra term. Adopting the integral from Equation (7.10) [Page 142] we get

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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 shall be called $n_n(T, z)$. In order for the occupation numbers of the single-particle levels not to be able to assume unphysical (negative) values, $-\infty < \mu < \min_i \varepsilon_i = 0$ has to be true. From this $0 < z < 1$ follows. We shall use this to further evaluate the function $g_l^{+1}(z)$.

The details of the calculation are found in Appendix (G.3) [Page 212]. The results are

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POLYLOGARITHM
(de Jonquière function)

$$g_l^{+1}(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^l} \; . \qquad\qquad (7.12)$$

This function has the following properties:

$$g_l^{+1}(z) \geq 0 \; ;$$
$$g_l^{+1}(0) = 0 \; ;$$
$$\frac{d}{dz} g_l^{+1}(z) \overset{(7.12)}{=} \frac{1}{z} g_{l-1}^{+1}(z) > 0 \; ;$$
$$g_l^{+1}(1) = \zeta(l) \; .$$

This mean that $g_l^{+1}(z)$ starts at zero for $z = 0$, is monotonically 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:

$$\zeta(3/2) = 2.612 \; ; \qquad\qquad \zeta(5/2) = 1.3415 \; .$$

Hereafter we shall at first consider three dimensional systems ($d = 3$), for which the following applies:

AVERAGE DENSITY
(for Bosons in 3d)

$$\tilde{n}(T, z) := \tilde{n}_0 + \tilde{n}_n(z) \; ; \qquad\qquad (7.13\text{a})$$
$$\tilde{n}_0 := \frac{1}{V} \frac{z}{1 - z} \; ; \qquad\qquad (7.13\text{b})$$
$$\tilde{n}_n(z) := \lambda_1^{-3} \, T^{3/2} \, g_{3/2}^{+1}(z) \; . \qquad\qquad (7.13\text{c})$$

Therefore, for the physically allowed values of z, we have $g_{3/2}^1(z) \leq \zeta(3/2)$. Thus, for the contributor $\tilde{n}_n(z) \leq \tilde{n}_C$ from 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 begins for

$$\tilde{n} \geq \lambda_T^{-3} \zeta(3/2)$$

$$\lambda_T^3 \geq \frac{\zeta(3/2)}{\tilde{n}} = \zeta(3/2) \underbrace{\frac{V}{\tilde{N}}}_{:=v} = \zeta(3/2) \, r^3 \; .$$

Here v is the average volume per particle and r is the average distance be-
tween particles. Bose condensation therefore starts when the thermic de
Broglie wavelength exceeds the average distance between particles.

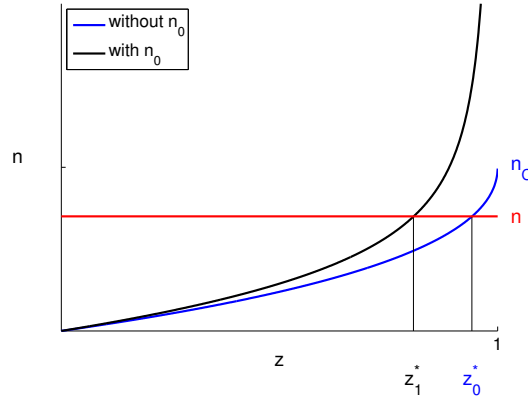**A) We shall start with $n < \tilde{n}_C$:**

Figure 7.1: *Density as a function of fuagcity z. The blue graph is the re-
sult without condensation contribution ($\tilde{n}_n(T, z)$) the black one contains the
condensation density.*

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 condensation contribution:

$$z_0^* < 1 \; . \tag{7.16}$$

The real solution for finite V is z_1^*. Now the additional term is monotonically
nondecreasing:

$$\frac{d}{dz} \frac{1}{1-z} = \frac{1}{(1-z)^2} > 0 \; .$$

Thus both contributors in Equation (7.13) [Page 146] are positive and mono-
tonically nondecreasing. For one, for all $V < \infty$ we have

$$z_1^* < z_0^* < 1$$

On the other hand, from this follows

$$\tilde{n}_0 = \frac{1}{V} \frac{z_1^*}{1 - z_1^*} \overset{z_1^* < z_0^*}{<} \frac{1}{V} \frac{z_0^*}{1 - z_0^*} \; .$$

Because of $z_0^* < 1$ (Equation (7.16) [Page 147]), $z_0^*/(1-z_0^*)$ is a finite constant C^* that is independent from V. Finally we get

$$\tilde{n}_0 < \frac{C^*}{V} \xrightarrow[V \to \infty]{} 0 \; .$$

From this follow, that in this case the condensation density vanishes in the themodynamic limit and thus the chemical potential is unambiguously determined by z_0^*.

For $\tilde{n} < \tilde{n}_C$ we have $\tilde{n}_0 = 0$.
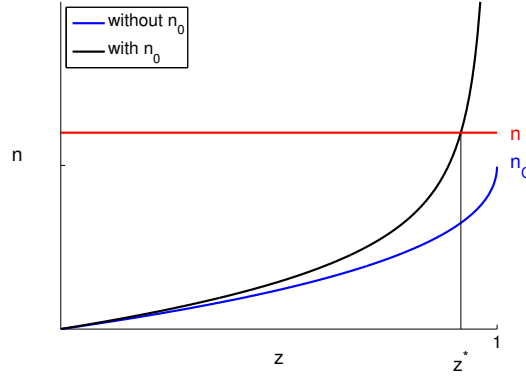
B) Now we consider $\tilde{n} > \tilde{n}_C$:

Figure 7.2: *Density as a function of fugacity z. The blue graph is the result without condensation contribution $(\tilde{n}_n(T,z))$, the black graph includes the condensation density.*

In this case we will show that the fugacity goes to 1 and the chemical potential goes to 0 and also that, in the thermodynamic limit, i.e. for $V \to \infty$, we have

$$\tilde{n}_0 = \tilde{n} - \tilde{n}_C > 0 \; .$$

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.

The fugacity z^* is a consequence of the equation

$$\tilde{n} = \frac{1}{V}\frac{z^*}{1-z^*} + \tilde{n}_n(T, z^*) \ . \tag{*}$$

We can see in the figure that $z^* \xrightarrow[V\to\infty]{} 1$. This is a consequence of the blue graph not contributing and the black graph approaching the vertical straight line at $z = 1$.

Mathematically, on can look at that as follows: From (*) we get

$$n = \frac{1}{V}\frac{z^*}{1-z^*} + n_n(T, z^*) < \frac{1}{V}\frac{z^*}{1-z^*} + \underbrace{n_n(T, 1)}_{=\tilde{n}_C}$$

$$\Rightarrow \qquad \left(n - \tilde{n}_C\right) < \frac{1}{V}\frac{z^*}{1-z^*}$$

$$(n - \tilde{n}_C)\left(1 - z^*\right) < \frac{1}{V}\, z^*$$

$$(n - \tilde{n}_C) < z^*\left(\frac{1}{V} + (n - \tilde{n}_C)\right)$$

$$\frac{(n - \tilde{n}_C)}{\frac{1}{V} + (n - \tilde{n}_C)} < z^* \le 1 \ .$$

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 shall perform a series expansion in μ^*.

$$\tilde{n} = \frac{1}{V}\frac{1 + \beta\mu^*}{(-\beta\mu^*)} + O(\mu^*) + \tilde{n}_C$$

$$= \frac{1}{V}\frac{1}{(-\beta\mu^*)} + \left(\tilde{n}_C - \frac{1}{V}\right) + O(\beta\mu^*)$$

$$\beta\mu^* = -\frac{1}{V(\tilde{n} - \tilde{n}_C + \frac{1}{V})} + O\left((\mu^*)^2\right)$$

$$\beta\mu^* = -\frac{1}{V(\tilde{n} - \tilde{n}_C)} + O(V^{-2}) + O\left((\mu^*)^2\right) \ . \tag{*}$$

In the leading order μ^* goes to zero with

$$\beta\mu^* = -\frac{1}{V}\frac{1}{\tilde{n} - \tilde{n}_C}$$

Therefore both terms that were omitted in (*) are of the order $O(V^{-2})$. From this we get the condensat density

$$\tilde{n}_0 = \frac{1}{V}\frac{z^*}{1 - z^*} = \frac{1}{V}\frac{1 + \beta\mu^*}{(-\beta\mu^*)} = \frac{1}{V}\frac{1}{(-\beta\mu^*)} - \frac{1}{V} = (\tilde{n} - \tilde{n}_C) - \frac{1}{V}$$

$$= (\tilde{n} - \tilde{n}_C) - \frac{1}{V} \; .$$

IN THE THERMODYNAMIC LIMIT THE FOLLOWING APPLIES
(in the condensation phase, i.e. $T < T_C$ or $n > \tilde{n}_C$)

$$\tilde{n}_0 = \tilde{n} - \tilde{n}_C - \frac{1}{V} \xrightarrow[V\to\infty]{} \tilde{n} - \tilde{n}_C \; ;$$

$$\beta\mu^* = -\frac{1}{V}\frac{1}{\tilde{n} - \tilde{n}_C} \xrightarrow[V\to\infty]{} 0 \; ; \tag{7.17}$$

$$z^* = 1 + \beta\mu^* \xrightarrow[V\to\infty]{} 1 \; .$$

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 142] the regular density is

$$\tilde{n}_n(z) = \Lambda_T^{-d} g_{d/2}^1(z) \; .$$

We had shown universally that $g_{d/2}^1(z)$ is a monotonically nondecreasing function in the variable z. This function corresponds to $\zeta(d/2)$ for $z = 1$. From Table (G.5) we infer that

$$\zeta(2/2) = \zeta(2/2) = \infty \; .$$

Thus, for all densities $\tilde{n}$ there is a solution for the equation

$$\tilde{n}_n(z^*) = \tilde{n} \; .$$

The rest of the argumentation is the same as in Section (7.2.1) [Page 147]. Therefore, in the thermodynamic limit we also have $z^* < 1$. As a consequence of this, in the thermodynamic limit the correction term vanishes in with $1/V$.

Isn't condensation trivial?

Have we not actually made a trivial observation? As with decreasing temperature the number of Bosons in the state of minimal single-particle energy $\varepsilon_0 = 0$ increases because of the Bose distribution. We get a typical temperature for this from the condition

$$\beta(\varepsilon_1 - \varepsilon_0) = \beta\varepsilon_1 \geq 1$$

$$\Rightarrow \qquad k_B T \leq \varepsilon_1 = \frac{2\pi\hbar^2}{m}\frac{\pi}{L^2} \;;$$

$$\text{resp.} \qquad 1 \leq \frac{2\pi\hbar^2\beta}{m}\frac{\pi}{L^2} = \frac{\lambda_{T_B}^2}{L^2}\pi$$

$$\text{thus} \qquad L \lesssim \lambda_T \;.$$

This transition takes place when the thermic de Broglie wavelength exceeds the dimensions 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. The ratio of the temperatures is

$$\frac{T_C}{T} = \frac{\lambda_T^2}{\lambda_C^2} = \frac{L^2}{L_1^2} = \left(\frac{V}{V_1}\right)^{2/3} = N^{2/3} \approx 10^{\frac{2\cdot24}{3}} = 10^{16} \;.$$

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 an actual phase transition.

BEC is a real phase transition

Dimension dependence of BEC

We shall consider the conditional equation for the chemical potential in Equation (7.13) [Page 146] again. $g_{\frac{d}{2}}(z = 1)$ diverges for dimensions $d = 1, 2$ because of

$$g_{\frac{d}{2}}(z = 1) = \zeta\left(\frac{d}{2}\right) = \sum_{n=1}^{\infty}\frac{1}{n^{d/2}} \;.$$

As was universally shown, g starts with zero and is monotonically nondecreasing for $z = 0$. Thus there always is a solution z^*, even without the condensation term. That in in this case no Bose condensation occurs is shown in Appendix (H) [Page 214].

