ΦSX

Advanced Topics of Theoretical Physics II

The statistical properties of matter

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with a guest chapter by Tom Kirchner

Caution! This is an unfinished draft version
Errors are unavoidable!

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don't panic!

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[1] To the title page: What is the meaning of ΦSX? Firstly, it sounds like "Physics". Secondly, the symbols stand for the three main pillars of theoretical physics: "X" is the symbol for the coordinate of a particle and represents Classical Mechanics. "Φ" is the symbol for the wave function and represents Quantum Mechanics and "S" is the symbol for the Entropy and represents Statistical Physics.

Contents

Chapter 1

Transition-state theory

1.1 Introduction: Rate laws

Chemical reactions or processes in materials are often thermally activated. That is the system remains in an initial state for some time until it accidentally overcomes a so-called reaction barrier separating the initial state from a final state. Examples for thermally activated processes are

- diffusion of dopants in a semiconductor
- the oxidation of a metal surface in contact with the atmosphere, that is corrosion,
- the reaction of gasoline and oxygen in a combustion engine
- cooking
- metabolic processes

All these processes have in common that they proceed faster if the temperature is increased.

Transition-state theory (TST) is the basis for the investigation of thermal activated processes of classical systems. It provides with the rate of chemical reactions or it provides diffusion constants.

Let us consider a set of molecules, say oxygen and hydrogen. These molecules can react to water, $\mathrm{H_2O}$ in the reaction

$$\mathrm{O_2} + 2\mathrm{H_2} \rightarrow 2\mathrm{H_2O} \tag{1.1}$$

We would like to know how fast this reaction proceeds. If there are initially N_0 hydrogen molecules and $\frac{1}{2}N_0$ oxygen molecules, we would like to know how long it takes at a given temperature until a certain percentage of water molecules are formed. Since the reaction only depends only on the number of **reactant molecules** O_2 and H_2, the number of hydrogen molecules consumed after a given time will follow an exponential law.[1]

$$\partial_t N(t) = \Gamma N(t) \tag{1.2}$$

where Γ is the reaction rate, that depends on temperature. From Eq. 1.2 we obtain the time dependence of he reactants

$$N(t) = N_0 \mathrm{e}^{-\Gamma t} \tag{1.3}$$

The goal of transition-state theory is the determination of the reaction rate Γ from a given potential energy surface.

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[1] To make the argument simple, we have ignored here the dependence on the concentration and we have ignored the back reaction.

1.2 Arrhennius law

Svante August Arrhenius (* 1859 near Uppsala; † 2. Oktober 1927 in Stockholm). Swedish Physicist and Chemist. Nobel price in Chemistry 1903

One of the main results of transition-state theory is a microscopic justification and theoretical quantification of the Arrhenius law, which says that the reaction rate $\Gamma(T)$ has an exponential dependence on the inverse temperature, that is:

ARRHENIUS LAW

$$\Gamma(T)=\Gamma_0\,\mathrm{e}^{-\frac{E_a}{k_BT}} \tag{1.4}$$

- The first term in Eq. 1.4, Γ_0 is the so-called **attempt frequency**, the **pre-exponential** or simply the **prefactor**. As we will see, it can be identified with an oscillation frequency as $\Gamma_0=\frac{\omega}{2\pi}$. It is the frequency with which the particle oscillates against the reaction barrier.
- The second factor $\mathrm{e}^{-\frac{E_a}{k_BT}}$ is called the **Boltzmann factor**. It is given by the activation energy E_a, the Boltzmann constant k_B and the temperature.

Reaction rates are usually represented in a **Arrhenius plot**, where $\ln[\Gamma]$ is plotted against the inverse temperature. In this representation, the Arrhenius law gives a straight line. The slope of the line leads directly to the activation energy.

The preexponential can also be written as[1, 2]

$$\Gamma_0=\underbrace{\frac{k_BT}{2\pi\hbar}}_{6\times10^{12}sec^{-1}}\mathrm{e}^{-\frac{S_a}{k_B}} \tag{1.5}$$

which defines the **entropy of activation** S_a as[3].

$$S_a=k_B\ln\left(\frac{2\pi\hbar}{k_BT}\Gamma_0\right) \tag{1.6}$$

The attempt frequency can be estimated from the vibrational frequencies. A typical oscillation frequency has an order of magnitude of 10^{-13} s, that is about 0.1 ps. Oscillation frequencies deviate from this value typically by less than a factor ten. This provides us with an order of magnitude estimate for the reaction rate as function of the activation energy, if the activation energy is known.

Consider the **residence time** or **waiting time** $t_{residence}=\frac{1}{\Gamma(T)}$ before the reaction occurs. We estimate the

RESIDENCE TIME

$$t_{residence}\approx10^{-13}\mathrm{e}^{\frac{E_a}{k_BT}}\mathrm{sec}=10^{-13}\mathrm{e}^{11604\frac{E_a[eV]}{T[K]}}\mathrm{sec} \tag{1.7}$$

The estimated residence times for three different temperature are shown in Fig. 1.2. They allow us to estimate, which processes may be important on which time scales. At room temperature, reactions up to 1.8 eV are relevant for technological degradation processes, given a 10 year lifetime of the product. At about 1000°C processes with barriers up to about 4 eV are acessible through 1 hour

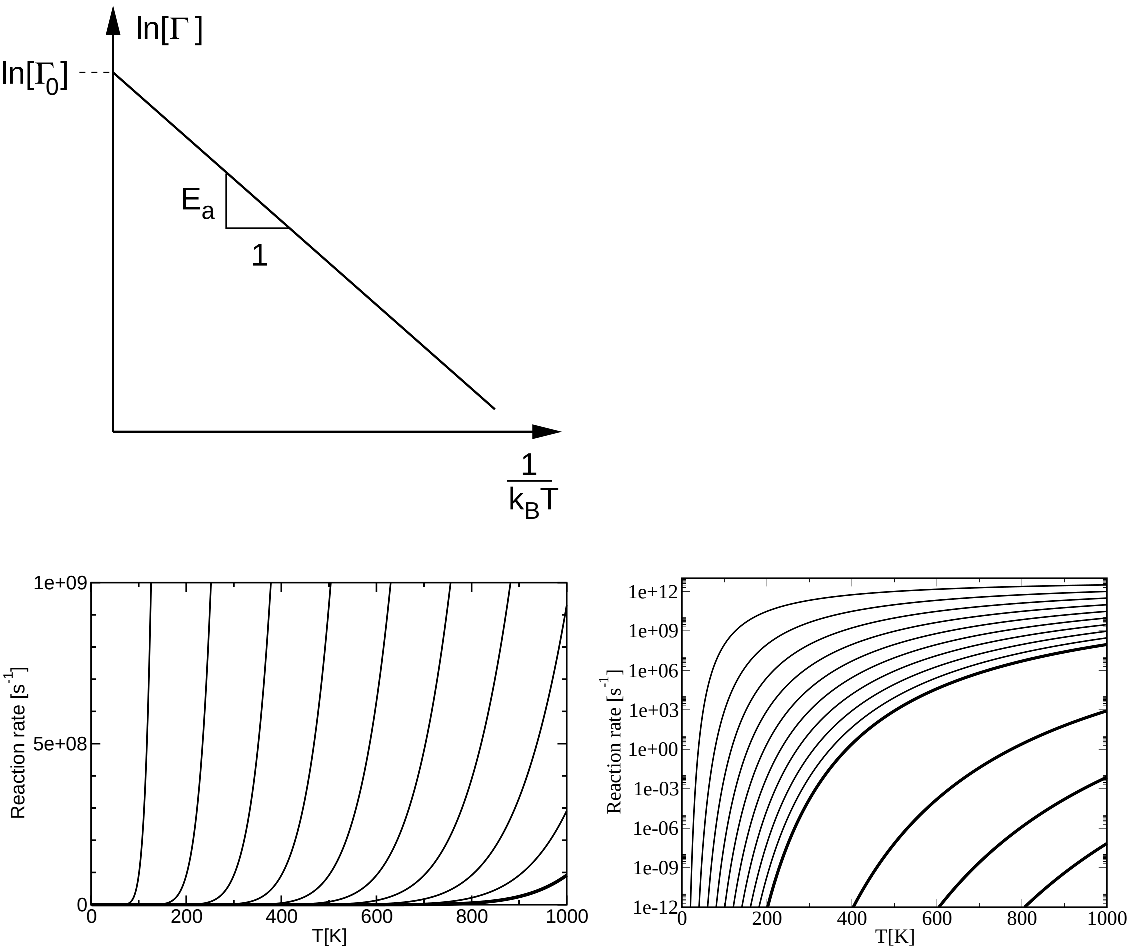

Fig. 1.1: Top: Arrhenius plot: The logarithm of the reaction rate or the diffusion constant is plotted versus the inverse temperature. In this representation the activation energy can immediately be obtained from the slope $E_a = \frac{\partial\Gamma}{\partial\frac{1}{k_BT}}$. From the abscizza, we obtain the pre-exponential. If the Arrhenius plot is not a straight line, this is an indication that there may be several processes with different activation energies. Bottom: Reaction rates in a normal (left) and semi-logarithmic (right) representation for activation energies between 0.1-0.9 eV in spacings of 0.1 eV (thin lines) and in spacings of 1 eV (thick lines).

baking. Only reactions with barriers less than 0.5 eV are accessible through direct first-principles simulations

The main reference for transition-state theory is the paper by Vineyard[4].

If an Arrhenius plot shows a curved line it can have two reasons. Either anharmonic effects become important at higher temperatures, or there are several competing mechanisms with different activation energies. A mechanism with large activation energy but also a large prefactor may be insignificant at low temperatures, but will dominate at higher temperatures, so that the reaction rate crosses over from the low-temperature mechanism to the high-temperature mechanism. Due to the logarithmic scale, only the dominant process contributes appreciably. For two processes we obtain an Arrhenius plot with approximately piecewise straight lines.

Important remark: The reaction rate given here is only valid for reactants that already exist in neighboring basins of the total energy surface. For reactions in the liquid or the gas, it needs to be augmented with the probability that the reactants are located in such neighboring basins.

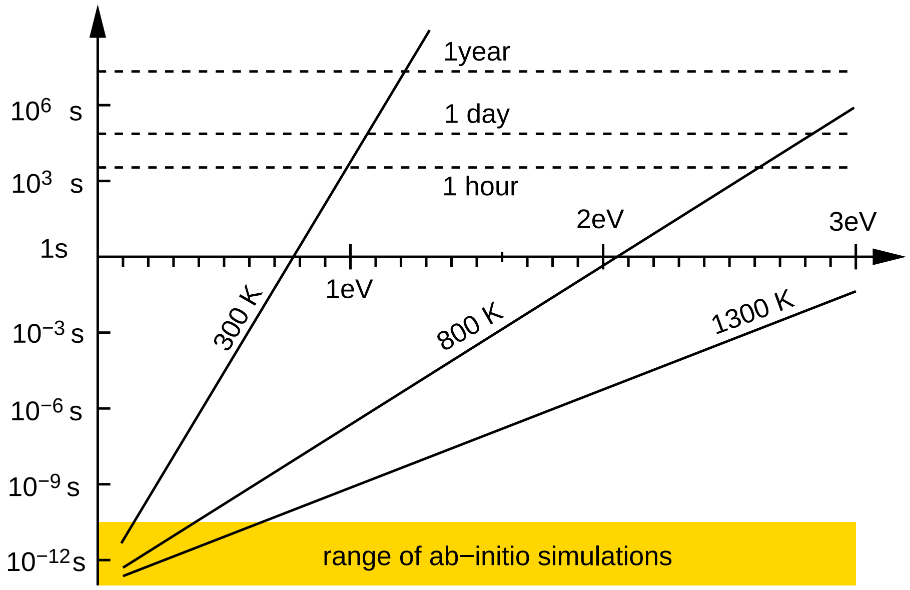

Fig. 1.2: Residence time $t_{residence}$ on a $\log_{10}$ scale as function of activation energy for different temperatures.

So far we have discussed the main conclusions of transition-state theory. In order to understand its limitations we will not derive the theory from first principles.

1.3 Transition-state theory one dimensional

Here, we develop the theory for a one-dimensional example, in order not to clutter the main concepts. Later, we will generalize transition-state theory to higher dimensions and many-particle systems.

Fig.1.3 shows a sketch of the one dimensional potential energy surface along with the parameters used in the derivation.

Firstly, we have to divide space into regions such that each region contains exactly one local minimum of the potential energy surface. In our example there are just two local minima, namely A and B. The state A refers to the left side of the reaction equation, namely O_2+H_2, while B refers to the right side, that is $2H_2O$.

An arbitrary point x_0 is attributed to a certain local minimum A in the following way: Follow the force $F = -\partial_x V$ from x_0 until the force vanishes. That is, solve the differential equation $\dot{x}(t) = -\partial_x V(x(t))$ with $x(0) = x_0$. If this path ends up in x_A, the point x_0 lies in Ω_A. If it ends up in point x_B, the initial point x_0 is attributed to B and $x_0 \in \Omega_B$.

Transition-state theory addresses the question, with which probability a particle located in Ω_A will end up in Ω_B after a given time interval T.

Formulation of the problem

The assumption of transition-state theory is that the system is in thermal equilibrium and forms a canonical ensemble. The rate of particles moving from Ω_A to Ω_B, is the equilibrium flux from Ω_A to Ω_B through the dividing "surface".