The ideal Bose gas has no BEC phase in 1d or 2d.

Different conditions for BEC

In Equation (7.14) [Page 146] we had the following condition for BEC:

$$\tilde{n} > \tilde{n}_C = \Lambda \, T^{3/2} \; .$$

From this, two conditions can be inferred

CONDITIONS FOR CONDENSATION

$$\tilde{n} > \tilde{n}_C(T) \qquad\qquad := \Lambda \, T^{3/2} \; ; \qquad (7.18)$$

$$T < T_C(\tilde{n}) \qquad\qquad := \left(\frac{\tilde{n}}{\Lambda}\right)^{2/3} \; ; \qquad (7.19)$$

$$\Lambda = \lambda_1^{-3} \, \zeta(3/2) \; ; \qquad (7.20)$$

$$\zeta(3/2) \, T_C^{3/2} = \tilde{n}\lambda_1^3 \; . \qquad (7.21)$$

In the condensation zone $T < T_C$ we have $z = 1$ in the thermodynamic limit (see Equation (7.17) [Page 150]) and for the condensation density we have

$$\tilde{n}_0 = \tilde{n} - \Lambda T^{3/2}$$

$$= \tilde{n}\left[1 - \left(\frac{T}{(\tilde{n}/\Lambda)^{2/3}}\right)^{3/2}\right] \stackrel{(7.19)}{=} \tilde{n}\left[1 - \left(\frac{T}{T_C}\right)^{3/2}\right] \; .$$

With this we have the

TEMPERATURE DEPENDENCE OF THE CONDENSATION DENSITY

$$\tilde{n}_0 = \tilde{n}\left[1 - \left(\frac{T}{T_C}\right)^{3/2}\right] \; .$$

This means that below T_C a macroscopic number of particles condense in the ground state $(k = 0)$.

We see that the condensation density becomes the total density for $T \to 0$. Thus, all particles condense in the ground state. In the condensation zone
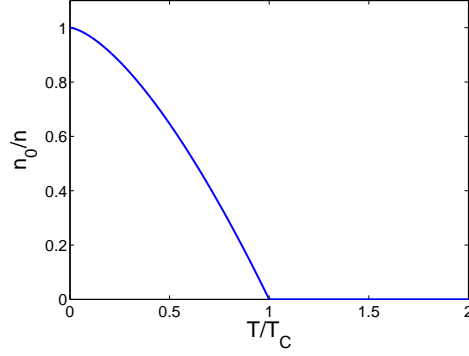
Figure 7.3: *Fraction of Bosons in the single-particle ground state (condensate fraction).*

the density of the regular fraction of the fluid is

$$\tilde{n}_n := \tilde{n} - \tilde{n}_0 = \lambda_T^{-3}\zeta(3/2) = \Lambda T^{3/2} \ . \tag{7.22}$$

With the values for ^{4}He, i.e. a density of $\rho = 75.4 \ kg \ m^{-3}$, a mass of $m_{^4\text{He}} = 6.6610^{-27}kg$ and $\zeta(5/2) = 1.3415$, the transition temperature for ^{4}He is $3.13K$. This is surprisingly close to the value for the λ transition in ^{4}He $(T_\lambda = 2.18K)$. At this point helium transitions from a suprafluid to a regular fluid. The physical properties of ^{4}He are fascinating, but would take too long to discuss in this lecture.

Outside the condensation zone the condensation density vanishes with V^{-1} and thus follows

$$\boxed{\begin{array}{c} \textsc{Density} \\ (\textit{outside the condensation phase, i.e. especially } T > T_C) \\[4pt] \hline \\[-6pt] \tilde{n}(T, z) = \lambda_1^{-3} \, T^{3/2} \, g_{3/2}^1(z) \; ; \hfill (7.23) \\[6pt] \tilde{n}_0 = 0 \; . \hfill (7.24) \end{array}}$$

7.2.2   Grand canonical potential

In Equation (7.7) [Page 141] we had already calculated the grand canonical potential without special consideration of the ε_0 terms. The result was

$$\frac{\beta \, \Omega(T, \mu, V)}{V} = -M_S \, \lambda_1^{-3} \, T^{3/2} \, g_{\frac{5}{2}}^\sigma(z) \; . \qquad (7.25)$$

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 132] 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 (7.25) [Page 154]. Within the condensation phase

$$1 - z = |\beta \mu| = \frac{(\tilde{n}_C - \tilde{n}_0)}{V} \; ; \text{and thus } \frac{\beta \Omega_{\varepsilon_0}}{V} \propto \frac{\ln(V)}{V} \xrightarrow[V \to \infty]{} 0 \; .$$

applies. The correction term therefore vanishes in the thermodynamic limit. Caution is to be exercised: If one intends to use the grand canonical potential to calculate other thermodynamic variables, such as the number of particles, via partial derivation, one may not yet omit the correction term. The reason for that is that when differentiated it may have a form, that does not vanish in the thermodynamic limit! This means that the thermodynamic limit should only be enforced once the final result is obtained.

7.2.3   Pressure

Because of $(p = -\Omega/V)$ we immediately get the pressure from the grand canonical potential. Here the form of the condensate term stays unchanged

and in the thermodynamic limit it does not contribute to the pressure. This is evident, as the particles in the condensate do not have any momentum $(k = 0)$. The pressure is therefore given by Equation (7.25) [Page 154]

PRESSURE AS A FUNCTION OF T AND z

$$p(T, z) = M_S \begin{cases} k_B \ \lambda_1^{-3} \ g_{5/2}^1(z) \ T^{5/2} \ ; & \text{outside the condensation phase} \\ k_B \ \lambda_1^{-3} \zeta(5/2) \ T^{5/2} \ ; & \text{within the condensation phase} \end{cases}.$$

$$(7.26)$$

---

p-T phase diagram

Since $g_{5/2}^1(z)$ is a monotonically nondecreasing function, the pressure increases with increasing z up to a maximum value for $z = 1$. At this point the condensation phase is entered. 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*)

$$p_C(T) = M_S \ k_B \ \lambda_1^{-3} \zeta(5/2) \ T^{5/2} \ . \qquad (7.27)$$

This pressure is also called **vapour pressure**. From that results the *p-T* phase diagram in Figure 7.4.

In order to express the pressure as a function of temperature and density (thermic equation of state), first Equation (7.23) [Page 154] has to be inverted for the density $n(T, z)$ in order to get $z(T, n)$. The result is then plugged into $p(T, z(n))$ resulting in $p(T, n)$. It is easier to numerically calculate $p(T, z)$ and $n(T, z)$ for a given z and with that enter a point in the p, n, T coordinate system. With that one can examine interesting steps, such as $p(T)\big|_n$ or $p(n)\big|_T$.
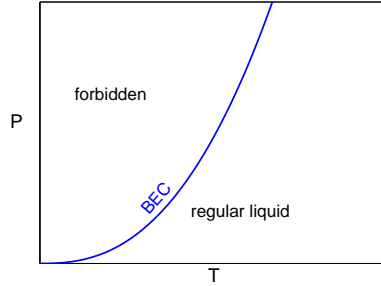
Figure 7.4: *p-T phase diagram. The area above the graph is inaccessible. in the lower area, for pairs of values of p and T a regular fluid is present. Exactly on the graph there is the two-phase area for which a mixture of regular fluid and condensate exists.*

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

$$\frac{\partial \tilde{n}(T,z)}{\partial z} = \lambda_T^{-3} \frac{d}{dz} g_{3/2}^1(z) = \lambda_T^{-3} \frac{g_{1/2}^1(z)}{z} > 0 \ .$$

From this follows

$$\left.\frac{\partial p}{\partial \tilde{n}}\right|_T = \left.\frac{\partial p}{\partial z}\right|_T \left.\frac{\partial z}{\partial \tilde{n}}\right|_T = k_B \Lambda \ T^{5/2} \frac{d g_{5/2}^1(z)}{dz} \frac{dz}{d\tilde{n}}$$

$$= k_B \Lambda \ T^{5/2} \underbrace{\frac{g_{3/2}^1(z)}{z} \frac{dz}{d\tilde{n}}}_{>0} > 0 \ .$$

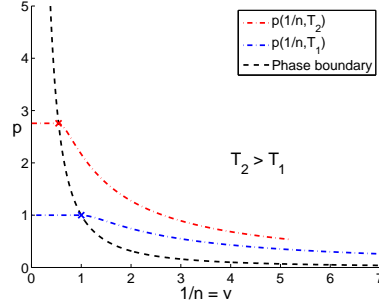Thus the pressure increases with increasing density, as one would intuitively infer because of reasons of stability.

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.*

Within the condensation phase, however, for fixed temperature the pressure is independent of the density. 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 $v_C = 0$.

For the transition point the following applies:

$$p_C = d_p T^{5/2} \; ; \qquad\qquad (Equation(7.27)[Page155])$$
$$\tilde{n}_C = d_n T^{3/2} \; ; \qquad\qquad (Equation(7.18)[Page152]) \; .$$

This yields a phase boundary at

$$\frac{p}{d_p} = \left(\frac{d_n}{\tilde{n}}\right)^{-5/3}$$

This is the dashed graph in Figure 7.5. In the condensation zone a mixture of phases is present.

7.2.4 Landau criterion

Now we shall consider the physical reason for the occurrence of friction free flux. For this we consider a macroscopic object of the mass M, which moves through a fluid with the velocity $\vec{V}$. The momentum of the object therefore is $\vec{P} = M\vec{V}$ and its cinetic energy is $E_{kin} = M\vec{V}^2/2$. We shall assume that the object moving within the fluid causes an excitation with the wave vector $\vec{k}$. The momentum of this *quasiparticle* then is $\vec{p} = \hbar\vec{k}$ and its energy is described by a dispersion relation $E(\vec{k})$. After the excitation of the quasiparticle, the macroscopic object shall move with the velocity $\vec{V}'$. Thus, its momentum now is $\vec{P}' = M\vec{V}'$ and its kinetic energy is $E'_{kin} = M\vec{V}'^2/2$. For this process, because of conservation of momentum we have

$$M\vec{V} = M\vec{V}' + \hbar\vec{k}$$

$$\vec{V}' = \vec{V} - \frac{\hbar\vec{k}}{M} \qquad (*)$$

and because of conservation of energy we have

$$\frac{1}{2}M\vec{V}^2 = \frac{1}{2}M\vec{V}'^2 + E(\vec{k}) \; ;$$

$$\frac{1}{2}M\vec{V}'^2 \overset{(*)}{=} \frac{1}{2}M\left(\vec{V}^2 + (\frac{\hbar}{M})^2\vec{k}^2 - 2\frac{\hbar}{M}\vec{V}\vec{K}\right)$$

$$= \frac{1}{2}M\vec{V}^2 + \frac{\hbar^2\vec{k}^2}{2M} - \hbar\vec{k}\vec{V} \; .$$

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 infer the following inequation:

$$\hbar|\vec{k}| \, |\vec{V}| \geq \hbar\vec{k}\vec{V} = E(\vec{k}) + \frac{\hbar^2\vec{k}^2}{2M} \geq E(\vec{k}) \; .$$

For the macroscopic object to be able to transfer energy to the fluid, the following has to be true:

CONDITION FOR DISSIPATION

$$|\vec{V}| \geq \min_{\vec{k}} \frac{E(\vec{k})}{\hbar|\vec{k}|} \ .$$

If this condition is not met, it is not possible to create the quasiparticle (the excitation) and therefore have a dissipative process. This critical velocity was first derived by Landau. If the right side of the equation has a lower limit, obviously, a minimal velocity of the object is needed to generate friction losses in the fluid. For velocities $V > V_{cr}$ quasiparticles can be created, i.e. the movement of macroscopic objects can be slowed. The other way around, this means that the macroscopic object can move in the fluid without friction for velocieties of $V < V_{cr}$. This minimal velocity is therefore

---

MINIMAL VELOCITY

$$V_{cr} = \min_{\vec{k}} \frac{E(\vec{k})}{\hbar|\vec{k}|} \ .$$

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 a always possible to gnereate dissipative processes.

In accordance with this the ideal Bose gas is never suprafluid, even with BEC.

For suprafluidity to occur it is therefore necessarry that there is no interaction between the particles.

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 suprafluid Helium, however, the dispersion relation $E(\vec{k})$ has a nonzero wave vector $\vec{k}$, a so called roton minimum. For $\vec{k} \to 0$ there is phonon

dispersion. For $\vec{k}$ at the roton minimum we have $E(\vec{k}_{rot}) < \hbar c |\vec{k}|$. From this follows

$$V_{cr} = \min_{\vec{k}} \frac{E(\vec{k})}{\hbar |\vec{k}|} = \frac{E(\vec{k}_{rot})}{\hbar |\vec{k}_{rot}|} < \frac{\hbar c |\vec{k}_{rot}|}{\hbar |\vec{k}_{rot}|} = c$$

that the critical velocity V_{cr} is smaller than the phonon velocity c. A quantitative comparison to experiments, however, shows that the Landau velocity V_{cr} for suprafluid Helium that results from this, is too great. When deriving the Landau criterion, the formation of vortexes is neglected. This would lead to a further reduction in the critical velocity.

According to Landau there has to be a critical velocity one energy gap above the ground state, from where phonons and rotons can be genergated. Those are responsible for the properties of the SF.
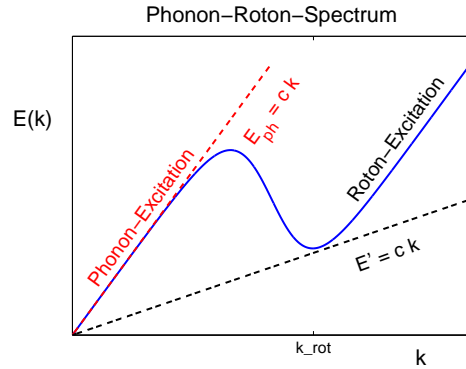

Figure 7.6: Phonon-roton dispersion

7.2.5   Thermodynamic potentials

Internal energy

We can get the internal energy from Equation (6.12) [Page 136] 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 140] we find that

$$U = -\frac{d}{2}\Omega = \frac{d}{2}pV \; .$$

For three dimensions we thus have the

CALORIC EQUATION OF STATE

$$U = \frac{3}{2}pV \; .$$

Plugging in the result for the pressure, we get

$$\frac{U}{Nk_B} = \frac{3}{2\tilde{n}}\lambda_1^{-3}T^{5/2} \; g_{5/2}^1(z) = \frac{3}{2}T\frac{\lambda_T^{-3}}{\tilde{n}} \; g_{5/2}^1(z) \; , \tag{7.28}$$

Here $z = 1$ has to be plugged in when considering the condensate zone. As a reminder: In the classical model the result for this was $U/(Nk_B) = \frac{3}{2}T$.

Heat capacity (specific heat)

Using Equation (7.28) [Page 161] we now calculate the heat capacity.

$$\frac{C_V}{Nk_B} := \frac{\partial(U/Nk_B)}{\partial T}\bigg|_{V,N} = \frac{\partial}{\partial T}\left(\frac{3}{2\tilde{n}}\lambda_1^{-3}T^{5/2} \; g_{5/2}^1(z)\right)\bigg|_{V,N} \; .$$

As V and N are kept constant, the density $\tilde{n}$ is constant too. Therefore, we get

$$\frac{C_V}{k_B N} = \frac{3}{2\tilde{n}} \; \lambda_1^{-3} \; \frac{\partial}{\partial T}\left(T^{5/2} \; g_{5/2}^1(z)\right)\bigg|_{V,N} \; . \tag{7.29}$$

We shall separately 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 (7.29) [Page 161] 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 (7.19) [Page 152] is

$$\tilde{n} = \lambda_1^{-3}\zeta(3/2)T_C^{3/2}$$

Therefore, we get

$$\frac{C_V}{Nk_B} = \underbrace{\frac{15}{4}\frac{\zeta(5/2)}{\zeta(3/2)}}_{=1.925}\left(\frac{T}{T_C}\right)^{3/2}\;. \tag{7.30}$$

As a reminder: In the classical model the result for this was $\frac{C_V}{Nk_B} = \frac{3}{2}$.

B) $\mathbf{T > T_C}$

For $T > T_C$ z also contributes to the derivation

$$\frac{C_V}{Nk_B} = \frac{15}{4\tilde{n}}\underbrace{\lambda_1^{-3}T^{3/2}}_{\lambda_T^{-3}}\,g_{5/2}^1(z) + \frac{3}{2\tilde{n}}\underbrace{\lambda_1^{-3}T^{5/2}}_{=T\lambda_T^{-3}}\,\underbrace{\frac{d}{dz}g_{5/2}^1(z)}_{\overset{(7.6)}{=}g_{3/2}^1(z)\,/z}\,\frac{dz}{dT}\bigg|_{V,N}$$

$$= \frac{15}{4\tilde{n}}\lambda_T^{-3}\,g_{5/2}^1(z) + \frac{3}{2\tilde{n}}T\,\lambda_T^{-3}\,g_{3/2}^1(z)\frac{z'}{z}\;.$$

Using Equation (7.23) [Page 154] $[\tilde{n} = \lambda_T^{-3}g_{3/2}^1(z)]$ this can be simplified even 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 just need z'/z. The fugacity is not only dependent on β, but also on μ. As N has to be constant, μ has to change with temperature. With Equation (7.23) [Page 154], from $n = N/V = const$ again follows

$$0 = \frac{d\tilde{n}}{dT} = \frac{d}{dT}\lambda_T^{-3}g_{3/2}^1(z) = \lambda_1^{-3}\,\frac{d}{dT}T^{3/2}g_{3/2}^1(z)$$

$$= \lambda_1^{-3}\left(\frac{3}{2}T^{1/2}g_{3/2}^1(z) + T^{3/2}\frac{d}{dz}g_{3/2}^1(z)z'\right)$$

$$= \lambda_1^{-3}\left(\frac{3}{2}T^{1/2}g_{3/2}^1(z) + T^{3/2}g_{1/2}^1(z)\,\frac{z'}{z}\right)\;;$$

$$\Rightarrow \qquad \frac{z'}{z} = -\frac{3}{2T}\frac{g_{3/2}^1(z)}{g_{1/2}^1(z)}\;.$$

Thus we have the final result for the

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HEAT CAPACITY

</div>

$$\frac{C_V}{Nk_B} = \begin{cases} \frac{15}{4} \frac{g^1_{5/2}(z)}{g^1_{3/2}(z)} - \frac{9}{4} \frac{g^1_{3/2}(z)}{g^1_{1/2}(z)} & \text{fÃ\frac{1}{4}r } T > T_C \qquad (a) \\ \frac{15}{4} \frac{\zeta(5/2)}{\zeta(3/2)} \left(\frac{T}{T_C}\right)^{3/2} & \text{fÃ\frac{1}{4}r } T \leq T_C \qquad (b) \end{cases} \qquad (7.31)$$

$$\frac{15}{4} \frac{\zeta(5/2)}{\zeta(3/2)} = 1.925 \ .$$

We now want to plot $C_V(T)$ as a function of T. As Equation (7.31) [Page 163] (b) is universally valid for all densities, this is easy for $T < T_C$. For $T > T_c$ we use the following approach: As we have already used on several occasions, for a predefined (fixed) density

$$\tilde{n} = \lambda_1^{-3} T^{3/2} g^1_{3/2}(z) \ .$$

is valid. This formula is valid for all $T \geq T_C$. We now specially choose $T = T_C$. In this case we have $z = 1$ and thus get

$$\tilde{n} = \lambda_1^{-3} T_C^{3/2} g^1_{3/2}(1) \ .$$

Dividing the two equations yields

$$1 = \left(\frac{T}{T_C}\right)^{3/2} \frac{g^1_{3/2}(z)}{\zeta(3/2)} \ ; \qquad \Rightarrow \frac{T}{T_C} = \left[\frac{g^1_{3/2}(z)}{\zeta(3/2)}\right]^{-2/3} \ . \qquad (7.32)$$

We shall rewrite this for the case $z \ll 1$ for later use.

$$g^1_{3/2}(z) = \zeta(3/2) \left(\frac{T}{T_C}\right)^{-3/2} \ ;$$

$$z \ll 1 \ \Rightarrow \qquad z = \zeta(3/2) \left(\frac{T}{T_C}\right)^{-3/2} \ . \qquad (7.33)$$

In order to plot the specific heat for $T \geq T_C$ we use the following approach: We predefine a value $z \in (0, 1)$. From Equation (7.32) [Page 163] we then calculate the corresponding temperature and evaluate C_V for z and this temperature. For the limit $T \to \infty$ or respectively $\beta \to 0$ we get $z \to 0$. For
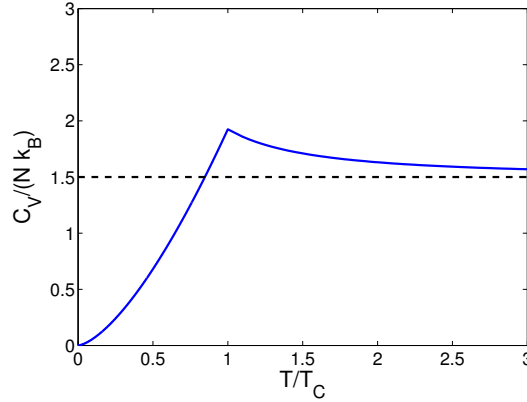
Figure 7.7: Heat capacity of the ideal Bose gas. Dashed line: Classical result

small values of z $g_l(z) \approx z$ applies and therefore in this limit we get

$$\frac{C_V}{Nk_B} \xrightarrow[T\to\infty]{} \frac{15}{4} - \frac{9}{4} = \frac{3}{2}.$$

As it should be, this is the classical result for the ideal gas for which $U = \frac{3}{2}Nk_BT$ applies.

The specific heat depicted in Figure **??** is similar to that of ^{4}He. However the latter diverges at T_C.

7.2.6 Entropy and latent heat

Starting from

$$\frac{\Omega(Z(V,\mu,T))}{Vk_BM_S} = -T\lambda_T^{-3}g_{5/2}^1(z) + \frac{1}{V}\ln(1-z)$$

$$= -T^{5/2}\lambda_1^{-3}g_{5/2}^1(z) + \frac{1}{V}\ln(1-z)$$

we calculate the entropy via $S = -\frac{\partial\Omega}{\partial T}\big|_{\mu,V}$

$$\frac{S}{Vk_BM_S} = \frac{\partial}{\partial T}\left(T^{5/2}\lambda_1^{-3}g_{5/2}^1(z)\right)\bigg|_{\mu,V} - \frac{\partial}{\partial T}\left(\frac{T}{V}\ln(1-z)\right)\bigg|_{\mu,V}$$

$$= \frac{\partial}{\partial T}\left(T^{5/2}\lambda_1^{-3}g_{5/2}^1(z)\right)\bigg|_{\mu,V} - \frac{1}{V}\ln(1-z). \qquad (7.34)$$

Considering the thermodynamic limit, we see the last term in Equation (7.34) [Page 164] vanish: For $T > T_C$ we have $z < 1$. Then it vanishes with $1/V$. For $T \leq T_C$ $z = 1 + O(V^{-1})$ applies and the correction term develops like

$\ln [V]/V \to 0$. However this also means that 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 (7.34) [Page 164] remains.

$$\frac{S}{Vk_BM_S} = \frac{\partial}{\partial T}\left(T^{5/2}\lambda_1^{-3}g_{5/2}^1(z)\right)\bigg|_{\mu,V} .$$ (7.35)

Again, we discuss the two temperature ranges sepertately.