From the classical limit of the canonical ensemble, we know that the probability distribution

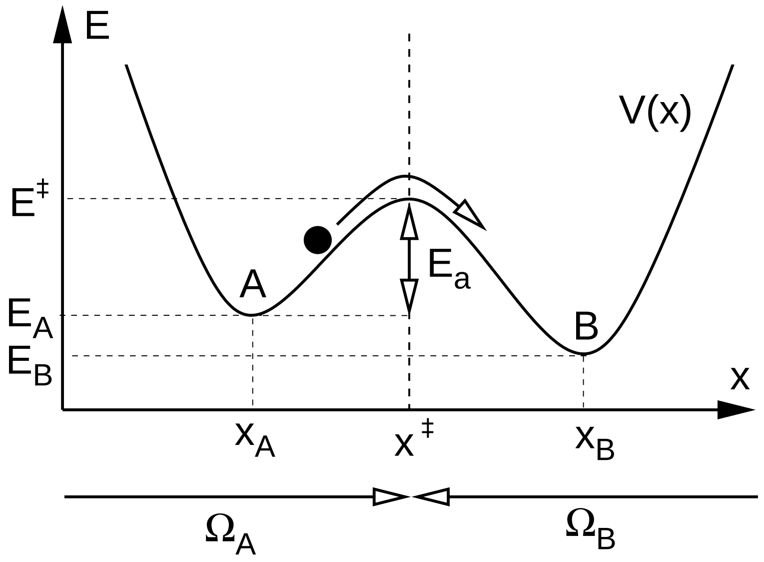

Fig. 1.3: Schematic drawing of the one-dimensional potential surface showing the main parameters entering transition-state theory in one dimension.

$P^{eq}(x,v)$ of the positions x and velocities v for a particle with mass m in a potential $V(x)$ is [2] given by

$$P^{eq}(x,v)=\frac{\mathrm{e}^{-\frac{1}{k_BT}\left(\frac{1}{2}mv^2+V(x)\right)}}{\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dv\;\mathrm{e}^{-\frac{1}{k_BT}\left(\frac{1}{2}mv^2+V(x)\right)}}$$

The numerator is the Boltzmann factor and the denominator is the normalization integral.

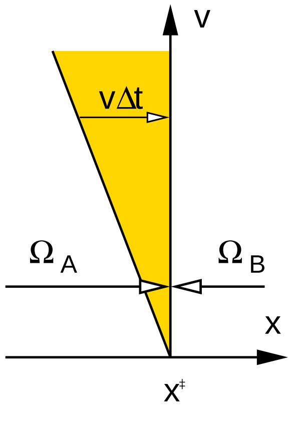

Fig. 1.4: Particles in the colored region of the x-v diagram will cross the barrier from left to right in the interval Δt.

What is the condition that a particle at position x in Ω_A with a velocity v moves from Ω_A to site Ω_B within a small time interval Δt? It must start out from the left of the barrier and after a time Δt it must end up to the right of the barrier. That is

$$x(t)<x^{\ddagger}\qquad\text{and}\qquad x(t+\Delta t)>x^{\ddagger}$$

where $x^{\ddagger}$ is the position of the barrier. For small time intervalls Δt we can form a Taylor expansion of $x(t+\Delta t)=x(t)+v\Delta t+O(\Delta t^2)$ and restrict ourselves to the first-order term.

Hence a particle must be on the left of the barrier, but not too far away so that it can still reach the barrier within the small time interval. Furthermore, the velocity must be oriented towards the barrier. Hence all particles with

$$x\in]x^{\ddagger}-v\Delta t,x^{\ddagger}]\qquad\text{and}\qquad v>0$$

will cross the barrier in the time intervall Δt. The points, that fulfill these conditions are shown schematically in Fig. 1.4.

Now, we need to integrate the probability distribution over the area in the x-v diagram depicted in Fig. 1.4 to obtain the probability $\Delta P_{AB}(\Delta t)$ for a particle to cross the barrier in the specified small

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[2] see ΦSX: Statistical Physics

time interval.

$$\lim_{\Delta t\to 0}\frac{1}{\Delta t}\Delta P_{A,B}(\Delta t)$$

will give us the equilibrium flux in thermal equilibrium. We want to know the number of particles crossing the barrier, relative to the number of particles in Ω_A. Thus we have to divide the equilibrium flux by the probability, that the particle is in Ω_A to obtain the rate.

$$\Gamma=\lim_{\Delta t\to 0}\frac{\Delta P_{A,B}(\Delta t)}{P_A\,\Delta t} \tag{1.8}$$

It may be instructive to compare this equation to the exponential law after bringing it into the following form.

$$\partial_t P_A=\lim_{\Delta t\to 0}\frac{\Delta P(\Delta t)}{\Delta t}=\Gamma P_A$$

Now we have defined the basic ingredients of the theory, so that we can work out the expressions:

Probability for a barrier crossing

If the system is in equilibrium we can determine the probability that a particle hops from B to site C as

$$\begin{aligned}
\Delta P_{AB}(\Delta t) &= \int_0^\infty dv\int_{x^\ddagger-v\Delta t}^{x^\ddagger} dx\; P^{eq}(x,v)\\
&= \frac{\int_0^\infty dv\int_{x^\ddagger-v\Delta t}^{x^\ddagger} dx\;\mathrm{e}^{-\frac{1}{k_BT}(\frac{1}{2}mv^2+V(x))}}{\int_\infty^\infty dv\int_{-\infty}^\infty dx\;\mathrm{e}^{-\frac{1}{k_BT}(\frac{1}{2}mv^2+V(x))}}\\
&= \frac{\int_0^\infty dv\;\mathrm{e}^{-\frac{mv^2}{2k_BT}}\int_{x^\ddagger-v\Delta t}^{x^\ddagger} dx\;\mathrm{e}^{-\frac{1}{k_BT}V(x)}}{\int_\infty^\infty dv\;\mathrm{e}^{-\frac{mv^2}{2k_BT}}\int_{-\infty}^\infty dx\;\mathrm{e}^{-\frac{1}{k_BT}V(x)}}\\
&\overset{Taylor}{=} \frac{\int_0^\infty dv\;\mathrm{e}^{-\frac{mv^2}{2k_BT}}\left(\int_{x^\ddagger-v\Delta t}^{x^\ddagger} dx\;\mathrm{e}^{-\frac{1}{k_BT}V(x^\ddagger)}+O(x-x^\dagger)\right)}{\left(\int_\infty^\infty dv\;\mathrm{e}^{-\frac{mv^2}{2k_BT}}\right)\left(\int_{-\infty}^\infty dx\;\mathrm{e}^{-\frac{1}{k_BT}V(x)}\right)}\\
&= \frac{\int_0^\infty dv\;\mathrm{e}^{-\frac{mv^2}{2k_BT}}\left(v\Delta t\;\mathrm{e}^{-\frac{1}{k_BT}V(x^\ddagger)}+O(\Delta t^2)\right)}{\left(\int_\infty^\infty dv\;\mathrm{e}^{-\frac{mv^2}{2k_BT}}\right)\left(\int_{-\infty}^\infty dx\;\mathrm{e}^{-\frac{1}{k_BT}V(x)}\right)}\\
&= \Delta t\underbrace{\frac{\int_0^\infty dv\;v\;\mathrm{e}^{-\frac{mv^2}{2k_BT}}}{\int_\infty^\infty dv\;\mathrm{e}^{-\frac{mv^2}{2k_BT}}}}_{\sqrt{\frac{k_bT}{2\pi m}}}\;\frac{\mathrm{e}^{-\frac{1}{k_BT}V(x^\ddagger)}}{\int_{-\infty}^\infty dx\;\mathrm{e}^{-\frac{1}{k_BT}V(x)}}
\end{aligned}$$

Now we have to perform the integrations over the velocity. They involve Gauss functions.

- The velocity integral in the numerator can be evaluated using the following identity.

$$\begin{aligned}
\partial_x\,\mathrm{e}^{-x^2} &= -2x\,\mathrm{e}^{-x^2}\\
\Rightarrow \int_0^\infty dx\;x\,\mathrm{e}^{-x^2} &= -\frac{1}{2}\int_0^\infty dx\;\partial_x\mathrm{e}^{-x^2}=-\frac{1}{2}\left[\mathrm{e}^{-x^2}\right]_0^\infty=\frac{1}{2}
\end{aligned}$$

- For the integral in the nominator we use the identity[5]

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

Thus we obtain the equilibrium flux through the dividing surface as

$$\lim_{\Delta t\to 0}\frac{\Delta P_{AB}(\Delta t)}{\Delta t} = \sqrt{\frac{k_bT}{2\pi m}}\frac{\mathrm{e}^{-\frac{1}{k_BT}V(x^\ddagger)}}{\int_{-\infty}^{\infty} dx\, \mathrm{e}^{-\frac{1}{k_BT}V(x)}} \tag{1.9}$$

Probability for the system being in the initial state

Next, we need to evaluate P_A, the probability that the particle is in Ω_A.

$$\begin{aligned}
P_A &= \frac{\int_{-\infty}^{\infty} dv \int_{\Omega_A} dx\, \mathrm{e}^{-\frac{1}{k_BT}(\frac{1}{2}mv^2+V(x))}}{\int_{-\infty}^{\infty} dv \int_{-\infty}^{\infty} dx\, \mathrm{e}^{-\frac{1}{k_BT}(\frac{1}{2}mv^2+V(x))}} \\
&= \frac{\left(\int_{-\infty}^{\infty} dv\, \mathrm{e}^{-\frac{mv^2}{2k_BT}}\right)\left(\int_{\Omega_A} dx\, \mathrm{e}^{-\frac{1}{k_BT}V(x)}\right)}{\left(\int_{-\infty}^{\infty} dv\, \mathrm{e}^{-\frac{mv^2}{2k_BT}}\right)\left(\int_{-\infty}^{\infty} dx\, \mathrm{e}^{-\frac{1}{k_BT}V(x)}\right)} \\
&= \frac{\int_{\Omega_A} dx\, \mathrm{e}^{-\frac{1}{k_BT}V(x)}}{\int_{-\infty}^{\infty} dx\, \mathrm{e}^{-\frac{1}{k_BT}V(x)}}
\end{aligned} \tag{1.10}$$

Reaction rate from transition-state theory

We combine the results obtained so far:

$$\begin{aligned}
\Gamma(T) &= \frac{1}{P_A}\lim_{\Delta t\to 0}\frac{\Delta P_{AB}(\Delta t)}{\Delta t} \overset{Eqs.\ 1.9,1.10}{=} \sqrt{\frac{k_bT}{2\pi m}}\frac{\mathrm{e}^{-\frac{1}{k_BT}V(x^\ddagger)}}{\int_{\Omega_A} dx\, \mathrm{e}^{-\frac{1}{k_BT}V(x)}} \\
&= \sqrt{\frac{k_bT}{2\pi m}}\frac{\mathrm{e}^{-\frac{1}{k_BT}(V(x^\ddagger)-E_A)}}{\int_{\Omega_A} dx\, \mathrm{e}^{-\frac{1}{k_BT}(V(x)-E_A)}}
\end{aligned}$$

Thus we obtain our final result for the

REACTION RATE FOR A ONE-DIMENSIONAL REACTION COORDINATE

$$\Gamma(T) = \underbrace{\sqrt{\frac{k_BT}{2\pi m}}\frac{1}{\int_{\Omega_A} dx\, \mathrm{e}^{-\frac{1}{k_BT}(V(x)-E_A)}}}_{\Gamma_0}\mathrm{e}^{-\frac{E_a}{k_BT}} \tag{1.11}$$

where $E_a = V(x^\ddagger) - E_A$ is the **activation energy**

Discussion

- The factor

$$\sqrt{\frac{k_BT}{2\pi m}} = \sqrt{\frac{\langle\frac{1}{2}mv^2\rangle}{\pi m}} = \sqrt{\frac{\langle v^2\rangle}{2\pi}}$$

has a physical meaning, since it is related to the mean velocity of the particle. If the potential would be completely flat except for hard walls enclosing Ω_A and Ω_B, the reaction rate would be $\Gamma = \sqrt{k_B T/(2\pi m)}\frac{1}{|\Omega_A|}$, where $|\Omega_A|$ is the 1-dimensional volume of Ω_A, that is its length.

If we consider an artificial problem with a constant potential

$$\Gamma = \sqrt{\frac{\langle v^2 \rangle}{2\pi}}\frac{1}{|\Omega_A|}$$

- the second factor

$$P^{\ddagger} = \frac{\mathrm{e}^{-\frac{E_a}{k_B T}}}{\int_{\Omega_A} dx\, \mathrm{e}^{-\frac{1}{k_B T}(V(x)-E_A)}}$$

  can be identified with the probability density to find a particle on top of the barrier, given that it is in Ω_A.

- If the temperature is sufficiently low, the integrand will only contribute near the minimum x_B so that we can apply the **harmonic approximation**. We perform a Taylor expansion of the potential about x_A

$$V(x) = V(x_A) + \frac{1}{2}m\omega^2(x-x_A)^2 + O(x-x_A)^3$$

  Where ω is the frequency of the particle, when it oscillates around x_A.

  A second consequence of the low temperature is that, within the harmonic approximation, the probability outside Ω_A is negligible, so that we can replace, within the harmonic approximation, the integral over Ω_A by an integral over all space.

  Within the harmonic approximation, the normalization integral can be rewritten as

$$\begin{aligned}\int_{\Omega_A} dx\, \mathrm{e}^{-\frac{V(x)-V(x_A)}{k_B T}} &\approx \int_{-\infty}^{\infty} dx\, \mathrm{e}^{-\frac{m\omega^2(x-x_A)^2}{2k_B T}} \\ &= \sqrt{\frac{2k_B T}{m\omega^2}}\int_{-\infty}^{\infty} dx\, \mathrm{e}^{-x^2} = \sqrt{\frac{2\pi k_B T}{m\omega^2}}\end{aligned}$$

  Thus we obtain the result in the harmonic approximation

$$\Gamma = \sqrt{\frac{k_B T}{2\pi m}\cdot\frac{m\omega^2}{2\pi k_B T}}\mathrm{e}^{-\frac{1}{k_B T}E_a} = \frac{\omega}{2\pi}\mathrm{e}^{-\frac{1}{k_B T}E_a} \tag{1.12}$$

  For a bond breaking event we can estimate prefactor from simple arguments. The period of a typical bond-stretch frequency is in the range of 0.1 ps. There is of course a large spread, but on a logarithmic scale the deviations are small compared to the size of the exponential factor. Thus we can estimate the preexponential to be of order $10^{13}\frac{1}{sec}$, which we used in the estimate of the residence time Eq. 1.7.

APPROXIMATE REACTION RATE

For simple process we can estimate the reaction rate from the activation energy as

$$\Gamma \approx 10^{13}\frac{1}{s}\mathrm{e}^{-\frac{1}{k_B T}E_a} \tag{1.13}$$

1.4 Transition-state theory multidimensional

1.4.1 Introduction

During a reaction event, a particle is rarely moving in one dimension. Furthermore there will be may atoms involved as for example a diffusing particle squeezes through a window of neighboring atoms.

Here we consider a reaction in N dimensions, where the N dimensions correspond to all the particle positions that are involved. We obtain a very similar result to the one-dimensional case. However

- the mass needs to be replaced by an effective mass, which includes the masses of all particles that participate in the reactive process.
- The activation energy is identified as the minimum energy, that is needed to cross the dividing surface.
- in addition to the activation energy, there is also an **entropy of activation**. See Eq. 1.6.

1.4.2 Explicit calculation

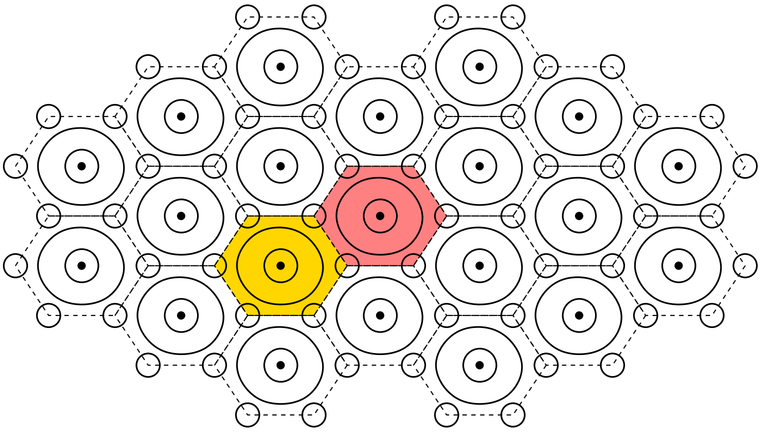


Fig. 1.5: Capture regions for a hexagonal two-dimensional array of local minima. It may describe for example the diffusion of an adatom on a graphite sheet. The solid lines are isocontours of the potential. The dashed lines are the dividing surfaces. The yellow and pink areas indicate two neighboring capture regions for local minima.

We divide the configuration space into **capture regions** Ω_i of local minima. Each point is uniquely attributed to a particular local minimum by following the down-hill trajectory $\dot{\vec{r}} = -\vec{\nabla} V(\vec{r})$ until it converges at one local minimum. The capture region of a local minimum contains all points for which those trajectories end in that minimum.

Probability for the system being in the initial state

Now we determine the probability P_i that the system is in a particular capture region

$$P_i = \int d^N r \int d^N v \; \theta_{\Omega_i}(\vec{r}) P(\vec{r}, \vec{v})$$

We use the probability density in coordinate and velocity space

$$P(\vec{r}, \vec{v}) = \mathcal{N} \mathrm{e}^{-\frac{1}{k_B t}\left(\frac{1}{2}\vec{v} m \vec{v} + V(\vec{r})\right)} \qquad (1.14)$$

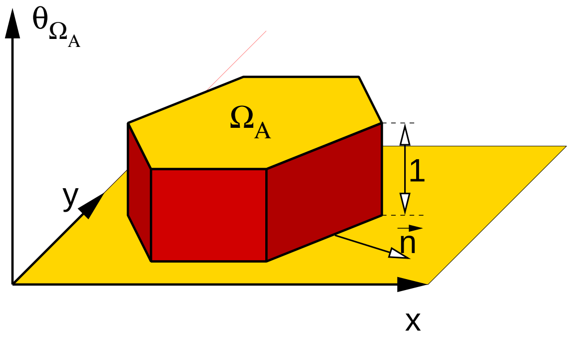


Fig. 1.6: Step function selecting one capture region Ω_A in two dimensions. $\vec{n}$ is the face normal.

and obtain

$$
\begin{aligned}
P_i &= \mathcal{N} \int_{\Omega_i} d^N r \int d^N v \; \mathrm{e}^{-\beta\left(\frac{1}{2}\sum_i m_i v_i^2 + V(\vec{r})\right)} \\
&= \mathcal{N} \int_{\Omega_i} d^N r \; \mathrm{e}^{-\beta V(\vec{r})} \prod_{i=1}^{N} \underbrace{\left(\int dv \; \mathrm{e}^{-\frac{m_i v_i^2}{2k_B T}} \right)}_{\sqrt{\frac{2k_B T}{m_i}} \cdot \sqrt{\pi}} \\
&= \mathcal{N} \int_{\Omega_i} d^N r \; \mathrm{e}^{-\beta V(\vec{r})} \sqrt{\frac{(2\pi k_B T)^N}{\det|\mathbf{m}|}} \\
&= \mathcal{N} \frac{(2\pi k_B T)^{\frac{N}{2}}}{\det|\mathbf{m}|} \int_{\Omega_i} d^N r \; \mathrm{e}^{-\beta V(\vec{r})}
\end{aligned}
\tag{1.15}
$$

We do not need to work out the normalization constant $\mathcal{N}$, because it will drop out of the final expression.

Probability for a barrier crossing

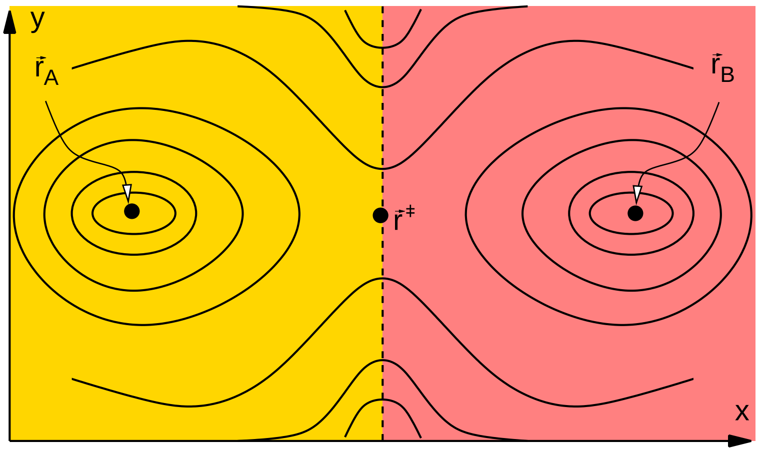


Fig. 1.7: Contour diagram of a saddle point

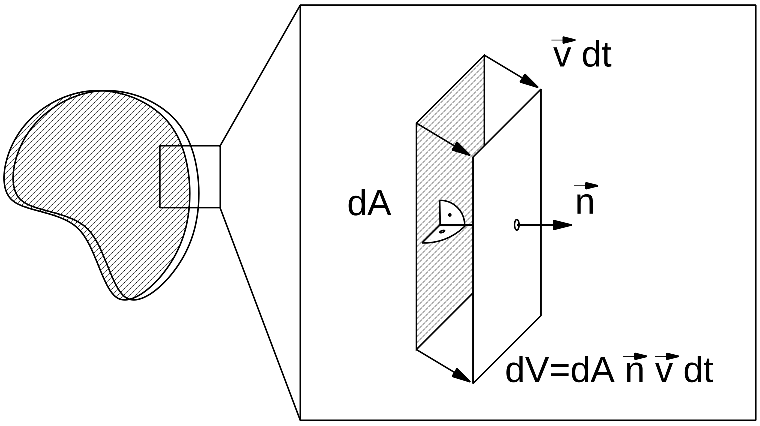


Fig. 1.8: Die Anzahl der Teilchen, die in einem Zeitintervall dt das Volumen Ω durch das Oberflächenelement dA verlassen, ist gleich der Dichte auf der Oberfläche multipliziert mit dem Volumen $dV = dA\vec n\vec v dt$. Dabei ist $\vec n$ der Normalenvektor auf der Oberfläche und $\vec v$ ist die Geschwindigkeit der Teilchen auf der Oberfläche. Alle Teilchen, die im Intervall dt durch die Oberflächenelement geflossen sind, liegen im Volumen dV. Durch Integration über die Oberfläche $\partial\Omega$ des Volumens Ω erhalten wir die Gesamtzahl $dN = \oint_{\partial\Omega} d\vec A\,\rho\vec v dt$ der Teilchen, die das Volumen im Zeitintervall verlassen. Dabei ist $d\vec A = dA\vec n$. Wir erhalten also $\dot N = \oint_{\partial\Omega} d\vec A\,\rho\vec v dt$

Next we determine the probability that the system leaves a given capture area

$$\Delta P_i = \int d^Nv \int_{\partial\Omega} dA\,(\vec v\vec n)\Delta t P(\vec r, \vec v)\theta(\vec v\vec n) \tag{1.16}$$

where $\vec n$ is the unit vector that stands perpendicular over the dividing surface and θ is the regular Heaviside function.[3] We introduce the mass matrix $\mathbf m$, which has the matrix elements $m_{i,j} = m_i\delta_{i,j}$. This is convenient because it allows to express the kinetic energy in matrix-vector notation $\frac12\sum_i m_i v_i^2 = \frac12\vec v\mathbf m\vec v$.

With Eq. 1.14 the reaction rate from Eq. 1.16 is

$$\begin{aligned}\frac{\Delta P_i}{\Delta t} &= \int d^Nv \int_{\partial\Omega} dA\,(\vec n\vec v)\mathcal N e^{-\beta(\frac12\vec v m\vec v + V(\vec r))}\theta(\vec n\vec v)\\ &= \mathcal N\int_{\partial\Omega} dA\, e^{-\beta V(\vec r)}\int d^Nv\,(\vec n\vec v)e^{-\beta\frac12\vec v m\vec v}\theta(\vec n\vec v)\end{aligned} \tag{1.17}$$

Now we introduce new coordinates and the mass matrix $\mathbf m$, which is diagonal and contains on the diagonal elements the masses corresponding to the respective coordinates.

$$\begin{aligned}\vec y &\overset{\text{def}}{=} \mathbf m^{\frac12}\vec v \qquad \Leftrightarrow \qquad y_i = \sqrt{m_i}v_i\\ \Rightarrow d^Ny &= \det\left|\mathbf m^{\frac12}\right| d^Nv = \sqrt{\det|\mathbf m|}d^Nv\end{aligned}$$

Secondly we introduce a transformed vector

$$\vec q \overset{\text{def}}{=} \mathbf m^{-\frac12}\vec n\frac{1}{\sqrt{\vec n\mathbf m^{-1}\vec n}}$$

The vector $\vec q$ is normalized, but is no more perpendicular to the dividing surface.

The factor μ is the

---

[3] $\theta(x<0) = 0;\theta(x) = \frac12$ and $\theta(x>0) = 1$.

EFFECTIVE MASS

$$\mu \overset{\text{def}}{=} \frac{1}{\vec{n}\mathbf{m}^{-1}\vec{n}} = \sum_i \left(\frac{n_i^2}{m_i}\right)^{-1}$$

The effective mass is defined on the dividing surface and it depends on the position on the dividing surface, because the normal vector changes with the orientation of the dividing surface.