A) $\mathbf{T < T_C}$

In the thermodynamic limit we here have $z = 1$, which is independent of T. With that we get

$$\frac{S}{Vk_BM_S} = \frac{5}{2}T^{3/2}\lambda_1^{-3}g_{5/2}^1(1) = \frac{5}{2}\lambda_T^{-3}\zeta(5/2) ,$$ (7.36)

or

$$\frac{S}{k_B} = V\ M_S\ \lambda_T^{-3} \cdot \ \frac{5}{2}\zeta(5/2) .$$

From Equation (7.22) [Page 153] we know that in the condensate the density of particles in the regular phase is $n_n = M_S\lambda_T^{-3}\zeta(3/2)$. Thus applies

$$\frac{S}{k_B} = \frac{5}{2}\frac{\zeta(5/2)}{\zeta(3/2)} \cdot N_n(T) ,$$

with $N_n(T)$ as 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 condensated state and one in the regular state is

$$\frac{\Delta S}{N_n} = \frac{5}{2}\frac{\zeta(5/2)}{\zeta(3/2)}\ k_B .$$

From this one gets the

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Latent heat
(*per particle*)

</div>

$$L := T\frac{\Delta S}{N} = \frac{5}{2} \frac{\zeta(5/2)}{\zeta(3/2)} \; k_B T \; . \tag{7.37}$$

</div>

This is the energy, which is emitted when a **normal particle** is converted to a **condensate particle**.

Thus we get a **mixed phase**, in which two phases coexist, as they do in a **phase transition of the first order** (for example water $\leftrightarrow$ ice)

B) Clausius-Clapeyron equation

In the zone of coexistence of a phase transition of the first oder the Clausius-Clapeyron equation should be valid. For this we need the derivation of the vapour pressure with respect to the temperature. With the vapour pressure from Equation (7.27) [Page 155] 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 (7.18) [Page 152]

$$n_C = M_S\lambda_T^{-3}\zeta(3/2)$$

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 using Equation (7.37) [Page 166] this can be rewritten to

$$\frac{dp_C(T)}{dT} = \frac{L}{T} \; n_C \; .$$

Eventually we need the difference between the specific volumes and both coexisting phases.

$$\Delta v = v_C - 0 = \frac{1}{n_C} \; .$$

Thus we indeed get the

CLAUSIUS-CLAPEYRON EQUATION
(for ideal Bosons)

$$\frac{dp_C(T)}{dT} = \frac{L}{T\Delta v} \ .$$

C) Finally we will now consider the temperature range $T > T_C$

Above T_C we have $z < 1$. The fugacity also contributes to the derivative in Equation (7.34) [Page 164].

$$
\begin{aligned}
\frac{S}{Vk_BM_S} &= \frac{\partial}{\partial T}\left(T^{5/2}\ \lambda_1^{-3}g_{5/2}^1(z)\right) \\
&= \frac{5}{2}\lambda_T^{-3}g_{5/2}^1(z) + \lambda_1^{-3}\ T^{5/2}\underbrace{\left(\frac{d}{dz}g_{5/2}^1(z)\right)}_{\overset{(7.6)}{=}=g_{3/2}^1(z)\ /z}\frac{dz}{dT} \\
&= \frac{5}{2}\lambda_T^{-3}g_{5/2}^1(z) + \lambda_T^{-3}\ T\ g_{3/2}(z)z^{-1}\ z\frac{(-\mu)}{k_BT^2} \\
&= \frac{5}{2}\lambda_T^{-3}g_{5/2}^1(z) + \underbrace{\lambda_T^{-3}g_{3/2}(z)}_{\tilde n}\frac{(-\mu T)}{k_BT^2} \\
&= \frac{5}{2}\lambda_T^{-3}g_{5/2}^1(z) - \beta\mu\tilde n\ .
\end{aligned}
$$

Comparing this result with the result for the condensate phase from Equation (7.36) [Page 165] we get

$$
\frac{S}{Vk_BM_S} = \begin{cases} \frac{5}{2}\lambda_T^{-3}g_{5/2}^1(1) & \text{fÃ}\frac{1}{4}\text{r } T \le T_C \\ \frac{5}{2}\lambda_T^{-3}g_{5/2}^1(z) - \beta\mu\tilde n & \text{fÃ}\frac{1}{4}\text{r } T > T_C \end{cases}
$$

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 heat. For $T \leq T_C$ 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 (7.19) [Page 152].

$$T_C^{-3/2} := \left\{ \left(\frac{\tilde{n}}{\Lambda}\right)^{2/3} \right\}^{-3/2} = \frac{\Lambda}{\tilde{n}} = \frac{\lambda_1^{-3}\zeta(3/2)}{\tilde{n}}$$

$$\Rightarrow \qquad \lambda_1^{-3} = \frac{\tilde{n}\,T_C^{-3/2}}{\zeta(3/2)} \; .$$

Thus the following is also valid:

$$\frac{S}{Vk_BM_S} = \tilde{n}\,\frac{5}{2}\,\frac{\zeta(5/2)}{\zeta(3/2)}\left(\frac{T}{T_C}\right)^{3/2} \; .$$

For the zone $T > T_C$ we predefine one allowed value for the fugacity ($z \in (0,1)$). Via Equation (7.32) [Page 163] we also assign the fugacity

$$\frac{T}{T_C} = \left[\frac{g_{3/2}^1(z)}{\zeta(3/2)}\right]^{-2/3} \tag{7.38}$$

to the temperature T/T_C that we use as the value of the abscissa in the plot. Furthermore, we eliminate the thermical de Broglie wavelength from the expression for the entropy

$$\frac{S}{Vk_BM_S} = \frac{5}{2}\lambda_T^{-3}g_{5/2}^1(z) - \ln[z]\tilde{n}$$

For $T > T_C$

$$\tilde{n} = \lambda_T^{-3}g_{3/2}^1(z) \Rightarrow \qquad \lambda_T^{-3} = \frac{\tilde{n}}{g_{3/2}^1(z)} \; .$$

applies according to Equation (7.23) [Page 154]. Thus, the expression for the entropy contains only the fugacity and the density.

$$\frac{S}{V k_B M_S} = \tilde{n} \left(\frac{5}{2} \frac{g^1_{5/2}(z)}{g^1_{3/2}(z)} - \ln [z] \right) ; \qquad (7.39)$$

$$\text{resp.} \qquad \frac{S}{N k_B M_S} = \frac{5}{2} \frac{g^1_{5/2}(z)}{g^1_{3/2}(z)} - \ln [z] . \qquad (7.40)$$

Having calculated the ratio T/T_C for a predefined z, we can easily evaluate this formula. The resulting graph is depicted in Figure 7.8.
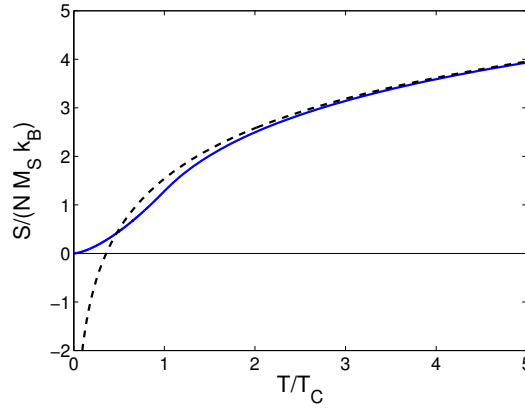

Figure 7.8: Entropy of an ideal Bose gas. Dashed line: classical result

Again, the comparison with the classical result for this is interesting. To this end we again assume that we have high temperatures. Thus we have $z \ll 1$. We also use the fact that we have $g^1_l(z) \approx 1$. We replace the argument of the logarithm in Equation (7.40) [Page 169] – z – according to Equation (7.33) [Page 163] with $\zeta(3/2)(T/T_C)^{-3/2}$ and therefore get

$$\frac{S}{V k_B M_S} = \frac{5}{2} + \frac{3}{2} \ln \left[\frac{T}{T_C} \right] - \ln [\zeta(3/2)] . \qquad (7.41)$$

Via Equation (7.21) [Page 152] we can now replace the combination of parameters $\tilde{n} \lambda_1^3$ with $\zeta(3/2) T_C^{3/2}$. This enables us to use the unit of temperature T_C (from the quantum mechanical calculation) in the classical case, even though in the classical case there is no phase transition. Thus we get

$$\frac{S}{N k_B M_S} = \frac{5}{2} + \frac{3}{2} \ln \left[\frac{T}{T_C} \right] - \ln [\zeta(3/2)] .$$

This is in agreement with the upper limit of the quantum mechanical result in Equation (7.41) [Page 169].

For the plot of the classical results we of course directly predefine T/T_C and not z.

In Figure 7.8 we also see that the quantum mechanical result approaches the classical result for $T/T_C > 1$. We also realise that the the classical result becomes invalid for low temperatures and that it has a diverging entropy. In contrast to the classical, the quantum mechanical result is in accord with the third law of thermodynamics. There the entropy goes to 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 an suprafluidity has already led to two Nobel prices:

- 2003: Alexei Abrikossow, Witali Ginsburg, Anthony James Leggett **for groundbreakin work on the theory of superconductors and suprafluids**.

- 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 suprafluid helium (He II). Those two phases are separated by the so called lambda phase transition, which is located at approximately $T = 2.2K$. The designation originates from the fact, that the
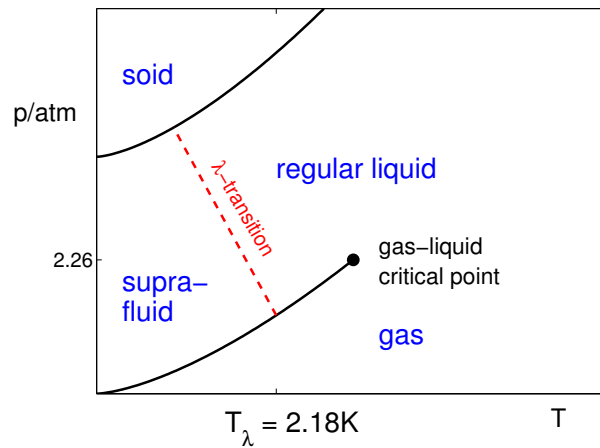

Figure 7.9: Phase diagram of ^{4}He.

temperature gradient of the heat capacity looks somewhat similar to the greek letter λ at T_C. Experimentally, one finds a logarithmic divergence at 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 with 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 supraflid 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 suprafluid phase having no entropy is the same.

However, there also is the following to consider:

- ^{3}He also becomes suprafluid for low temperatures. However, here we have a system of Fermions, for which there is no Bose-Einstein condensation in its basic form.

- The λ transition is no phase transition of the first order 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 suprafluid. One can even show that suprafluidity 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 an enclosed, laser cooled, diluted atomic gas. Because of their magnetic field, 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 apply, are used.

- All atoms have a magnetic moment, which is essential for magnetic enclosure.

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 traps the atoms within a parabolic potential. This means, that they are harmonic oscillators. 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 thermically occupied levels is $\nu_{max} = \frac{k_B T}{\hbar\omega}$ without BEC. Thus, the dimensions without BEC would be

$$R_T = \sqrt{\frac{k_B T}{\hbar\omega}}\, a_0 \gg a_0 \ .$$

Fherefore, for $T > T_C$ one 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} atoms 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 $n = (10^{11} - 10^{15})\mathrm{cm}^{-3}$ (instead of 10^{24}).

The magnetic field that is used for this creates a harmonic potential, which we shall – for the sake of simplicity – assume to be isotropic.

$$V(\vec{x}) = \frac{m\omega^2}{2}\vec{x}^{\,2} \ .$$

With this 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 similay to how it was for free Bosons. For condensation to occur, the fugacity has to be $z = 1$ in the thermodynamic limit, as only then we have $n_0 > 0$. 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 134] without special treatment of the ε_0-term.

$$N_n(T_C, z = 1) = \sum_{l_1,..,l_d=0}^{\infty} \frac{1}{e^{\beta_C \hbar \omega \sum_i l_i} - 1} \; .$$

As the calculation of the density of states is a bit more elaborate, we shall use another method, which uses the summation formula from Appendix (E) [Page 205]. 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 208] we convert the sum into an integral.

$$\tilde{N} \overset{!}{=} \left(\frac{k_B T_C}{\hbar\omega} \right)^d \int_0^{\infty} \cdots \int_0^{\infty} \frac{1}{e^{\sum_i x_i} - 1} d^d x \; . \tag{7.42}$$

The relative uncertainty for this is – according to Appendix (E) [Page 205] – of the order

$$\delta = \frac{\hbar\omega}{k_B T_C} \; . \tag{7.43}$$

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 for the approximation of the sum with the simple integral. We shall now calculate the integral from Equation (7.42) [Page 173].

$$\begin{aligned}
\tilde{N} &= \left(\frac{k_B T_C}{\hbar\omega} \right)^d \int_0^{\infty} \cdots \int_0^{\infty} \frac{e^{-\sum_l x_i}}{1 - e^{-\sum_l x_i}} \, d^d x \\
&= \left(\frac{k_B T_C}{\hbar\omega} \right)^d \sum_{m=0}^{\infty} \int_0^{\infty} \cdots \int_0^{\infty} e^{-(m+1)\sum_l x_l} \, d^d x \\
&= \left(\frac{k_B T_C}{\hbar\omega} \right)^d \sum_{m=0}^{\infty} \left(\int_0^{\infty} e^{-(m+1)\, x} \, dx \right)^d \\
&= \left(\frac{k_B T_C}{\hbar\omega} \right)^d \sum_{m=0}^{\infty} \left(\frac{1}{m+1} \right)^d \; .
\end{aligned}$$

Thus, the searched-after result is:

TRANSITION TEMPERATURE FOR BEC IN A HARMONIC TRAP

$$\tilde{N} = \left(\frac{k_B T_C}{\hbar\omega} \right)^d \zeta(d) \ . \tag{7.44}$$

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 microkelvin. Of course this is a crude estimate, as the interaction between particles was nelected. The values, however, are of the right order of magnitude.

Equation (7.44) [Page 174] makes it seem like as if, because of the changed enclosure potential there was a different universal power law[2] at work for T_C than for Equation (7.19) [Page 152]. 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 (7.44) [Page 174] 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 oscillators 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 extent at the temperature T_C. The corresponding thermodynamic expectation value for r^2 yields

$$\langle r^2 \rangle_{T_C} = 3a_0^2 \langle n \rangle_{T_C} = \frac{3a_0^2}{e^{\beta\hbar\omega} - 1} \overset{\beta_C \hbar\omega \ll 1}{=} \frac{3a_0^2 k_B T_C}{\hbar\omega} \ .$$

---

[2]This is insofar surprising, as the power is independent of the curvature of the potential.

In the end we thus get the average volume for 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 (7.44) [Page 174], 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 changed.

7.2.9   Why does BEC only occur in quantum systems?

The reason for this is the indistinguishability of the particles. Once more we shall 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 $0, \dots, \infty$. However, for the (micro-) canonical ensemble the condition for the number of particles has to 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 and the Boltzmann factor together yield

$$P(\{n_i\}) = \frac{1}{Z} \frac{N!}{\prod_i n_i!} e^{-\beta E(\{n_i\})} \ .$$

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 can be simplified to

$$P(\{n_i\}) = \frac{N!}{\prod_i n_i!} L^{-N} \ .$$

We assume 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 an equal distribution with

$$m := \frac{N}{L}$$

particles per single-particle level. Now we calculate the ratio of the probability of the equal distribution and 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 implementation we shall discuss thermal radiation. An example for thermal radiation is infrared 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 heatsource 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 electromagnetic 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 where they form a 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 reservoires of photons.

For photons, conservation of particles does not apply (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. As in the following case N is variable,

$$\left(\frac{\partial F(T, N, V)}{\partial N} \right) \Bigg|_{T,V} = 0 \ ,$$

has to apply. On the other hand, the left side of this equation is – per definition – the cemical potential. Thus applies in the case that there is no conservation of particles

$$\mu = 0 \ ;$$
$$F = \Omega \ .$$

The photons in the cavity interact with the atoms in the walls. With that, 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 wave numbers

$$k_\alpha = \frac{\pi}{L_\alpha} l_\alpha \ , \tag{7.45}$$

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 taken from Equation (F.1) [Page 210] in Appendix (F.2) [Page 210].

Now we 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)

$$\rho(\varepsilon) = C_{ph} \, \varepsilon^2 \; ; \tag{7.46}$$

$$F_\rho(\varepsilon) = \frac{C_{ph}}{3} \, \varepsilon^3 \; ; \tag{7.47}$$

$$C_{ph} = \frac{V}{\pi^2 (\hbar c)^3} \; . \tag{7.48}$$

7.3.2 Grand canonical potential

Using Equation (6.11) [Page 136] and Equation (6.14) [Page 137], 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

$$\Omega(T, V) \stackrel{(7.47)}{=} -\frac{V}{3\pi^2 \, (\hbar c)^3} \int_0^\infty \frac{1}{e^{\beta\varepsilon} - 1} \varepsilon^4 \, \frac{d\varepsilon}{\varepsilon}$$

$$\stackrel{(G.4)}{=} -\frac{V}{3\pi^2 \, (\hbar c)^3} \, (k_B T)^4 \zeta(4) \Gamma(4) \; . \tag{7.49}$$

With $\zeta(4) = \pi^4/90$ and $\Gamma(4) = 6$ we finally get

$$\Omega(T, V) = -\frac{V\pi^2}{45} \frac{(k_B T)^4}{(\hbar c)^3} \; .$$

GRAND CANONICAL POTENTIAL

$$\Omega(T,V) = -V\,\frac{\alpha}{3}\,T^4 \ ; \tag{7.50}$$

$$\alpha := \frac{\pi^2}{15}\frac{(k_B)^4}{(\hbar c)^3} \ ; \qquad \text{(Stefan-Boltzmann constant)} . \tag{7.51}$$

7.3.3   Radiation pressure

From Equation (7.50) [Page 180] we can immediately read off the radiation pressure.

RADIATION PRESSURE

$$p = -\Omega/V = \frac{\alpha}{3}\,T^4 \ .$$

7.3.4   Entropy

The entropy can also be derived from the grand canonical potential with ease.

$$S(T,V) = -\left(\frac{\partial\Omega}{\partial T}\right)\bigg|_V .$$

It is sufficiently consistent with the formula

ENTROPY

$$S(T,V) = \frac{4\alpha}{3}VT^3$$

7.3.5   Spectral emittance (Planck's law of radiation)

According to Equation (6.12) [Page 136] 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 emittance is this average energy per unit of volume and thus

$$S(\varepsilon) = \frac{1}{V} \, \rho(\varepsilon) \, \varepsilon \, \langle n_\varepsilon \rangle_{T,\mu} \tag{7.52}$$

This 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 (7.52) [Page 181]. In the case of the spectral emittance 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 emittance, i.e. the average energy per unit of volume that is emitted in the form of quanta of energy ε, together with the density of states from Equation (7.48) [Page 179] gives

---

PLANCK'S LAW OF RADIATION

$$S(\varepsilon, T) d\varepsilon = \frac{\varepsilon^3}{\pi^2 (\hbar c)^3} \, \frac{1}{e^{\beta \varepsilon} - 1} \, d\varepsilon \; ; \tag{7.53}$$

$$S(\omega, T) d\omega = \frac{\hbar \omega^3}{\pi^2 \, c^3} \, \frac{1}{e^{\beta \hbar \omega} - 1} \, d\omega \; .$$

Now we shall consider the two border cases $\hbar \omega \gg k_B T$ and $\hbar \omega \ll k_B T$, which are of historical importance. For the first case we get the

---

WIEN APPROXIMATION

$$S(\omega, T)d\omega = \frac{\hbar\omega^3}{\pi^2 \, c^3} \, e^{-\beta\hbar\omega} \, d\omega \; ; \qquad \text{for} \ \ \hbar\omega \gg k_B T \, .$$

---

and for the second case the

CLASSICAL RAYLEIGHT-JEANS FORMULA

$$S(\omega, T)d\omega = \frac{\omega^2 k_B T}{\pi^2 \, c^3} \; ; \qquad \text{fÃ}\frac{1}{4}\text{r} \ \hbar\omega \ll k_B T \, .$$

7.3.6   Internal energy and average number of particles

Now we actually calculate the internal energy. For this we only have to integrate Planck's law (Equation (7.53) [Page 181]) 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 (7.49) [Page 179]. The expression we have here differs only by a factor (-3). Therefore we have:

INTERNAL ENERGY

$$U = -3\Omega = V\alpha T^4 \; ; \qquad \text{(Stefan-Boltzmann law)} \, .$$

Average number of particles

Finally, according to Equation (6.13) [Page 136], the average number of particles is

$$
\begin{aligned}
\langle N \rangle &= \int \frac{1}{e^{\beta\varepsilon} - 1} \, \rho(\varepsilon)d\varepsilon \\
&\overset{(G.4)}{=} C_{ph} \int \frac{1}{e^{\beta\varepsilon} - 1} \, \varepsilon^3 \frac{d\varepsilon}{\varepsilon} \\
&= C_{ph} \, (k_B T)^3 \, \zeta(3) \, \Gamma(3) \\
&\overset{(7.48)}{=} \frac{V \, 2}{\pi^2 (\hbar c)^3} \, (k_B T)^3 \, \zeta(3) \; .
\end{aligned}
$$

AVERAGE NUMBER OF PARTICLES
(*of 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 themperature we get

$$
\langle N \rangle \approx 5 \cdot 10^8 \; .
$$

within $1cm^3$.