With these definitions Eq 1.17 obtains the form

$$\begin{aligned}\frac{\Delta P_i}{\Delta t} &= \mathcal{N} \int_{\partial\Omega} dA\, \mathrm{e}^{-\beta V(\vec{r})} \frac{1}{\sqrt{\det|\mathbf{m}|}} \int d^N y\; (\vec{n}\mathbf{m}^{-\frac{1}{2}}\vec{y})\mathrm{e}^{-\frac{1}{2k_BT}y^2}\theta(\vec{n}\mathbf{m}^{-\frac{1}{2}}\vec{y}) \\ &= \mathcal{N} \int_{\partial\Omega} dA\, \mathrm{e}^{-\beta V(\vec{r})} \frac{1}{\sqrt{\mu\det|\mathbf{m}|}} \int d^N y\; (\vec{q}\vec{y})\mathrm{e}^{-\frac{1}{2k_BT}y^2}\theta(\vec{q}\vec{y}) \end{aligned} \tag{1.18}$$

Next we rotate our coordinate system for $\vec{y}$ such that the first component is parallel to $\vec{q}$

$$\vec{w} \overset{\text{def}}{=} \mathbf{U}\vec{y}$$

The matrix $\mathbf{U}$ is unitary, so that $\mathbf{U}^\top = \mathbf{U}^{-1}$ and it is chosen such that

$$\mathbf{U}\vec{q} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$$

so that $\vec{q}\vec{y} = \vec{q}\mathbf{U}^\top\mathbf{U}\vec{y} = \vec{q}\mathbf{U}^\top\vec{w} = (\mathbf{U}\vec{q})\,\vec{w} = w_1$

$$\begin{aligned}\frac{\Delta P_i}{\Delta t} &= \mathcal{N} \int_{\partial\Omega} dA\, \mathrm{e}^{-\beta V(\vec{r})} \frac{1}{\sqrt{\mu\det|\mathbf{m}|}} \int d^N w\; (\vec{q}\mathbf{U}^\top\vec{w})\mathrm{e}^{-\frac{1}{2k_BT}\vec{w}\mathrm{U}\mathrm{U}^\top\vec{w}}\theta(\vec{q}\mathbf{U}^\top\vec{w}) \\ &= \mathcal{N} \int_{\partial\Omega} dA\, \mathrm{e}^{-\beta V(\vec{r})} \frac{1}{\mu\sqrt{\det|\mathbf{m}|}} \int d^N w\; \theta(w1)w_1\mathrm{e}^{-\frac{1}{2k_BT}\vec{w}^2} \\ &= \mathcal{N} \int_{\partial\Omega} dA\, \mathrm{e}^{-\beta V(\vec{r})} \frac{}{\sqrt{\mu\det|\mathbf{m}|}} \underbrace{\left[\int dw_1\; \theta(w1)w_1\mathrm{e}^{-\frac{1}{2k_BT}w_1^2}\right]}_{2k_BT\cdot\frac{1}{2}} \prod_{i=2}^{N} \underbrace{\left[\int dw_i\; \mathrm{e}^{-\frac{1}{2k_BT}w_i^2}\right]}_{\sqrt{2k_BT}\cdot\sqrt{\pi}} \\ &= \mathcal{N} \int_{\partial\Omega} dA\, \mathrm{e}^{-\beta V(\vec{r})} \frac{1}{\sqrt{\mu\det|\mathbf{m}|}} k_BT\left(\sqrt{2\pi k_BT}\right)^{N-1} \\ &= \mathcal{N}\sqrt{\frac{(2\pi k_BT)^N}{\det|\mathbf{m}|}} \int_{\partial\Omega} dA\, \mathrm{e}^{-\beta V(\vec{r})} \sqrt{\frac{k_BT}{2\pi\mu}} \end{aligned}$$

Reaction rate from transition-state theory

If we combine this result with the probability Eq. 1.15 for the system being in the initial state we obtain the

REACTION RATE FROM TRANSITION-STATE THEORY IN MANY DIMENSIONS

$$\Gamma=\frac{1}{P_i}\frac{\Delta P_i}{\Delta t}=\int_{\partial\Omega} dA\,\sqrt{\frac{k_BT}{2\pi\mu}}\,\underbrace{\frac{\mathrm{e}^{-\beta V(\vec r)}}{\int_{\Omega_i} d^Nr'\,\mathrm{e}^{-\beta V(\vec r\,')}}}_{P^{\ddagger}(\vec r)} \tag{1.19}$$

The transition rate is related to the probability that a particle reaches the dividing surface and the mean velocity perpendicular to the dividing surface.

Harmonic approximation

Editor: This section is under construction!

Now we can introduce the harmonic approximation by approximating the potential at the transition state and in the local minimum by a Taylor series.

$$\begin{aligned}
V(x)&=V(x_{BC})+\frac{1}{2}\frac{\partial^2V}{\partial x_i\partial x_j}(x_i-x_{BC,i})(x_j-x_{BC,j})+O(\vec r-\vec r_{BC})\\
&=V(x_{BC})+\frac{1}{2}D^{BC}_{i,j}y^{BC}_i y^{BC}_j+O(\vec y^2)\\
y^{BC}_i&\stackrel{\mathrm{def}}{=}\sqrt{m_i}(x_i-x_{BC,i})\\
V(x)&=V(x_B)+\frac{1}{2}\frac{\partial^2V}{\partial x_i\partial x_j}(x_i-x_{B,i})(x_j-x_{B,j})+O(\vec r-\vec r_B)\\
&=V(x_B)+\frac{1}{2}D^{B}_{i,j}y^{B}_i y^{B}_j+O(\vec y^2)\\
y^{B}_i&\stackrel{\mathrm{def}}{=}\sqrt{m_i}(x_i-x_{B,i})
\end{aligned}$$

In the harmonic approximation the dividing surface is planar so that the effective mass is a constant

$$\begin{aligned}
\frac{\Delta P_{BC}}{\Delta t}&=\sqrt{\frac{k_BT}{2\pi\mu}}\frac{\int d^{3N-1}A_x\,\mathrm{e}^{-\beta\frac{1}{2}\frac{\partial^2V}{\partial x_i\partial x_j}(x_i-x_{BC,i})(x_j-x_{BC,j})}}{\int d^{3N}r\,\mathrm{e}^{-\beta\frac{1}{2}\frac{\partial^2V}{\partial x_i\partial x_j}(x_i-x_{B,i})(x_j-x_{B,j})}}\mathrm{e}^{-\beta(V_{BC}-V_B)}P_B\\
&=\sqrt{\frac{k_BT}{2\pi\mu}}\frac{\int d^{3N-1}A_x\,\mathrm{e}^{-\beta\frac{1}{2}\frac{\partial^2V}{\partial x_i\partial x_j}(x_i-x_{BC,i})(x_j-x_{BC,j})}}{\int d^{3N}r\,\mathrm{e}^{-\beta\frac{1}{2}\frac{\partial^2V}{\partial x_i\partial x_j}(x_i-x_{B,i})(x_j-x_{B,j})}}\mathrm{e}^{-\beta(V_{BC}-V_B)}P_B
\end{aligned}$$

1.4.3 Entropy of reaction

1.5 Limitations of transition-state theory

1.5.1 Harmonic approximation

Often the errors of the harmonic approximation are identified with the errors of the transition-state theory. This is a mistake. Nevertheless, in practice the harmonic approximation is usually used and it error bars must be understood.

Typically the harmonic approximation is good, if the activation energy is large compared to the temperature. This is the case for systems with low rates. In that case the probability distribution will be localized around the minima, so that higher order terms are negligible.

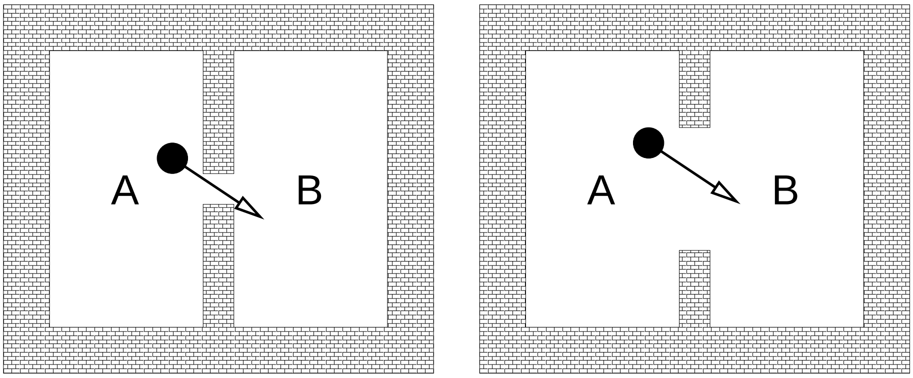


Fig. 1.9: Illustration of a system with a small (left figure) and a large (right figure) entropy of reaction. The entropy of reaction is related to the "width of the door" through which the particle have to pass. (The model of a particle in a box allows to remove the potential effects completely, so that only entropic terms remain.)

1.5.2 Correlated jumps

Sofar we have identified the reaction rate to the equilibrium flux through a dividing surface. However, it may be that the particle becomes reflected and crosses the barrier backwards. Such an event would be an unsuccessful reaction event. We call these events **correlated return jumps**. Similarly a particle may immediately pass on into a third local minimum, which is also a correlated event. Such correlated events must be taken into account if the reaction rates shall be compared to experiment.

Correlated events take place if the particle does not dissipate its energy sufficiently fast. In order to jump, the particle must have a large energy. While still being "hot", it may be able to overcome other barriers as well.

In most cases correlated events only contribute little to the overall reaction rate. Since they are very difficult to evaluate they are usually ignored.

A proper analysis considers the full time dependence of the probabilities in the original an the neighboring capture regions.

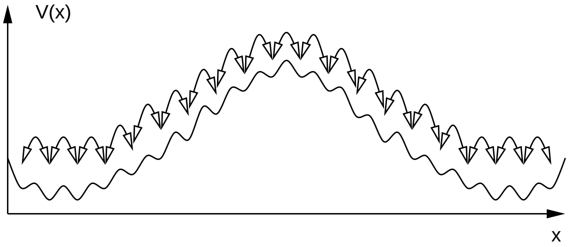
$$P(x, t=0) = \int dx\; P^{eq}(x, v)\theta_{\Omega_A}(x)$$

$$P_i(t) = \int dx\; P(x, t)\theta_{\Omega_i}(x)$$

In order to determine correlated events in a simulation, one starts several trajectories at the dividing surface, with velocities determined by the Boltzmann distribution and a position probability given by the Boltzmann factor $e^{-\frac{1}{k_BT}V(\vec{r})}$. Then one follows the trajectories over time, and monitors the correlation function.

Two limiting cases where transition-state theory fails

There are two extreme cases, where correlated events are important. For one-dimensional systems there is no energy dissipation. Thus a system that reacts, will with certainty overcome another barrier or return. Thus, essentially all events must be considered unsuccessful. The calculated rate would be zero. While purely one-dimensional systems are rarely relevant in practice, there are systems that behave similarly. Consider a very dilute gas of clusters. Each cluster has its own energy and can only dissipate its energy by radiation, which is a very slow process, or by collisions with molecules or other cluster. If the gas is sufficiently dilute, one has to consider each cluster to be in a microcanonical ensemble, which changes the statistics of the transitions in a fundamental way. Thus one has to be very careful when trying to estimate reaction rates of reaction products from such experiments.



Another extreme case is present, when the barrier is wide an flat, and the system couples strongly to its environment. In that case the particle will proceed in a Brownian motion type of trajectory. Such a trajectory will also cross any dividing surface many times, before is leaves the barrier in a diffusive motion. Also here the assumption of an equilibrium flux strongly overestimates the reaction rate. The typical example is the folding and unfolding of proteins. The total energy surface actually consists of many small minima, to that the system in effect will perform a kind of diffusive motion.

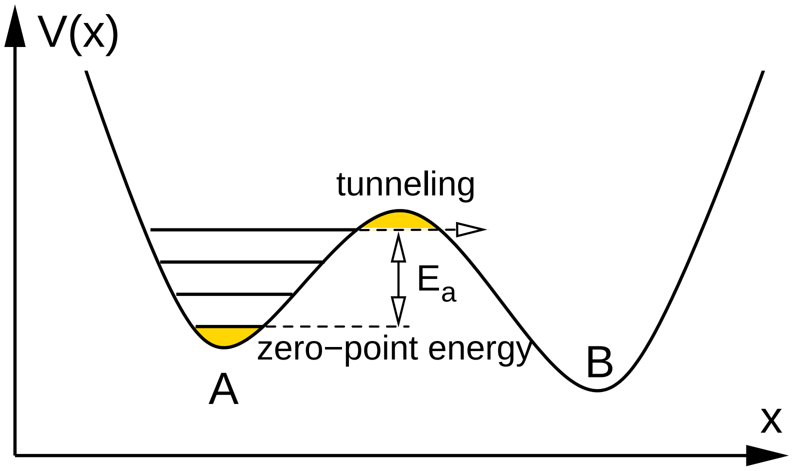
1.5.3 Quantum effects

Quantum effects may be important for light particles such as hydrogen or even lighter particles. The quantum effects are

- The lowering of the barrier due to zero-point energy.

- The increase of the reaction rate through tunneling.

Expressions that include quantum effects can be found in the literature.



Even for light particles, quantum effects become unimportant at higher energies. The reason is that the classical limit is at the same time the high-temperature limit of thermodynamics. Thus while the particles still behave quantum mechanically, their statistical behavior is very similar to that of a classical particle.

1.6 Methods to determine transition states

1.6.1 Drag method

1.6.2 Nudged elastic band

1.6.3 Dimer method

1.7 Free energy integration

1.8 Estimate correlation factor

1.9 Capture cross section

Chapter 2

Diffusion

2.1 Introduction

Let us consider an impurity in a crystal. It is often important to determine the concentration profile of such impurities.

In semiconductor technology, it is important to understand the dopant profile, depending on the process parameters. It is also important if harmful elements can diffuse into a sensitive area of a semiconductor device.

Modern metallic materials are complex alloys. The components can for example segregate to grain boundaries, dislocations or the surface. There they are important for example to pin dislocation or to make them mobile, which affects the plastic behavior of the material. The composition on the surface of the material influences its local hardness and the corrosion resistance of the material.

Corrosion is a process where for example oxygen is converged diffuses towards the interface of the metal with the protective oxide. There it reacts and transform more of the metal into an oxide, that is rust. Thus the understanding of diffusion is crucial to understanding corrosion.

Let us consider a single diffusing atom in a crystal. We assume that we know the positions of the local minima $\vec{r}_i$ in the potential energy surface and the diffusion rates $\Gamma_{i\rightarrow j}$ from one minimum to the next.