7.4 Work, heat and entropy

Here we will discuss the change of state for an ideal gas, for which we know that in the thermic equilibrium and in d spatial dimensions, the energy is given by

$$E = \frac{d}{2} N k_B T \ . \tag{7.54}$$

The following equation of state also applies:

$$pV = N k_B T \ .$$

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. Now we shall derive this relation.
We consider an ideal gas inside a cuboid-shaped box. One of the walls shall be movable perpendicular to its plane. This direction shall be defined as the x-direction. Now we shall move the piston with a very small but constant velocity u, thusly reducing the volume of the box adiabatically. A particle shall move in the direction of the piston. The x-component of its velocity is v_x. We quickly switch to the frame of reference 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 the velocity

$$\tilde{v}'_x = -v_x - u \ .$$

Transforming this velocity into the original frame of reference we get

$$v'_x = -v_x - 2u \ .$$

The transfer of momentum caused by the collision with the static piston is

$$\Delta P_x = -2m v_x \ .$$

The number of particles that collide with the wall in the time dt is

$$dN = \rho A v_x dt \ ,$$

However, these are only the ones with a positive v_x. A is the surface of the piston. The average momentum transfer in the time dt yields – when divided by the time

$$F_x = \frac{d}{dt} P_x^{\text{ges}} = -2m A \langle v_x^2 \rangle' \rho \ .$$

One should note that for the averaging $\langle \cdot \rangle'$ only the part of the velocity distribution with $v_x > 0$ is used. Thus $\langle v_x \rangle'$ is nonzero. However, $\langle v_x^2 \rangle' = \langle v_x^2 \rangle$ applies. According to Newton's law the force F_x that affects the piston is also the force, which is transferred to the particles. The elastic collisions with the wall therefore create the pressure

$$p = \frac{|F_x|}{A} = 2m\langle v_x^2 \rangle' \rho = m\langle v_x^2 \rangle \rho \; . \qquad (7.55)$$

In the second step we introduced the total velocity distribution. Furthermore, the ideal gas law applies:

$$m\langle v_x^2 \rangle \rho = 2\langle \left(\frac{m}{2} v_x^2 \right) \rangle \frac{N}{V}$$
$$= 2\frac{E_{kin,x}}{V} = 2\frac{Nk_BT}{2V}$$
$$\Rightarrow \quad pV = Nk_BT \; .$$

applies, which is the ideal gas law. Now we will discuss the extra term we get from the movement of the piston. As a consequence of the collision, the cinetic energy of a particle changes according to

$$\Delta E_{kin,x} = \frac{m}{2}\left(\left(v_x + u \right)^2 - v_x^2 \right)$$
$$= 2mv_xu + O(u^2) \; .$$

Because the movement of the piston shall be adiabatic, we can neglect $O(u^2)$. Multiplying this with the number of particles, which collide with the wall in the time interval dt we get

$$dE_{kin,x} = \rho Av_x dt(2mv_x u)$$
$$= 2m\rho v_x^2 \, A \, u \, dt$$

Now $udt = -dx$ is the distance that the piston moves in dt, thereby decreasing the volume. We now plug in Equation (7.55) [Page 185] and finally get

$$d\langle E_{kin,x} \rangle = -pdV$$

This is the microscopic derivation of the formula, which we had already derived macroscopically. The ideal gas has only cinetic energy. The change in its energy that is caused by the work of the piston therefore is

$$dE = -pdV = -dW \; .$$

This is the connection 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 $dW > 0$:

$$dW = pdV = \begin{cases} > 0 & \text{wenn } dV > 0 \\ < 0 & \text{wenn } dV < 0 \end{cases} .$$

With the work of the piston, the energy changes. As for the ideal gas it is dependent only on T – N is constant – we get

$$dE = \frac{3}{2}Nk_B \, dT = -pdV .$$

Now we shall work out the relation between T and V. To this end we substitute p with Nk_BT/V and get

$$\frac{3}{2}Nk_B \, dT = -\frac{Nk_BT}{V} \, dV$$
$$\frac{dT}{T} = -\frac{2}{3}\frac{dV}{V}$$
$$\ln(T) = C + \ln\left(V^{-2/3}\right)$$
$$T \propto V^{-2/3} .$$

Applying that to a reference state (T_0, V_0)

$$\frac{T}{T_0} = \left(\frac{V}{V_0}\right)^{-2/3}$$

follows. Finally we will derive the relation of pressure and volume for adiabatic changes in the volume. For that purpose we use the ideal gas law and substitute the temperature on the left side of the last equation by

$$T = \frac{pV}{Nk_B} .$$

Thus

$$\frac{T}{T_0} = \frac{p}{p_0}\frac{V}{V_0} = \left(\frac{V}{V_0}\right)^{-2/3}$$

$$\frac{p}{p_0} = \left(\frac{V}{V_0}\right)^{-5/3} \tag{7.56}$$

follows. This means $p \propto V^{-5/3}$.

Next we consider a isothermal change of state. For this, the temperature shall remain constant. This is possible only when coupled to a heat bath. If the temperature of the ideal gas does not change, because of the equation of state we get

$$d(pV) = d(Nk_BT) = 0$$
$$\Rightarrow \quad pdV = -Vdp$$
$$\frac{dV}{V} = -\frac{dp}{p} \ .$$

This gives

$$\frac{p}{p_0} = \left(\frac{V}{V_0}\right)^{-1}$$

In this case, the change in pressure is smaller than for adiabatic compression. The behaviour is to be understood as such: At first the particles gain cinetic energy because of the work of the piston, but then it is passed on to the heat bath. The increase in cinetic energy in the case of adiabatic compression leads to an additional contribution to the pressure.

Now all of the additional cinetic energy shall be transmitted to the heat bath. Such a change in energy, which is not dependent on work is called heat. Heat transport generally is the transport of energy due to temperature differences between different thermodynamic subsystems. This transferred energy is called heat. One differentiates between three types of transport:

1. Heat transport (which was discussed just now)

2. Thermal radiation. This follows from radiation (see black-body radiation)

3. Convection. A circulating fluid (gas) transports energ from a warmer region to a colder one. There it loses cinetic energy and then returns to the warmer region.

Now we continue with the ideal gas. The (cinetic) energy of the system does not change for constant T. Therefore

$$dE = dQ - dW \qquad (7.57)$$

applies. Here dE is the change in the total energy of the system and dQ is the heat the system absorbs. If dQ is positive, heat is emitted. Otherwise, heat is absorbed. Later we will define the term more rigorously. dW is the work that the system perfoms, or is performed within 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 haver $dQ = 0$ as the system is isolated. Then

$$dE = -dW = -pdV$$

applies. Then we rearrange Equation (7.57) into the form

$$dQ = dE + dW \ .$$

With this we can understand the change in the heat of the gas to be the difference between the energy change in the system – which is defined by the energy – and the work performed by the gas.

The heat transfer to the bath can also be understood as microscopic work of fluctuating forces. For this we can picture the impenetrable walls of the container as a thin elastic foil of uniform density. This wall is surrounded by particles belonging to the bath. If a particle of the system collides with this wall, it creates waves (phonons) that disperse the energy of the scattering particle. At some point, however, a particle of the bath will collide with the

wall in a suitable way. In doing so it collides with the wave, wich causes the wave to loose energy and the bath particle to gain energy. Unlike how it was for the collision with the moving piston, those force transfers fluctuate. On a microscopic level we are just dealing with mechanical forces, however, they fluctuate. In contrast to the work of the piston, those forces cannot be controlled anymore. Heat is then the average work of those fluctuating forces.

7.4.1   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 no fragmentation with respect to the influences of E_n, dV and dT, but with respect to wheter P_n does or does not change. Otherwise, with $P_n = e^{-\beta E_n}/Z$, changing E_n would also lead to a change in P_n. I.e. if we do not change V and therefore E_n, in dE_1 P_n is still assumed to remain constant. This is, for example, achieved by simultaneously changing the temperature. In quantum mechanics this corresponds to the expression for the eigenbasis of $\hat{H}$. We still observe an ideal gas. The (self-)energies change with the volume only if we have

$$dE_1 = \sum_n P_n \frac{dE_n}{dV} dV$$

The change of the eigenvalues of $\hat{H}$ with changing volume has to be

$$dE_n = \frac{dE_n}{dV} dV = \underbrace{\frac{dE_n}{dV}}_{=K_n} A \, dx \ .$$

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 walls. For the states being occupied with a probability of P_n,

$$\sum_n P_n p_n$$

corresponds to the average pressure p. Therefore

$$dE_1 = \sum_n P_n dE_n$$
$$= -pdV = -dW$$

is valid and with that, because of $dE = dQ - dW$ we should get

$$dQ = \sum_n dP_n E_n \ .$$

At least this is consistent with the adiabatic changes. Adiabatic meaning that the canges 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

$$P_n = \frac{e^{-\beta E_n}}{Z}$$
$$\ln(P_n) = -\beta E_n - \ln(Z)$$

Thus we get

$$dS = -k_B \sum_n dP_n \big(-\beta E_n - \ln(Z) \big)$$

$$= \frac{1}{T} \sum_n dP_n E_n + k_B \ln(Z) \underbrace{\sum_n dP_n}_{=0}$$

$$TdS = \sum_n dP_n E_n = dE_2 = dQ \ .$$

With that the following connection between heat transfer and changes in entropy can be found:

$$dQ = T dS$$

or

$$dS = \frac{dQ}{T} \; .$$

Those relations apply only for irreversible 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 shall be derived.

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

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 192] with x^m and sum over m. For interchanging sum and derivative the left 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 took into consideration that $\Phi(x, t)$ is a function of two variables and that, therefore, we have only one partial derivative. If the same

operations are performed on the right side we get

$$\frac{\partial}{\partial t}\Phi(x,t) = (\lambda_2 - \lambda_1) \underbrace{\sum_{m=0}^{N} P(\mathcal{N}_1^{(t)} = m)\, x^m\, m}_{=x\frac{\partial}{\partial x}\Phi(x,t)} - \lambda_2 N \underbrace{\sum_{m=0}^{N} P(\mathcal{N}_1^{(t)} = m)\, x^m}_{=\Phi(x,t)}$$

$$+ \lambda_1 \sum_{m=0}^{N-1} P(\mathcal{N}_1^{(t)} = m+1)\, x^m\, (m+1) + \lambda_2 N \sum_{m=1}^{N} P(\mathcal{N}_1^{(t)} = m-1)\, x^m$$

$$- \lambda_2 \sum_{m=1}^{N} P(\mathcal{N}_1^{(t)} = m-1)\, x^m (m-1)\ .$$

Here we used the fact that we have $P(\mathcal{N}_1^{(t)} = 0) = 0$ and $P(\mathcal{N}_1^{(t)} = N+1) = 0$. 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 do compensate each other.

$$\frac{\partial}{\partial t}\Phi(x,t) = (\lambda_2 - \lambda_1)\, x\frac{\partial}{\partial x}\Phi(x,t) - \lambda_2 N\Phi(x,t)$$

$$+ \lambda_1 \underbrace{\sum_{n=0}^{N} P(\mathcal{N}_1^{(t)} = n)\, x^{n-1}\, n}_{\frac{\partial}{\partial x}\Phi(x,t)}$$

$$+ \lambda_2 N \underbrace{\sum_{n=0}^{N} P(\mathcal{N}_1^{(t)} = n)\, x^{n+1}}_{=x\Phi(x,t)} - \lambda_2 \underbrace{\sum_{n=0}^{N} P(\mathcal{N}_1^{(t)} = n)\, x^{n+1} n}_{=x^2\frac{\partial}{\partial x}\Phi(x,t)}\ ;$$

$$\frac{\partial}{\partial t}\Phi(x,t) = (\lambda_2 - \lambda_1)\, x\frac{\partial}{\partial x}\Phi(x,t) - \lambda_2 N\Phi(x,t) + \lambda_1\frac{\partial}{\partial x}\Phi(x,t) + \lambda_2 N x\Phi(x,t) - \lambda_2 x^2\frac{\partial}{\partial x}\Phi(x,t)$$

$$= \frac{\partial}{\partial x}\Phi(x,t)\Big((\lambda_2 - \lambda_1)\, x + \lambda_1 - \lambda_2 x^2\Big) + \Phi(x,t)\Big(-\lambda_2 N + \lambda_2 N x\Big)$$

$$= -\lambda_2\frac{\partial}{\partial x}\Phi(x,t)\Big(x^2 - (1-\frac{\lambda_1}{\lambda_2})\, x - \frac{\lambda_1}{\lambda_2}\Big)\lambda_2 N\Phi(x,t)\Big(x-1\Big)\ .$$