The goal of this section is to arrive at a continuum description for the diffusion, where the individual sites are no more resolved.

2.2 Diffusion equation

The macroscopic diffusion equation describes the dynamics of the probability density of a diffusing species. It can be derived from the **continuity equation**, which is also called **Fick's second law**

$$\partial_t \rho(\vec{r}, t) + \vec{\nabla}\vec{j}(\vec{r}, t) = 0 \tag{2.1}$$

and a linear relation between the current density $\vec{j}(\vec{r}, t)$ and the concentration gradient, which is **Fick's first law**

$$\vec{j}(\vec{r}, t) = -\mathbf{D}\vec{\nabla}\rho(\vec{r}, t) \tag{2.2}$$

The coefficient $\mathbf{D}$ is the **diffusion constant**. In general the diffusion constant is a tensor. If the problem is isotropic, however, this tensor is proportional to the unit matrix, that is $\mathbf{1}D$. In this case the scalar D is also called the diffusion constant.

The continuity equation is simply the expression of particle conservation, that is the number of particles in a given volume is equal to the current through its surface.

$$\partial_t N_\Omega(t) = \int_\Omega d^d r\ \rho(\vec{r},t) \overset{Eq.\ 2.1}{=} -\int_\Omega d^d r\ \vec{\nabla}\vec{j}(\vec{r},t) \overset{Gauss}{=} -\int_{\partial\Omega} d\vec{A};\vec{j}(\vec{r},t) = -J_{surf,\partial\Omega}$$

Here $J_{surf,\partial\Omega}$ is the particle current through the surface of the volume from the inside to the outside.

Fick's first law is based on the assumption that there is no current in the absence of a concentration gradient, so that the concentration gradient is the driving force. For a small driving force the linear relation is assumed to be sufficient.

The continuity equation and Fick's first law can be combined to the diffusion equation

$$\partial_t \rho(\vec{r},t) \overset{Eq.\ 2.1}{=} -\vec{\nabla}\vec{j}(\vec{r},t) \overset{Eq.\ 2.2}{=} +\vec{\nabla}\mathbf{D}\vec{\nabla}\rho(\vec{r},t)$$

If we add an additional current, so that Eq. 2.2 is changed to

$$\vec{j}(\vec{r},t) = -\mathbf{D}\vec{\nabla}\rho(\vec{r},t) + \vec{v}(\vec{r},t)\rho(\vec{r},t)$$

we arrive at the

FOKKER-PLANCK EQUATION[a]

$$\partial_t \rho = \vec{\nabla}\mathbf{D}\vec{\nabla}\rho - \vec{\nabla}\left(\vec{v}\rho\right) \tag{2.3}$$

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[a] ADRIAAN FOKKER, 1987-1972, DUTCH PHYSICIST AND MUSICIAN. COUSIN OF ANTHONY FOKKER, THE FOUNDER OF THE FOKKER AIRCRAFT COMPANY.

In the absence of a velocity field, that is for $\vec{v}=0$, we can directly obtain the probability density as

$$\rho(\vec{r},t) = \Big[(4\pi t)^d \det[D]\Big]^{-\frac{1}{2}} \mathrm{e}^{-\frac{\vec{r}\mathrm{D}^{-1}\vec{r}}{4t}}$$

which can be verified by insertion into Eq. 2.3 with $\vec{v}=0$.

This solution is also the Green's function of the Fokker-Planck equation in the absence of a drift velocity, that is

$$G(\vec{r},t,\vec{r'},t_0) = \Big[(4\pi t)^d \det[D]\Big]^{-\frac{1}{2}} \mathrm{e}^{-\frac{(\vec{r}-\vec{r'})\mathrm{D}^{-1}(\vec{r}-\vec{r'})}{4(t-t_0)}}$$

We can see that the Green's function obeys

$$\begin{aligned}\left[\partial_t - \vec{\nabla}\mathbf{D}\vec{\nabla}\right] G(\vec{r},t,\vec{r}_0,t_0) &= \delta(\vec{r}-\vec{r}_0)\delta(t-t_0)\\ G(\vec{r},-\infty,\vec{r}_0,t_0) &= 0\end{aligned}$$

For a given initial density $\rho(\vec{r},t_i)$ we can determine the density at a later time by an integral equation

$$\rho(\vec{r},t) = \int d^3r'\ G(\vec{r},\vec{r'})\rho(\vec{r'},t_i)$$

Of interest is the mean square displacement of an atom in a diffusion process. The mean square displacement can be directly obtained from any dynamical simulation and it can be related to other physical relations.

$$\begin{aligned}
\langle\vec{r}^2\rangle &= \frac{\int d^dr\ \vec{r}^2\rho(\vec{r},t)}{\int d^dr\ \rho(\vec{r},t)} = \frac{\int d^dr\ \vec{r}^2\mathrm{e}^{-\frac{\vec{r}\mathrm{D}^{-1}\vec{r}}{4t}}}{\int d^dr\ \mathrm{e}^{-\frac{\vec{r}\mathrm{D}^{-1}\vec{r}}{4t}}} = \frac{\int d^dx\ \left(\sum_{i=1}^d x_i^2\right)\mathrm{e}^{-\sum_{i=1}^d\frac{x_i^2}{4D_it}}}{\int d^dx\ \mathrm{e}^{-\sum_{i=1}^d\frac{x_i^2}{4D_it}}}\\
&= \sum_{i=1}^d \frac{\int d^dx\ x_i^2\mathrm{e}^{-\sum_{j=1}^d\frac{x_j^2}{4D_jt}}}{\int d^dx\ \mathrm{e}^{-\sum_{j=1}^d\frac{x_j^2}{4D_it}}} = \sum_{i=1}^d \frac{\int dx_i\ x_i^2\mathrm{e}^{-\frac{x_i^2}{4D_it}}}{\int d^dx\ \mathrm{e}^{-\frac{x_i^2}{4D_it}}} = \sum_{i=1}^d 2D_it\\
&= 2t\mathrm{Tr}[D]
\end{aligned}$$

We used a transformation on the eigenmodes $\vec{u}_i$ of the diffusion constant so that $\vec{r}=\sum_{i=1}^d\vec{u}_ix_i$. The eigenvalue equation has the form $\mathbf{D}\vec{u}_n=\vec{u}_nD_n$ with eigenvalues D_n and orthonormal eigenvectors $\vec{u}_n$, so that $\vec{r}^2=\vec{x}^2$. We exploited that the trace of a matrix is the sum of its eigenvalues, that is $Tr[D]=\sum_i D_i$.

Thus we obtain

$$D\overset{\mathrm{def}}{=}\frac{1}{d}Tr[\mathbf{D}]=\frac{\langle\vec{r}^2\rangle}{2dt} \tag{2.4}$$

which allows to estimate the diffusion constant from a dynamic simulation. A special case of Eq. 2.4 is the three dimensional case

$$D=\frac{\langle\vec{r}^2\rangle}{6t}$$

which is often quoted. Note, however, that this equation only holds for isotropic processes in three dimensions.

2.2.1 Extension of the Fokker Planck equation to an external potential

We consider external forces act on the diffusing particles. We use the knowledge of the equilibrium distribution in order to estimate the corresponding terms

$$\rho_{eq}(\vec{r})=\mathcal{N}\mathrm{e}^{-\frac{V(\vec{r})}{k_BT}}$$

We require now that the equilibrium distribution is also the stationary distribution of the Fokker Planck equation.

$$\vec{\nabla}\boldsymbol{D}\vec{\nabla}\rho_{eq}(\vec{r})=\vec{\nabla}\boldsymbol{D}\left(-\frac{1}{k_BT}\vec{\nabla}V\right)\rho_{eq}(\vec{r})$$

FOKKER-PLANCK EQUATION WITH FORCES

$$\partial_t\rho=\vec{\nabla}\mathbf{D}\vec{\nabla}\rho-\vec{\nabla}\left(\left[\vec{v}+\frac{D}{k_BT}\vec{F}\right]\rho\right) \tag{2.5}$$

2.3 Diffusion equation from Master equation

Let us start with the kinetic equation, which directly follows from the expressions of the transition-state theory. This is the so-called **Master equation**.

$$\partial_t P_i = \sum_j \left(P_j\Gamma_{j\to i} - P_i\Gamma_{i\to j}\right) \tag{2.6}$$

The variable P_i is the probability for the system being in the capture region of site i and $\Gamma_{i\to j}$ is the hopping rate from site i to site j. The master equation simply says that the number of particles at a given site increases when particles hop from the neighboring site into the site i and it decreases, when particles hop form site i to a neighboring site.

Our goal is to derive the diffusion equation from this master equation. As transition-state theory allows to derive the master equation from first principles, this step will provide us with a justification of the diffusion equation from first principles and a precise definition of the parameters, such as drift velocity and diffusion constant.

For a system that is out of thermal equilibrium, we can express the probability at a given site by an enhancement factor $\alpha(\vec{r})$ and the probabilities in thermal equilibrium P_i^{eq}, so that

$$P_i = P_i^{eq}\alpha(\vec{r}_i)$$

In thermal equilibrium, the enhancement factor α is spatially uniform. Close to thermal equilibrium, α will only vary slowly. Still, the equilibrium probabilities P_i^{eq} may still vary strongly throughout space: Consider for example a system with metastable sites with quite different energies.

Next we insert the Ansatz into the master equation, Eq. 2.6. In order to simplify the notation we introduce $\alpha_i \overset{\text{def}}{=} \alpha(\vec{r}_i, t)$.

$$P_i^{eq}\partial_t\alpha_i = \sum_j \left(P_j^{eq}\alpha_j\Gamma_{j\to i} - P_i^{eq}\alpha_i\Gamma_{i\to j}\right) \tag{2.7}$$

Now we exploit the condition of **detailed balance**

DETAILED BALANCE

The principle of detailed balance says that there is no net current in thermal equilibrium.

$$P_i^{eq}\Gamma_{i\to j} = P_j^{eq}\Gamma_{j\to i} \tag{2.8}$$

Detailed balance is a sufficient, but not a necessary condition for a stationary probability distribution.

The reason for requiring detailed balance in thermal equilibrium is that currents result in dissipation, which is impossible in state of thermal equilibrium as that is a state of maximum entropy. Detailed balance follows directly from transition-state theory.

Insertion of the condition of detailed balance, Eq. 2.8, into the above master equation Eq. 2.7 yields

$$P_i^{eq}\partial_t\alpha_i = \sum_j P_i^{eq}\Gamma_{i\to j}\left(\alpha_j - \alpha_i\right) \tag{2.9}$$

In the next step we expand $\alpha_j = \alpha(\vec{r}_j)$ about $\vec{r}_i$ up to second order in $\vec{r}_j - \vec{r}_i$. Due to this assumption our derivation is limited to slowly varying enhancement factors $\alpha(\vec{r})$.

$$\begin{aligned}
P_i^{eq}\partial_t\alpha_i &\overset{\text{Eq. 2.9}}{=} \sum_j P_i^{eq}\Gamma_{i\to j}\left(\alpha_i + (\vec{r}_j-\vec{r}_i)\,\vec{\nabla}\big|_{\vec{r}_i}\alpha + \frac{1}{2}\left((\vec{r}_j-\vec{r}_i)\,\vec{\nabla}\right)^2\Big|_{\vec{r}_i}\alpha + O(|\vec{r}_j-\vec{r}_i|^2) - \alpha_i\right)\\
&= \sum_j P_i^{eq}\Gamma_{i\to j}\left((\vec{r}_j-\vec{r}_i)\,\vec{\nabla}\big|_{\vec{r}_i}\alpha + \frac{1}{2}Tr\left[(\vec{r}_j-\vec{r}_i)\otimes(\vec{r}_j-\vec{r}_i)\right]\vec{\nabla}\otimes\vec{\nabla}\big|_{\vec{r}_i}\alpha\right) \qquad (2.10)
\end{aligned}$$

where $\otimes$ denotes the dyadic product defined by $\left(\vec{a}\otimes\vec{b}\right)_{i,j} = a_i b_j$ and $Tr[\mathbf{A}] = \sum_i A_{i,i}$ is the trace.

Now we introduce a smoothening procedure with some function $f(\vec{r})$, and average Eq. 2.10 with f:

$$\begin{aligned}
\partial_t \sum_i f(\vec{r}-\vec{r}_i) P_i^{eq} \alpha_i &= \sum_{i,j} f(\vec{r}-\vec{r}_i) P_i^{eq} \Gamma_{i\to j} \left((\vec{r}_j - \vec{r}_i)\, \vec{\nabla}\big|_{\vec{r}_i} \alpha \right) \\
&+ \mathrm{Tr} \left(\sum_{i,j} f(\vec{r}-\vec{r}_i) P_i^{eq} \Gamma_{i\to j} \frac{1}{2} \left[(\vec{r}_j - \vec{r}_i) \otimes (\vec{r}_j - \vec{r}_i) \right] \vec{\nabla} \otimes \vec{\nabla}\big|_{\vec{r}_i} \alpha \right) \qquad (2.11)
\end{aligned}$$

Now we make a fairly drastic approximation namely to replace the enhancement factor α and its derivative at $\vec{r}_i$ by its value at $\vec{r}$, the center to the function $f(\vec{r}-\vec{r}_i)$.

$$\begin{aligned}
\partial_t \alpha(\vec{r},t) \sum_i f(\vec{r}-\vec{r}_i) P_i^{eq} &= \underbrace{\left[\sum_{i,j} f(\vec{r}-\vec{r}_i) P_i^{eq} \Gamma_{i\to j} (\vec{r}_j - \vec{r}_i) \right]}_{\vec{A}} \vec{\nabla}\alpha \\
&+ Tr \left(\underbrace{\left[\sum_{i,j} f(\vec{r}-\vec{r}_i) P_i^{eq} \Gamma_{i\to j} \frac{1}{2} \left[(\vec{r}_j - \vec{r}_i) \otimes (\vec{r}_j - \vec{r}_i) \right] \right]}_{B} \vec{\nabla} \otimes \vec{\nabla}\alpha \right) \qquad (2.12)
\end{aligned}$$

In the next simplification, we will show that the right-hand side of Eq. 2.12 can be simplified. We need the identity $\vec{\nabla}\mathbf{B} = \vec{A}$ between the variables $\vec{A}$ and $\boldsymbol{B}$, which have been defined in the equation Eq. 2.12 given above.

$$\vec{A}\vec{\nabla}\alpha + Tr\left[\boldsymbol{B}\vec{\nabla}\otimes\vec{\nabla}\alpha\right] \overset{\vec{\nabla}\mathrm{B}=\vec{A}}{=} \vec{\nabla}\left(\boldsymbol{B}\vec{\nabla}\alpha\right) \qquad (2.13)$$

which is verified best by writing out the components

$$\underbrace{\left(\sum_i \partial_i B_{i,j}\right)}_{A_j} \sum_j \partial_j\alpha + \sum_{i,j} B_{i,j}\partial_j\partial_i\alpha = \sum_{i,j}\left[\partial_i\left(B_{i,j}\partial_j\alpha\right) - B_{i,j}\partial_i\partial_j\alpha + B_{i,j}\partial_j\partial_i\alpha\right] = \sum_{i,j}\partial_i\left(B_{i,j}\partial_j\alpha\right)$$

The derivation of $\vec{\nabla}\mathbf{B} = \vec{A}$ is a bit involved.

$$\begin{aligned}
\vec{\nabla}\mathbf{B} &= \sum_{i,j} \vec{\nabla} f(\vec{r}-\vec{r}_i) \frac{1}{2} \sum_j P_i^{eq} \Gamma_{i\to j} (\vec{r}_j - \vec{r}_i) \otimes (\vec{r}_j - \vec{r}_i) \\
&\overset{\vec{a}(\vec{b}\otimes\vec{c})=(\vec{a}\vec{b})\vec{c}}{=} \frac{1}{2} \sum_{i,j} \left[(\vec{r}_j - \vec{r}_i)\, \vec{\nabla} f(\vec{r}-\vec{r}_i) \right] P_i^{eq} \Gamma_{i\to j} (\vec{r}_j - \vec{r}_i) \\
&= -\frac{1}{2} \sum_{i,j} \left(f(\vec{r}-\vec{r}_j) - f(\vec{r}-\vec{r}_i) + O(\vec{r}_i - \vec{r}_j)^2 \right) P_i^{eq} \Gamma_{i\to j} (\vec{r}_j - \vec{r}_i) \\
&\approx -\frac{1}{2} \sum_{i,j} f(\vec{r}-\vec{r}_j) P_i^{eq} \Gamma_{i\to j} (\vec{r}_j - \vec{r}_i) + \frac{1}{2} \sum_{i,j} f(\vec{r}-\vec{r}_i) P_i^{eq} \Gamma_{i\to j} (\vec{r}_j - \vec{r}_i) \\
&\overset{\text{Eq. 2.8}}{=} -\frac{1}{2} \sum_{i,j} f(\vec{r}-\vec{r}_j) P_j^{eq} \Gamma_{j\to i} (\vec{r}_j - \vec{r}_i) + \frac{1}{2} \sum_{i,j} f(\vec{r}-\vec{r}_i) P_i^{eq} \Gamma_{i\to j} (\vec{r}_j - \vec{r}_i) \\
&\overset{i\to j}{=} \frac{1}{2} \sum_{i,j} f(\vec{r}-\vec{r}_i) P_i^{eq} \Gamma_{i\to j} (\vec{r}_j - \vec{r}_i) + \frac{1}{2} \sum_{i,j} f(\vec{r}-\vec{r}_i) P_i^{eq} \Gamma_{i\to j} (\vec{r}_j - \vec{r}_i) \\
&= \sum_{i,j} f(\vec{r}-\vec{r}_i) P_i^{eq} \Gamma_{i\to j} (\vec{r}_j - \vec{r}_i) = \vec{A} \qquad (2.14)
\end{aligned}$$

With this identity Eq. 2.14, the proof of Eq. 2.13 is completed and we obtain from Eq. 2.12

$$\partial_t\alpha(\vec{r},t)\sum_i f(\vec{r}-\vec{r}_i)P_i^{eq}=\vec{\nabla}\left(\underbrace{\left[\sum_{i,j} f(\vec{r}-\vec{r}_i)P_i^{eq}\Gamma_{i\rightarrow j}\frac{1}{2}\left(\vec{r}_j-\vec{r}_i\right)\otimes\left(\vec{r}_j-\vec{r}_i\right)\right]}_{B}\vec{\nabla}\alpha\right) \tag{2.15}$$

Let us now define a number of quantities:

- We define the density as

$$\rho(\vec{r})\overset{\text{def}}{=}\alpha(\vec{r})\underbrace{\sum_i f(\vec{r}-\vec{r}_i)P_i^{eq}}_{\rho^{eq}} \qquad \text{with} \qquad \int d^3r\; f(\vec{r})=1 \tag{2.16}$$

- Correspondingly the equilibrium density is

$$\rho^{eq}(\vec{r})\overset{\text{def}}{=}\underbrace{\sum_i f(\vec{r}-\vec{r}_i)P_i^{eq}}_{\rho^{eq}} \tag{2.17}$$

  To obtain the density, defined as number of particles per volume or probability density, we have to require that $f(\vec{r})$ integrates to one. This ensures that the density has the unit “one divided by volume”. Furthermore

$$\begin{aligned}\sum_i f(\vec{r}-\vec{r}_i)P_i &= \sum_i f(\vec{r}-\vec{r}_i)\int_{\Omega_i} d^3r\; p(\vec{r}')\\ &\approx \sum_i\int_{\Omega_i} d^3r\; f(\vec{r}-\vec{r}')p(\vec{r}')=\int d^3r\; f(\vec{r}-\vec{r}')p(\vec{r}')=\rho(\vec{r})\end{aligned}$$

  where $p(\vec{r})$ is the probability density.

- We define the **diffusion constant** as

DIFFUSION CONSTANT FROM MASTER EQUATION

$$\mathbf{D}(\vec{r})=\frac{\sum_{i,j} f(\vec{r}-\vec{r}_i)P_i^{eq}\Gamma_{i\rightarrow j}\frac{1}{2}\left[(\vec{r}_j-\vec{r}_i)\otimes(\vec{r}_j-\vec{r}_i)\right]}{\sum_i f(\vec{r}-\vec{r}_i)P_i^{eq}} \tag{2.18}$$

  and the

- **drift velocity**

$$\vec{v}(\vec{r})\overset{\text{def}}{=}D(\vec{r})\frac{\vec{\nabla}\rho^{eq}}{\rho^{eq}} \tag{2.19}$$

With these definitions (Eqs. 2.16,2.17, 2.18,2.19) provided above, Eq.2.15 attains the form of the **Fokker-Planck equation**

$$\begin{aligned}\partial_t\rho &= \vec{\nabla}\left(\mathbf{D}\rho^{eq}\vec{\nabla}\frac{\rho}{\rho_0}\right)=\vec{\nabla}\left(\mathbf{D}\vec{\nabla}\rho\right)-\vec{\nabla}\left(\mathbf{D}\rho\frac{\vec{\nabla}\rho^{eq}}{\rho^{eq}}\right)\\ &\overset{Eq.\ 2.19}{=}\vec{\nabla}\left(\mathbf{D}\vec{\nabla}\rho\right)-\vec{\nabla}\left(\vec{v}\rho\right)\end{aligned}$$

which is identical to Eq. 2.3. Here, however, we have derived it from microscopic defined quantities. The identity confirms that the quantities defined in Eqs.. 2.16,2.17, 2.18,2.19 are indeed identical to those used in the empirically derived Fokker Planck equation of Eq. 2.3.

Let us investigate the drift velocity

$$\begin{aligned}\frac{\vec{\nabla}\rho^{eq}}{\rho^{eq}} &= \frac{\vec{\nabla}\sum_i f(\vec{r}-\vec{r}_i)P_i^{eq}}{\sum_i f(\vec{r}-\vec{r}_i)P_i^{eq}} = \frac{\vec{\nabla}\int d^3r'\; f(\vec{r}-\vec{r}')\mathcal{N}\mathrm{e}^{-\beta V(\vec{r}')}}{\int d^3r'\; f(\vec{r}-\vec{r}')\mathcal{N}\mathrm{e}^{-\beta V(\vec{r}')}} \\ &= \frac{\int d^3r'\; f(\vec{r}-\vec{r}')\vec{\nabla}'\mathrm{e}^{-\beta V(\vec{r}')}}{\int d^3r'\; f(\vec{r}-\vec{r}')\mathrm{e}^{-\beta V(\vec{r})}} = \frac{1}{k_BT}\frac{\int d^3r'\; f(\vec{r}-\vec{r}')\mathrm{e}^{-\beta V(\vec{r}')}\left(-\vec{\nabla}\vec{V}\right)}{\int d^3r'\; f(\vec{r}-\vec{r}')\mathrm{e}^{-\beta V(\vec{r})}}\end{aligned}$$

With the definition of the force as

$$\vec{F}(\vec{r})\overset{\text{def}}{=}\frac{\int d^3r'\; f(\vec{r}-\vec{r}')\mathrm{e}^{-\beta V(\vec{r}')}\left(-\vec{\nabla}\vec{V}\right)}{\int d^3r'\; f(\vec{r}-\vec{r}')\mathrm{e}^{-\beta V(\vec{r})}} \tag{2.20}$$

we can express the **drift velocity** as

DRIFT VELOCITY

$$\vec{v}(\vec{r}) = \frac{1}{k_BT}\mathbf{D}(\vec{r})\vec{F}(\vec{r})$$

Note, however, that the diffusion constant itself is strongly dependent on temperature!

Let us return to the definition of the diffusion constant Eq. 2.18 and obtain a back-on-the envelope expression for it. To simplify the problem we assume that all sites and all jump rates are identical. Our goal is to work out the trace of the diffusion constant:

ESTIMATE OF THE DIFFUSION CONSTANT

$$Tr[\mathbf{D}] = \frac{1}{2}\Gamma\sum_j(\vec{r}_j-\vec{r}_i)^2 = \frac{n}{2}\Gamma\ell^2$$

n is the number of different transitions from a given site, ℓ is the jump length and Γ is the jump-rate for a given transition.

We can now use our simple estimate for the reaction rate used in Eq. 1.7

$$\Gamma \approx 10^{13}\mathrm{e}^{-11604\frac{E_a[eV]}{T[K]}}\,\frac{1}{sec}$$

and an estimate of the interatomic distance $\ell \approx 2$ as an estimate of the jump length to obtain a simple expression for the Diffusion constant

$$\frac{1}{3}Tr[\mathbf{D}] \approx 4n\times10^{-9}\mathrm{e}^{-11604\frac{E_a[eV]}{T[K]}}\,\frac{m^2}{sec}$$

Let us consider the case of carbon diffusion in iron. I found two values[1]

T[° C]	D[m^2/sec]
800	15×10^{-13}
1100	450×10^{-13}

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[1] Source: `http://de.wikipedia.org/wiki/Diffusionskoeffizient`

from which we can derive the activation energy from an Arrhenius construction

$$E_a[eV] = \frac{\ln[\frac{450}{15}]}{11604(\frac{1}{1078} - \frac{1}{1378})} = 1.451346$$

2.4 Relation to the Schrödinger equation

The Fokker Planck equation provides an important link between Statistical Physics and quantum mechanics. Links between Statistical Physics and quantum mechanics have been abundant an very fruitful, because many of the techniques can be, more or less directly, be transferred from one field to the other.

Consider the Fokker-Planck equation with an isotropic and spatially constant diffusion constant in the absence of a drift velocity

$$\partial_\tau \rho = D\vec{\nabla}^2 \rho$$

We have used the symbol τ instead of t because we will interpret it as imaginary time of the Schrödinger equation.

Now we perform a **Wick rotation**, that is we consider τ as **imaginary time** $\tau = it$.(thus $\partial_\tau = -i\partial_t$)

$$i\hbar\partial_t \rho = -\hbar D\vec{\nabla}^2 \rho$$

This equation is identical to the Schrödinger equation of a free particle

$$i\hbar\partial_t \psi = -\frac{\hbar^2}{2m}\vec{\nabla}^2 \psi$$

if we identify the density with a wave function, the diffusion constant by $D = \frac{\hbar}{2m}$.

If we consider the Schrödinger equation of a particle in a potential

$$i\hbar\partial_t \psi = \left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r})\right]\psi$$

and perform the Wick rotation, we obtain

$$\partial_\tau \psi = \frac{\hbar}{2m}\vec{\nabla}^2 \psi - \frac{1}{\hbar}V(\vec{r})\psi \qquad \Leftrightarrow \qquad \partial_\tau \rho = D\vec{\nabla}^2 + Q(\vec{r})\rho$$

Thus the potential term does not fit into the Fokker-Planck equation. We can interpret $Q(\vec{r})\rho(\vec{r},t)$ as sources and sinks of particles in the Fokker-Planck equation.