We now define $\tau = \lambda_2 t$ and $q = \frac{\lambda_1}{\lambda_2}$. With that we get

$$\frac{d}{d\tau}\Phi(x,\tau) = -\Phi'(x,\tau)\left(x^2 - (1-q)\,x - q\right) + N\Phi(x,\tau)\left(x - 1\right).$$

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 standardisation, $\Phi(1,t) = 1$, we finally get

$$\Phi(x,\infty) = (1+q)^{-N}\,(x+q)^N$$
$$= \left(\frac{1}{1+q}x + \frac{q}{1+q}\right)^N = \left(\frac{1}{1+q}x + 1 - \frac{1}{1+q}\right)^N.$$

We shall remind ourselves of the generating functional of the binomial distribution

$$P(n|N, q_1, q_2) \longrightarrow \quad \Phi_b(x) = (1 - q_1 + q_1 x)^N\,.$$

Obviously we get $q_1 = \frac{1}{1+q} = \frac{\lambda_2}{\lambda_1+\lambda_2}$. We have already derivated $\lambda_\alpha = c/V_\alpha$. From this follows

$$q_1 = \frac{\frac{1}{V_2}}{\frac{1}{V_1} + \frac{1}{V_2}} = \frac{V_1}{V}$$
$$q_2 = \frac{V_2}{V}\,,$$

and thus the stationary distribution we sought is

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

A.2   Average time until equilibrium

Here we will solve Equation (1.5) [Page 10] in order to determine the average 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 $N = 2N'$.

$$D_n = D_{n+1} - \frac{n}{2N'}\left(D_{n+1} - D_{n-1}\right) + 1 . \qquad (A.2)$$

The series expansion of $D_{n\pm1}$ around n yields

$$D_n = D_n + D'_n + \frac{1}{2}D''_n - \frac{n}{N'}D'_n + 1$$
$$0 = D''_n + 2(1 - \frac{n}{N'})D'_n + 2 . \qquad (A.3)$$

With $G := D'$ we have to solve the linear inhomogenous differential equation of the first order

$$G'_n + 2(1 - \frac{n}{N'})G_n = -2 \qquad (A.4)$$

At first we consider the homogenous differential equation

$$G' = -2(1 - \frac{n}{N'})G$$
$$\frac{dG}{G} = 2\frac{n - N'}{N'} \, dn$$
$$\ln(G) = c + \frac{(n - N')^2}{N'}$$
$$G = ge^{\frac{(n-N')^2}{N'}} .$$

For the inhomogenous differential we let g be dependent on n and thus get

$$G' = G\frac{2(n - N')}{N'} + g'e^{\frac{(n-N')^2}{N'}}$$
$$G' + \frac{2(N' - n)}{N'}G = -2 \quad \Rightarrow \quad g' = -2e^{-\frac{(N'-n)^2}{N'}}$$
$$g = a - 2\int_{-\infty}^{n} e^{-\frac{(N'-t)^2}{N'}} \, dt .$$

for Equation (A.4) [Page 195]. From the substitution

$$\frac{(N'-t)^2}{N'} =: z^2 \; ;$$
$$N' - t = \sqrt{N'}z \; ;$$
$$dt = -\sqrt{N'}dz$$

we get

$$g = a + 2\sqrt{N'} \int_{-\infty}^{\frac{N'-n}{\sqrt{N'}}} e^{-z^2} \, dz = \tilde{a} + 2\sqrt{N'} \int_0^{\frac{N'-n}{\sqrt{N'}}} e^{-z^2} \, dz$$
$$= \tilde{a} + \sqrt{N'\pi} \; \Phi\left(\frac{N-n}{\sqrt{N'}}\right) \; .$$

Thus

$$D'_n = G_n = \left(\tilde{a} + \sqrt{N'\pi} \; \Phi\left(\frac{N'-n}{\sqrt{N'}}\right)\right) e^{\frac{(N'-n)^2}{N'}}$$

is valid for the output variable. Actually we are interested in $n = 0$. For that situation Equation (A.2) [Page 195] is

$$D_0 = D_1 + 1$$
$$D_1 - D_0 = -1$$
$$D'_0 = -1 \; .$$

With these starting conditions we determine the parameter $\tilde{a}$

$$D'_0 = \left(\tilde{a} + \sqrt{N'\pi} \; \Phi\left(\sqrt{N'}\right)\right) e^{N'} = -1$$
$$\tilde{a} = -\sqrt{N'\pi} \; \Phi\left(\sqrt{N'}\right) - e^{-N'} \; .$$

Thus the differential equation becomes

$$D'_n = -\left[e^{\frac{(N'-n)^2}{N'}-N'} + \sqrt{N'\pi}\left(\Phi\left(\sqrt{N'}\right) - \Phi\left(\frac{N'-n}{\sqrt{N'}}\right)\right)e^{\frac{(N'-n)^2}{N'}}\right]$$
$$D_n = C + \int_0^n D'_z dz$$
$$D_{N'} = 0 \; \Rightarrow \quad C = -\int_0^{N'} D'_z dz$$
$$D_n = -\int_n^{N'} D'_z dz \; .$$

The sought after average runtime is

$$D_0 = \int_0^{N'} \left(e^{\frac{(N'-t)^2}{N'} - N'} + \sqrt{N'\pi} \left(\Phi(\sqrt{N'}) - \Phi(\frac{N'-t}{\sqrt{N'}}) \right) e^{\frac{(N'-t)^2}{N'}} \right) dt \ .$$

Again, we use the substitution

$$\frac{(N'-t)^2}{N'} = z^2 \ ; \quad N' - t = \sqrt{N'}z \ ; \quad dt = -\sqrt{N'}dz$$

and get

$$D_0 = \sqrt{N'} \int_0^{\sqrt{N'}} \left(e^{z^2 - N'} + \sqrt{N'\pi} \left(\Phi(\sqrt{N'}) - \Phi(z) \right) e^{z^2} \right) dz \ .$$

When substituting $z = t\sqrt{N'}$, the first summand yields

$$D_0^{(1)} = \sqrt{N'} \int_0^{\sqrt{N'}} e^{z^2 - N'} dn = N' \int_0^1 e^{-N'(1-t^2)} dt$$

$$= \sqrt{N'} DawsonF(\sqrt{N'}) \overset{N' \to \infty}{\longrightarrow} \frac{1}{2} \ .$$

The other summands are

$$D_0^{(2)} = N'\sqrt{\pi} \int_0^{\sqrt{N'}} e^{z^2} \left(\Phi(\sqrt{N'}) - \Phi(z) \right) dz$$

$$= N'\sqrt{\pi} \int_0^{\sqrt{N'}} e^{z^2} \left(\left(\Phi(\sqrt{N'}) - 1 \right) - \left(\Phi(z) - 1 \right) \right) dz$$

$$= -2N' \int_0^{\sqrt{N'}} e^{z^2} \left(\int_{\sqrt{N'}}^\infty e^{-x^2} dx - \int_z^\infty e^{-x^2} dx \right) dz$$

$$= -2N' \int_0^{\sqrt{N'}} e^{z^2} \left(\int_0^\infty e^{-(t+\sqrt{N'})^2} dt - \int_0^\infty e^{-(t+z)^2} dt \right) dz \ . \qquad (A.5)$$

The first term yields

$$T_1 := -2N' \int_0^{\sqrt{N'}} e^{z^2} \int_0^\infty e^{-(t+\sqrt{N'})^2} dt\,dz = -2N' \left(\int_0^{\sqrt{N'}} e^{z^2 - N'} dz \right) \left(\int_0^\infty e^{-t^2 - 2t\sqrt{N'}} dt \right)$$

$$= -2N' \left(\sqrt{N'} \int_0^1 e^{-N'(1-x^2)} dx \right) \left(\int_0^\infty e^{-t^2 - 2t\sqrt{N'}} dt \right)$$

$$= -2 \left(N' \int_0^1 e^{-N'(1-x^2)} dx \right) \left(\sqrt{N'} \int_0^\infty e^{-t^2 - 2t\sqrt{N'}} dt \right)$$

$$= -2 \underbrace{\left(\sqrt{N'} Dawson(\sqrt{N'}) \right)}_{\to 1/2} \underbrace{\left(e^{N'} \sqrt{N'} \frac{\sqrt{\pi}}{2} (1 - \Phi(\sqrt{N'})) \right)}_{\to 1/2} \overset{N' \to \infty}{\longrightarrow} -\frac{1}{2}$$

The second term in Equation (A.5) [Page 197] yields

$$T_2 := 2N' \int_0^{\sqrt{N'}} e^{z^2} \int_0^\infty e^{-(t+z)^2} dtdz = 2N' \int_0^{\sqrt{N'}} \int_0^\infty e^{-t^2 - 2tz} dtdz$$

$$= 2N' \int_0^\infty dt\, e^{-t^2} \int_0^{\sqrt{N'}} e^{-2tz} dz = 2N' \int_0^\infty dt\, e^{-t^2} \frac{1 - e^{-2t\sqrt{N'}}}{2t}$$

$$= N' \int_0^\infty e^{-\frac{t^2}{N'}} \frac{1 - e^{-2t}}{t} \, dt \ .$$

We split the integral in two parts in order to get the divergence under control.

$$T_2 = N' \left(\int_0^\xi e^{-\frac{t^2}{N'}} \frac{1 - e^{-2t}}{t} \, dt \ + \int_\xi^\infty e^{-\frac{t^2}{N'}} \frac{1 - e^{-2t}}{t} \, dt \right) \ .$$

Now we define $1 \ll \xi \ll \sqrt{N'}$ in order to get $t^2/N' \ll 1$ in the first integral. The first integral thus gives

$$\int_0^\xi e^{-\frac{t^2}{N'}} \frac{1 - e^{-2t}}{t} \, dt = \int_0^\xi \frac{1 - e^{-2t}}{t} \, dt$$

$$= \gamma + \ln(2\xi) + \underbrace{\Gamma(0, 2\xi)}_{\ll 1 \ (\text{da } \xi \gg 1)} \ .$$

Here $\gamma = 0.5771$ is the Euler constant and $\Gamma(\nu, x)$ is the incomplete gamma function. The second integral respectively yields

$$\int_\xi^\infty e^{-\frac{t^2}{N'}} \frac{1}{t} \, dt = \frac{1}{2} \int_{\frac{\xi^2}{N'}}^\infty \frac{e^{-z}}{z} \, dz$$

$$= \frac{1}{2} \Gamma(0, \frac{\xi^2}{N'})$$

$$= -\frac{1}{2}(\gamma + \ln(\xi^2/N'))$$

$$= -\frac{\gamma}{2} - \ln(\xi) + \frac{1}{2} \ln(N') \ .$$

With that we have

$$T_2 = N' \left(\frac{\gamma}{2} + \ln(2) + \frac{1}{2} \ln(N') \right)$$

and the final result is

$$
\begin{aligned}
D_0 &= D_0^1 + T_1 + T_2 \\
&= \frac{1}{2} - \frac{1}{2} + N'\left(\frac{\gamma}{2} + \ln(2) + \frac{1}{2}\ln(N')\right) \\
&= N'\left(\frac{\gamma}{2} + \ln(2) + \frac{1}{2}\ln(N')\right) \\
&= \frac{N}{2}\left(\frac{\gamma}{2} + \ln(2) + \frac{1}{2}\ln(\frac{N}{2})\right) \\
&= \frac{N}{4}\left(\underbrace{\gamma + \ln(2)}_{1.27} + \ln(N)\right) .
\end{aligned}
$$

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 $N_1 = N'$ with t rw-steps shall be $n(t)$. The rate of change approximately corresponds to the drifting velocity, namely $P_r - P_l = (1 - \frac{n}{2N'}) - \frac{n}{2N'} = 1 - \frac{n}{N'}$. Therefore we have

$$
\begin{aligned}
\dot{n} &= 1 - \frac{n}{N'} \\
\frac{dn}{1 - \frac{n}{N'}} &= dt \\
n(t=0) &= 0 \\
t &= -N'(\ln(1 - \frac{n}{N'}) = N'(\ln(N') - \ln(N' - n)) .
\end{aligned}
$$

The time until $n = N' - 1$ therefore is $t = N'\ln(N')$.