There is a simple physical picture of Eq. 2.21. Consider ρ as the density of animals in a population. Q can be interpreted as an effective reproduction rate. If it is positive, the population grows , because the death rate is slower than the reproduction rate. If Q is negative the animals die faster than they reproduce, and the population will die out. Thus a positive potential, corresponding to a negative Q describes a hostile environment, and a negative potential describes a fertile environment. The diffusion term would then describe that the animals wander around randomly to explore new territory. This travel instinct describes that also hostile environments are populated to a certain extent. It also has the important consequence that new areas of fertile regions are explored and populated.

One important difference between Fokker-Plank and Schrödinger equation is that the Schrödinger equation h=can have positive and negative values, while the density is always positive definite.

Chapter 3

Monte Carlo Method

The diffusion equation can be looked upon in two ways:

- One considers the diffusion equation in the 3N-dimensional space of the N-particle system. In this case we need to solve a differential equation in a 3N+1 dimensional space for N particles. The solution provides the probability density in 3N dimensional space as function of time. This problem is nearly intractable, because the density cannot be stored except for systems with the very few particles.[1] The problem is analogous to the problem of solving the Schrödinger equation for an interacting many-particle system.
- Alternatively, we can consider the diffusion equation in 3-dimensional space. Then the solution is interpreted as the particle density. However, in that case we need to assume that the particles are non-interacting. This assumption is valid only for very dilute densities, such as the concentration of dopant atoms in a semiconductor device. However, the effect that two atoms cannot occupy the same site on a lattice, is ignored.

Often we are interested in the formation of islands on a surface, or the formation of new materials. In this case the diffusion equation becomes useless for practical purposed.

An alternative method to tackle this problem is the Monte-Carlo method.

The basic feature of the kinetic Monte Carlo method have been developed in 1966 by Young and Elcock.[6] In 1975 the method has been reinvented independently[7] and termed "The N-fold Way".

A very good source on the Monte-Carlo method is the book by Landau and Binder[8]. An introduction into the kinetic Monte Carlo method has been given by Voter[9]. See also the classical paper by Fichthorn et al[10].

3.1 Basic principles

The basic idea of the Monte Carlo method is to directly simulate the **master equation** as a random process.

$$\partial_t P_i = \sum_j \left(P_j \Gamma_{j\rightarrow i} - P_i \Gamma_{i\rightarrow j} \right)$$

Note that each state i is a N-particle state, described by 3N spatial coordinates on a lattice.

The formulation of the master equation as a differential equation is a bit artificial, because the real process is not continuous but discrete and stochastic. In the Monte Carlo simulation return to description of the diffusion process as a a random process.

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[1] If one describes a probability density of 10 particles on a grid with 100 gridpoints in each direction, one has to store 10^{60} numbers. On a computer a Gigabyte (GB) of memory can hold about 10^9 numbers. Thus we would need a computer with 10^{52} GB of storage. to simply hold the density.

Imagine the model for radioactive decay as a simple example for a random process: Initially, the nucleus is in a certain state, which can undergo a radioactive reaction to form a more stable nucleus, while emitting an electron, neutron, photon etc. The probability that the nucleus is in the initial state shall be $P_a(t)$ and the probability that it is in the final state is $P_b(t)$. The rate constant from the initial to the final state is named Γ and we assume that the back reaction has a rate that is so low that it can be ignored. The master equation for this problem is

$$\begin{aligned}\partial_t P_a &= -P_a\Gamma\\ \partial_t P_b &= +P_a\Gamma\end{aligned}$$

At a given time, the nucleus is in the initial or in the final state. We describe the state of the nucleus by a discrete variable $\sigma(t)$, which is equal to one, if the nucleus is in the initial state and zero otherwise. As a function of time $\sigma(t)$ will remain for a period time in its initial state and suddenly switch to zero.

While we cannot predict at what time nucleus will decay, we know the probability that a nucleus decays in a certain time period Δt, namely

$$W\overset{\text{def}}{=}\Gamma\Delta t$$

We can implement a random process, if we divide the time axis into discrete time intervals Δt. In each time interval we choose a random number, which has the value 1 with probability W and zero otherwise. If this random number is equal to one and the particle is in the initial state, we change the state of the nucleus to its final state. If the random number is zero, we leave the nucleus in its current state.

In practice we generate a random number r with equal probability in the interval $[0,1]$. Such **random number generators** exist in most computer languages. In order to induce the decay with probability $\Gamma\Delta t$, we induce the decay if $r < \sigma(t_i)\Gamma\Delta t$. It is important that $\Gamma\Delta t << 1$. Then the transition occurs with probability $\sigma(t_i)\Gamma\Delta t$ and with probability $1-\sigma(t_i)\Gamma\Delta t$ the system remains in the same state.

If we average over many (N)such processes, we obtain the probability

$$P_a(t) = \lim_{N\to\infty}\frac{1}{N}\sum_{i=1}^{N}\sigma_i(t)$$

that obeys the master equation Eq. 3.1. We can estimate the transition rate from

$$\begin{aligned}\partial_t P_a(t) &= \lim_{\Delta t\to 0}\frac{P_a(t+\Delta t)-P_a(t)}{\Delta t} = \lim_{\Delta t\to 0}\frac{1}{\Delta t}\lim_{N\to\infty}\frac{1}{N}\sum_{i=1}^{N}(\sigma_i(t+\Delta t)-\sigma_i(t))\\ &= \lim_{\Delta t\to 0}\frac{1}{\Delta t}\lim_{N\to\infty}\frac{1}{N}\sum_{i=1}^{N}(-\sigma_i(t)\Gamma\Delta t) = \lim_{\Delta t\to 0}(-P_a(t)\Gamma)\\ &= -P_a(t)\Gamma\end{aligned}$$

The random process described here is a so-called **Markov process**. If the probabilities for the transitions only depend on the current distribution of particles, but not on what happened in the past, the process is called a Markov process.

Thus we have learned how the master equation can be described by a random process, and how the process is implemented in practice using random numbers.

However the problem we applied it to was trivial and the methodology was very inefficient, because most of the time, nothing happens during the random process.

3.2 Random number generators

On the computer, one cannot construct true **random numbers**. However a good approximation are pseudo-random numbers. Pseudo-random number generators construct a sequence of numbers with the proper distribution, that, however, eventually repeats itself. Random-number generators are formulated such that they create a set of integer values R in a certain interval $[0, R_{max}[$. This interval is then mapped into the interval $[0, 1[$ by division by R_{max}.

The algorithms underlying random-number generators seem to be utterly simple. However, the difficulties come with the detail, algorithmic and numerical. People say that a large fraction of the published Monte Carlo results are invalid due to a poor choice of the random-number generator. I will not go into every detail, but I will mention some frequent algorithms, and then provide one implementation in App. A.1. This implementation may not be the best, but it seems to provide a reliable standard.

3.2.1 Congruential method

The most common method is the **linear congruential generator**, invented by D. Lehmer in 1951, which produces a series

$$R_{n+1} = (aR_n + b) \mod m$$

The modulo operation in an expression $x \mod y$ determines the remainder of x/y after subtracting the integer part.

The values of a and b must be chosen properly. Park and Miller[11] developed the “Minimal Standard Linear Congruential Generator”, which uses the values $a = 16807$, $b = 0$, and $m = 2^{31} - 1$.

Congruential methods can be mixed. One can, for example, generate a table of random numbers and use a second random number generator to randomly choose numbers from the table.

3.2.2 Shift register algorithms

Another class of random number generators are the **shift register algorithms**. The shift register algorithm works as follows:

1. construct a series of random numbers
2. continue the series using

$$R_n = R_{n-p} \oplus R_{n-q}$$

where the $\oplus$ operation is the bitwise exclusive-or operation, also denoted "XOR". The **exclusive-or** also called the **exclusive disjunction** is a logical function of two logical variables a and b, that produces the value true, if $a \neq b$ and the value false otherwise.

a	b	$a \oplus b$
true	true	false
true	false	true
false	true	true
false	false	false

Other notations are $a \oplus b = a\, XOR\, b = (a \neq b) = a + b$. It can be represented by the unary logical “not” ($\neg$) operation and the binary logical “or” ($\vee$) and “and” ($\wedge$) operations as

$$a \oplus b = (a \wedge \neg b) \vee (\neg a \wedge b)$$

The exclusive or of two integer numbers is performed by first converting the number into its binary representation $r = \sum_{n=0} c_n 2^n$ where c_n can have values 0 or 1, and the coefficients c_n are written from right to left with increasing n. A value $c_n = 1$ is interpreted as logical value "true" and $c_n = 0$ is interpreted as logical value "false". Then the exclusive or is applied bitwise, that is for each n.

The exclusive or of two integer numbers that may have values 0 or 1, can also be represented as

$$a \oplus b = a + b \text{ modulo } 2$$

As an example

$$14 \oplus 9 = 1110 \oplus 1001 = 0111 = 7$$

Only certain pairs p and q in the shift register algorithm provide good random numbers. A common set used in the random number generator "R250", is $p = 250$ and $q = 103$.

3.2.3 Mersenne twister

Recently, I found on the internet reports of the Mersenne twister, which has been developed in 1997 by M. Matsumoto and T. Nishimura. The commonly used variant of the Mersenne twister is called MT19937. The Mersenne twister has a repeat period of $2^{19937} - 1$ and is said to have superior properties regarding equidistribution, speed, and that it passes a number rather stringent tests of statistical randomness.

3.2.4 Random numbers with non-uniform distributions

So-far we discussed random-number generators that are equi-distributed in the interval $[0, 1[$. That is the probability distribution is

$$p(x) = \theta(x)\theta(1 - x)$$

where $\theta(x)$ is the Heaviside function[2]

Often, one needs random numbers with a specified distribution $p(x)$. Such random numbers can be constructed from equi-distributed random numbers as described in the following:

Our starting point is a sequence of equi-distributed random numbers x in the interval $[0, 1]$. That is, the probability distribution $p(x)$ of the equi-distributed random numbers is $p(x) = 1$. Our goal is to find a mapping $y(x)$, which converts the sequence of equi-spaced random numbers into the sequence of random numbers y with the specified probability distribution $q(y)$ on the interval $[a, b]$. The probability distribution $q(y)$ must be normalized so that

$$\int_a^b dy q(y) = 1 \tag{3.1}$$

We start out from the condition that the probability for a random number y to fall within an interval of width $dy = \frac{dy}{dx} dx$ at $y(x)$ is equal to the probability that the variable x falls into the interval of width dx at x.

$$q(y)dy = p(x)dx = p(x(y)) \underbrace{\frac{dx}{dy} dy}_{dx}$$

$$\Rightarrow \qquad \frac{dx}{dy} = \frac{q(y)}{p(x(y))} \overset{p(x)=1}{=} q(y)$$

$$\Rightarrow \qquad x(y) = \underbrace{x(a)}_{=0} + \int_a^y dy' \left. \frac{dx}{dy} \right|_{y'} = \int_a^y dy' \, q(y') \tag{3.2}$$

---

[2] The Heaviside function vanishes for negative arguments, and is equal to zero for positive arguments.

After obtaining $x(y)$ from the integral, we invert the function to obtain $y(x)$. This is our desired mapping of the random numbers.

From a sequence of random numbers x in the interval $[0, 1]$, we obtain the sequence of random numbers $y(x)$ by simply applying the mapping $y(x)$ to each random number x. The resulting sequence of random numbers y has the probability distribution $q(y)$ on the interval $[a, b]$.

3.3 The Ising model

Let us therefore introduce the two-dimensional Ising model, which allows us to explore already a number of interesting phenomena and real processes.

Model description of the Ising model

We apply our simulation to the two-dimensional square **Ising model**. The Ising model is considered the prototypical model system for a magnetic material.

A state of the Ising model is given by the orientation of spins arranged on a lattice. A single spin at the lattice position α is described by σ_α which can gave two values. The values may be the spin orientations ↑ and ↓, or they may be bits such as 0 and 1. A many particle state is a set of the spin values on all lattice sites, that is $\vec{\sigma} = (\sigma_1, \sigma_2, \ldots \sigma_N)$.

The total energy of a many particle state is

$$E(\vec{\sigma}_i) = \sum_\alpha \left[-H\sigma_{\alpha,i} - \frac{1}{2} J \sum_{\beta \in NN(\alpha)} \sigma_{\alpha,i}\sigma_{\beta,i} \right]$$

Here B is a magnetic field. The sum over β runs over all nearest neighbors of the site α.

In particular we will focus here on Ising model on the two-dimensional square lattice.

Applications of the Ising model

While the Ising model has been developed as a model for magnetism, it is actually a poor model for magnetic systems. The only real magnetic system it can realistically describe, are dilute spins in a magnetic field, where the interactions are so small that phase transitions are not of interest.

However the Ising model is a perfect model for the motion of atoms on a lattice. Consider adsorbed ad-atoms on a surface. The atoms can occupy only certain lattice sites. A given lattice site can be either occupied or unoccupied, which corresponds to the two states of the ising model, spin up or spin down. The interaction describes the binding between two adatoms adsorbed on neighboring sites.

The classical Ising model describes a problem where the diffusion between sites is low, and that states changes by adsorption and desorption of adatoms.

We will later see that we can extend the Ising model to a model where atoms change sites, which describes the diffusion of atoms on a surface. We can furthermore also mix diffusion and adsorption-desorption processes to describe for example the growth of a material during molecular beam epitaxy.