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

$$\Omega_d = \frac{2 \, \pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2})} \; ; \tag{C.1}$$

$$V_d(R) = R^d \, \frac{\pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2} + 1)} \; ; \tag{C.2}$$

$$= R^d \, \frac{\pi^{\frac{d}{2}}}{(\frac{d}{2})!} \; ; \qquad\qquad (\text{für gerades } d) \; . \tag{C.3}$$

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

$$F(\lambda) := \mathrm{tr}\left\{ \mathrm{e}^{\alpha(\hat{A}+\lambda\hat{B})} \right\} .$$

For this we want to calculate the derivation with respect to λ. As the operators generally do not commute, the exponential function cannot be factorised. 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

$$F(\lambda) = \lim_{M\to\infty} \mathrm{tr}\left\{ \left(\mathrm{e}^{\epsilon\hat{A}}\mathrm{e}^{\epsilon\lambda\hat{B}} \right)^M \right\} = \lim_{M\to\infty} \mathrm{tr}\left\{ \prod_{k=1}^{M} \mathrm{e}^{\epsilon\hat{A}}\mathrm{e}^{\epsilon\lambda\hat{B}} \right\} .$$

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:

$$
\begin{aligned}
\frac{d}{d\lambda}F(\lambda) &= \lim_{M\to\infty} \sum_{l=1}^{M} \mathrm{tr}\left\{ \left[\prod_{k=1}^{l-1} e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}}\right] \left[\frac{d}{d\lambda}e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}}\right] \left[\prod_{k=l+1}^{M} e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}}\right]\right\} \\
&= \lim_{M\to\infty} \sum_{l=1}^{M} \mathrm{tr}\left\{ \left[\prod_{k=1}^{l-1} e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}}\right] \left[e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}}\epsilon\hat{B}\right] \left[\prod_{k=l+1}^{M} e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}}\right]\right\} \\
&= \epsilon \lim_{M\to\infty} \sum_{l=1}^{M} \mathrm{tr}\left\{ \prod_{k=1}^{l} e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}}\left[\hat{B}\right] \prod_{k=l+1}^{M} e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}}\right\}.
\end{aligned}
$$

Because the trace is invariant to cyclical permutation of the factors we get

$$
\begin{aligned}
\frac{d}{d\lambda}F(\lambda) &= \epsilon \lim_{M\to\infty} \sum_{l=1}^{M} \mathrm{tr}\left\{ \hat{B}\left(e^{\epsilon\hat{A}}e^{\epsilon\lambda\hat{B}}\right)^{M}\right\} \\
&= \epsilon \underbrace{\sum_{l=1}^{M}}_{=\frac{\alpha}{M}\ M=\alpha} \mathrm{tr}\left\{ \hat{B}e^{\alpha(\hat{A}+\lambda\hat{B})}\right\}.
\end{aligned}
$$

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

$$
\frac{d}{d\lambda}F(\lambda) = \alpha\,\mathrm{tr}\left\{ \hat{B}e^{\alpha(\hat{A}+\lambda\hat{B})}\right\}.
$$

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:

$$S = \underbrace{\sum_{l_1=N_{1,a}}^{N_{1,b}} \cdots \sum_{l_d=N_{d,a}}^{N_{d,b}}}_{:=\sum_{\vec{l}}} f(\vec{x}_{\vec{l}}) \ ;$$

$$\vec{x}_{\vec{l}} := (\delta_1 l_1, \dots, \delta_d l_d)^T \ ;$$

$$\delta_i \ll 1 \ .$$

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

---

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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)

</div>

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

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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)

</div>

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

---

**SUMMATION FORMULA IN $\mathbb{N}_0^d$**

$$\sum_{\vec{l}} f(\vec{x}_l) = \frac{1}{\Delta V} \int_0^\infty \cdots \int_0^\infty f(\vec{x}) d^d x \cdot \left(1 + O(\delta)\right). \qquad \text{(E.3)}$$

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

$$
\begin{aligned}
F_d(E) &:= M_S \sum_{\vec{l}} \theta\left[\frac{\hbar^2 \vec{k}^2(\vec{l})}{2m} < E\right] \\
&= M_S \frac{V}{(2\pi)^d} \sum_{\vec{l}} \theta\left[\frac{\hbar^2 \vec{k}^2(\vec{l})}{2m} < E\right] \triangle^d k \\
&= \frac{M_S V}{(2\pi)^d} \int \theta\left[E - \frac{\hbar^2 \vec{k}^2}{2m}\right] d^d k \\
&= \frac{M_S V}{(2\pi)^d} V_d\left(R = \sqrt{2mE/\hbar^2}\right) \\
&= \frac{M_S V}{(2\pi)^d} \frac{(2mE)^{\frac{d}{2}}}{\hbar^d} \frac{\pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2}+1)} \\
&= M_S V\left(\frac{2\pi m}{h^2}\right)^{\frac{d}{2}} \frac{2}{d\,\Gamma(\frac{d}{2})} E^{\frac{d}{2}} .
\end{aligned}
$$

We get the density of states by deriving with respect to 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

DISTRIBUTION FUNCTION
(for linear dispersion (3d))

$$\rho(\varepsilon) = C_{ph} \, \varepsilon^2 \, ;$$

$$F(\varepsilon) = \frac{C_{ph}}{3} \, \varepsilon^3 \, ;$$

$$C_{ph} := \frac{V}{2\pi^2 \, \hbar^3 \, c^3} \, .$$

(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 $l > 1$.

$$\frac{d}{dz} g_l^{(\sigma)}(z) = \frac{1}{\Gamma(l)} \int_0^\infty \frac{e^t - \sigma z + \sigma z}{(e^t - \sigma z)^2} t^{l-1} \, dt = \frac{1}{\Gamma(l)} \int_0^\infty \frac{e^t}{(e^t - \sigma z)^2} t^{l-1} \, dt$$

$$= -\frac{1}{\Gamma(l)} \int_0^\infty t^{l-1} \frac{d}{dt} \frac{1}{e^t - \sigma z} dt$$

$$\stackrel{\text{part.Int.}}{=} -\frac{1}{\Gamma(l)} \underbrace{t^{l-1} \frac{1}{e^t - \sigma z} \Big|_0^\infty}_{0} + \frac{(l-1)}{\Gamma(l)} \int_0^\infty t^{l-2} \frac{1}{e^t - \sigma z} dt$$

$$= \frac{1}{\Gamma(l-1)} \int_0^\infty t^{l-2} \frac{1}{e^t - \sigma z} dt = \frac{1}{z} g_{l-1}^\sigma(z) \ M.$$

G.2 Series expansion for the quantum mechanical gamma function

We shall perform a series expansion in z around $z = 0$ for $z \ll 1$.

$$
\begin{aligned}
g_l^\sigma(z) &= \frac{1}{\Gamma(l)} \int_0^\infty t^{l-1} \frac{z}{e^t - \sigma z} dt = \frac{z}{\Gamma(l)} \int_0^\infty e^{-t} t^{l-1} \frac{1}{1 - \sigma z e^{-t}} dt \\
&= \frac{z}{\Gamma(l)} \int_0^\infty e^{-t} t^{l-1} \left(\sum_{n=0}^\infty \left[\sigma z e^{-t} \right]^n \right) dt \\
&= \frac{1}{\Gamma(l)} \sum_{n=0}^\infty z^{n+1} \sigma^n \int_0^\infty e^{-(n+1)t} t^{l-1} dt \\
&= \frac{\sigma}{\Gamma(l)} \sum_{m=1}^\infty [z\sigma]^m \int_0^\infty e^{-mt} t^{l-1} dt \\
&= \frac{\sigma}{\Gamma(l)} \sum_{m=1}^\infty \frac{[z\sigma]^m}{m^l} \underbrace{\int_0^\infty e^{-x} x^{l-1} dx}_{=\Gamma(l)} \ .
\end{aligned}
$$

The result is

SERIES EXPANSION OF $g_l^\sigma(z)$
(in z around z = 0)
$$g_l^\sigma(z) = \sigma \sum_{m=1}^\infty \frac{[z\sigma]^m}{m^l} \qquad \text{(G.1a)}$$
$$= z + \sigma \frac{z^2}{2^l} + \dots \qquad \text{(G.1b)}$$

G.3 Bosonic gamma function

In the case of Bosons ($\sigma = +1$), the series expansion from Equation (G.1) 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:

$$\text{POLYLOGARITHM}$$
$$(\textit{de Jonquière function})$$

$$g_l^{+1}(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^l} \; . \tag{G.3}$$

Especially for $z = 1$ we get

$$\text{BOSONIC GAMMA FUNCTION}$$

$$g_l^{+1}(1) = \sum_{n=1}^{\infty} \frac{1}{n^l} = \zeta(n) \; . \tag{G.4}$$

Here $\zeta(l)$ is the Riemann ζ-function. Some values of the ζ-function that we will need, are

---

$$\text{SPECIAL VALUES OF THE RIEMANN } \zeta\text{-FUNCTION}$$

$$\zeta(1) = \infty \tag{G.5a}$$
$$\zeta(2) = 1.645 \tag{G.5b}$$
$$\zeta(3) = 1.202 \tag{G.5c}$$
$$\zeta(1/2) = \infty \tag{G.5d}$$
$$\zeta(3/2) = 2.612 \tag{G.5e}$$
$$\zeta(5/2) = 1.3415 \; . \tag{G.5f}$$

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

$$\langle n_{\varepsilon_0}\rangle = \frac{1}{e^{-\beta\mu}-1} = \frac{1}{(-\beta\mu)\left[1 + O(|\beta\mu|)\right]} = V\left(\tilde{n} - \tilde{n}_C\right)\left[1 + O(\frac{1}{V})\right] ;$$

$$\langle n_{\varepsilon_{\vec{k}_{\vec{l}}}}\rangle = \frac{1}{e^{\beta(\varepsilon_{\vec{k}_{\vec{l}}}-\mu)}-1} = \frac{1}{\beta(\varepsilon_{\vec{k}_{\vec{l}}}-\mu)}\left[1 + O(\frac{1}{V})\right] ;$$

$$\frac{\langle n_{\varepsilon_0}\rangle}{\langle n_{\varepsilon_{\vec{k}_{\vec{l}}}}\rangle} = \frac{\varepsilon_{\vec{k}_{\vec{l}}}-\mu}{-\mu}\left[1 + O(\frac{1}{V})\right] = \left[\frac{\varepsilon_{\vec{k}_{\vec{l}}}}{-\mu}+1\right]\left[1 + O(\frac{1}{V})\right] = \left[\frac{\beta\varepsilon_{\vec{k}_{\vec{l}}}}{-\beta\mu}+1\right]\left[1 + O(\frac{1}{V})\right]$$

$$= \left[\beta\varepsilon_{\vec{k}_{\vec{l}}}\left(V(\tilde{n} - \tilde{n}_C)\right)+1\right]\left[1 + O(\frac{1}{V})\right]$$

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	$k_B = 1.3806504 \quad \cdot 10^{-23}$	J/K
	$k_B = 8.617343 \qquad \cdot 10^{-5}$	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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