The three Ising model can for example describe the formation of different phases from a alloy with different type of atoms. The “spin-up” state would in this case describe a lattice site occupied by a atom of type A and in the “spin-down” state it would be occupied by atom of type B.

3.4 Metropolis algorithm

In order to develop the concepts, let us start with the most simple Monte-Carlo algorithm, namely the **Metropolis algorithm**[12].

The methodology described in Section 3.1 is inefficient, because it as an extremely low **acceptance ratio**. Essentially all the time is spent with repeatedly drawing random numbers, while the state changes with very small probability. Furthermore the time step is determined by the fasted process, which leads to an even less efficient description of processes with lower rate.

The Metropolis algorithm sacrifices the dynamic interpretation of the stochastic process, but considers it only as a tool to determine the properties of an ensemble in thermal equilibrium. As long as one is not interested in time-correlation functions of the type $\langle A(0)B(t)\rangle_T$, the time scales are irrelevant in thermal equilibrium. The only quantity of interest is the equilibrium distribution P_i^{eq}, which is defined by the stationary master equation

$$\sum_j \left(P_j^{eq}\Gamma_{j\to i} - P_i^{eq}\Gamma_{i\to j} \right) = 0$$

A sufficient condition for the equilibrium distribution is the requirement of detailed balance

$$P_j^{eq}\Gamma_{j\to i} - P_i^{eq}\Gamma_{i\to j} = 0$$

We observe immediately, that the jump rates $\Gamma_{i\to j}$ can be changed nearly arbitrarily, as long as the ratio

$$\Gamma_{i\to j}/\Gamma_{j\to i}$$

remains unchanged.

This allows us to scale the jump rates up such that for each pair of states, one of the jump probabilities $\Gamma\Delta t$ becomes equal to 1, that is

$$\Gamma'_{i\to j} = \frac{1}{\Delta t}\frac{\Gamma_{i\to j}}{\max\{\Gamma_{i\to j},\Gamma_{j\to i}\}} \qquad \text{and} \qquad \Gamma'_{j\to i} = \frac{1}{\Delta t}\frac{\Gamma_{j\to i}}{\max\{\Gamma_{i\to j},\Gamma_{j\to i}\}}$$

Thus the new jump probabilities are

$$W'_{i\to j} = \Gamma'_{i\to j}\Delta t = \min\left\{1, \frac{\Gamma_{i\to j}}{\Gamma_{j\to i}}\right\} \tag{3.3}$$

$$W'_{i\to j} = \Gamma'_{j\to i}\Delta t = \min\left\{1, \frac{\Gamma_{j\to i}}{\Gamma_{i\to j}}\right\} \tag{3.4}$$

We see that the Metropolis algorithm maximizes the acceptance ratio, by pairwise scaling up the reaction rates to the maximum possible values compatible with the requirement of detailed balance. While doing this, the time scales of the processes are completely mixed up, so that any prediction about sequence of events is unphysical.

The ratio of the forward and backward jump rates between two sites is independent of the energy of the transition state, but it is given alone by the equilibrium probability of a state. This is again a direct consequence of the condition of detailed balance, Eq. 2.8.

$$\frac{\Gamma_{i\to j}}{\Gamma_{j\to i}} = \frac{P_j^{eq}}{P_i^{eq}}$$

The equilibrium probabilities can be expressed in turn by the free energies

$$P_i^{eq} = \mathcal{N} e^{-\frac{1}{k_BT}F_i(T)} = \frac{1}{Z}\int_{\Omega_i} d^{3N}r\ e^{-\frac{1}{k_BT}E(\vec{r})}$$

This gives the adjusted jump probabilities as

$$W'_{i\to j} = \min\left\{1, \mathrm{e}^{-\frac{1}{k_BT}(F_j(T)-F_i(T))}\right\}$$

Thus if the diffusion event lowers the free energy, it is accepted with certainty. If on the other hand the event would increase the free energy, it may be accepted as well, but only with probability $\mathrm{e}^{-\frac{1}{k_BT}(F_j(T)-F_i(T))}$.

In the Metropolis algorithm a transition is always accepted if it lowers the energy. However, with a certain probability, the system can also increase its energy. This allows the system to overcome barriers and thus explore the configuration space for lower minima of the total energy. Note that these barriers are not to be confused with the barriers described in transition-state theory. Rather they describe valleys

3.4.1 Machinery of the Metropolis algorithm

This provides us with the Metropolis algorithm

1. Construct a starting configuration, that is an arbitrary many particle state.
2. Select a certain transition between many particle states. In the following we denote the initial state as i and the final state as j.
3. Determine the energy difference $F_j - F_i$
4. Determine the transition probability as

   $$W_{i,j} = \min\left[1, \mathrm{e}^{-\frac{1}{k_BT}(F_j(T)-F_i(T))}\right]$$

   and accept the move with this probability.

   This is implemented in the following way:

   - If the energy is lowered by the transition, accept the transition with certainty.
   - if the energy increases by the transition accept the transition with probability $W_{i\to j} = \mathrm{e}^{-\frac{1}{k_BT}(F_j(T)-F_i(T))}$. In order to decide if the transition is accepted or not, draw a random number between 0 and 1. Accept the move if the random number is smaller than $\mathrm{e}^{-\frac{1}{k_BT}(F_j(T)-F_i(T))}$ and discard the move if it is larger. Most computer languages offer an intrinsic random number generator, that creates a sequence of pseudo-random numbers in the interval $[0, 1]$.
5. calculate the observable quantities for the resulting state and add it to the average. Also, if the move has been deferred, the observable of the current state has to be added. That is a certain state may be counted several times.
6. proceed with step 2 using the current state instead of the initial state.

3.4.2 Monte Carlo versus direct integration

The reader may now ask, why we are not simply average over all states, as we need to know the probability for each state anyway. The reason is that Monte Carlo is more efficient. Consider the number of states for a 2-dimensional ising model with $50 \times 50 = 2500$ lattice points. Since each site can be in one of two states, there are $2^{2500} \approx 10^{750}$ different states. A Monte Carlo step takes about 2×10^{-7} sec on my laptop. This corresponds to about 10^{14} time steps per year. Thus it will take 10^{731}years to complete the calculation by directly averaging over states. Monte Carlo does the same job in less than a minute.

Why is Monte Carlo so efficient? Monte Carlo visits states with little probability very rarely. Thus it concentrates on those parts of the sum that is relevant.

The reader may ask if Monte Carlo does not count states several times, leading to an inherent inefficiency. Again the answer is related to the dimension of the configuration space: In the above example each state has 2500 transitions to a neighboring many-particle state. Hence, the probability that it hops directly back to the same state is only a fraction of a promille. The probability to return after the particle hopped a few steps further is even lower. Thus it is extremely rare that Monte Carlo visits the same state twice.

This observation has implications on a general problem-solving process. If one is faced with a difficult problem, it is advantageous to proceed by trial and error, which corresponds to the Monte Carlo approach and is related to brain storming. It is important to try new things as much as possible. This step is sensible if the space of possible solutions is very large, that is the dimensionality is large. However, after a while of poking around, one should attempt to find a systematic approach, that is one should attempt to lower the dimension of the search space.

It also reflects on the scientific process, a permanent frustration to every organization. Organizations always attempt to identify the "best way for research" and they fail consistently. The reason is that the scientific process is efficient, because people have rather different strategies. In basic science, it is often not even clear what to look for. There are people to stay away from the main stream and frequently try out radically new ideas. They are likely to find from time to time radically new things. However they do not stay there very long and soon start with something new. There are also other scientists, that do smaller steps and investigate problems in more depth. This is important to explore whether a certain approach is not only new but also whether it has a wider applicability. Finally, there is the engineering approach, which deals with problems, for which the basic route to the solution is clear, but the process has to be optimized. This is an example of a low-dimensional process, where a systematic exploration is most successful. None of the three models to do research is efficient by itself. Only if they work together the full efficiency of the scientific process, which at times seems rather chaotic, is guaranteed.

3.4.3 Application to the two-dimensional Ising model

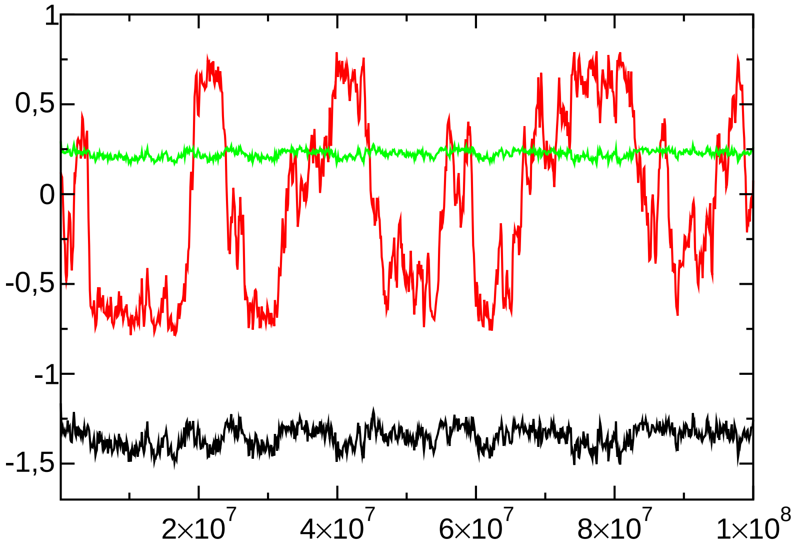

Fig. 3.1: Monte Carlo simulation on a 50 $\times$ 50 two dimensional square lattice. Black line: average total energy per site as function of number of MC steps. Red: averaged magnetization. Green: acceptance ratio. Averaging has been done over 10^5 MC-steps.

The code of the following simulation is given in App. B.1. We have chosen $H = -0.02$, $J = 1$ and $k_BT = 2.3$. The temperature is close to the Curie temperature of the ising model.

The magnetization as function of time is shown in Fig. 3.1. Observe in Fig. 3.1 that the magnetization per site jumps between 0.7 and -0.7. This is indicative of a ferromagnetic material. We also see on p. 40 that the spins have arranged in ferromagnetic domains. The domains are connected across the boundaries of the unit cell, which shows us that the cell is too small and that the simulation suffers from **finite size effects**.

Note however, that this simulation only shows a section of a trajectory of 10^8 Monte Carlo moves, It seems to be sufficient to show the characteristic behavior, however, it is insufficient to average properly over the periods during which the materials is polarized in one or the other direction.

The acceptance ratio lies at 0.25, that is a move is accepted every fourth move time slice. This is a quite satisfactory value. At lower temperatures and with larger magnetization the acceptance ratio would drop to a fairly low value, rendering the Metropolis algorithm fairly inefficient for those cases.

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Snapshot of a Monte Carlo simulation of the 2-dimensional square Ising model. We observe that Weiss domains have developed. The existence of Weiss-domains indicates that the temperature of the simulation is below the Curie temperature

3.5 Kinetic Monte Carlo method

The Metropolis algorithm is very inefficient at low temperatures. The system progresses very slowly, because most attempts for a transition are unsuccessful. One says that the **acceptance ratio**, the ratio of accepted versus deferred transitions, is very low.

As an example, consider the Ising model below the Curie temperature. The system consists of ferromagnetic domains. Most of the spins are parallel with their neighbors, so that a spin flip has a large energy cost and consequently a low acceptance ratio. Only a few spins at the domain boundary can revert their spin with reasonable probability, because their neighbors are partly parallel and partly antiparallel. A spin flip shifts the domain boundary, but it has only a minor effect on its size. In the low-temperature limit and in the absence of magnetic fields, the energy is proportional to the size of the domain boundaries.

Even though we have artificially modified the jump rates in Eq. 3.4, the Monte Carlo method described before is a time-step based method. We step forward on an artificial time axis and estimate, whether a transition occurs or not. A better way to deal with the problem is kinetic Monte Carlo. Kinetic Monte Carlo describes the process on the physical time axis. It can however also be performed with scrambled jump rates a la Eq. 3.4 as in the Metropolis algorithm to bring the processes onto the same time scale. Then, the method is called N-fold way.[3] Here one determines, which transition is the next to occur, and then estimate the time lag up to this process.

In order to make the simulation tractable, we divide the transitions into classes so that all transitions in each class have the same transition probabilities. In each step one selects first a class of transitions. Out of this class we then select at random one transition out.

The main advantage of the kinetic Monte Carlo method, is that it allows to study processes in real time, and thus provides realistic dynamical information.

3.5.1 Selecting a transition

Consider now that the system is initially in state X_i. The probability that it ends up in state X_j with time period Δ is $\Gamma_{i\rightarrow j}\Delta$. Remember that $\Gamma_{i\rightarrow j}$ is the jump rate for the transition between the two states. The probability that the *next* event is a transition to X_j is

$$W_{i\rightarrow j}=\frac{\Gamma_{i\rightarrow j}\Delta}{\sum_{k\neq i}\Gamma_{i\rightarrow k}\Delta}=\frac{\Gamma_{i\rightarrow j}}{\sum_{k\neq i}\Gamma_{i\rightarrow k}}$$

This probability is independent of the time step Δ.[4]

Now we pick one of the possible events considering the probabilities. Numerically we choose a random number x between zero and one. If

$$\sum_{k=1}^{j-1}P_k<x<\sum_{k=1}^{j}P_k$$

then the transition to state j is chosen. As demonstrated in figure 3.2, this procedure picks the transition to state X_j exactly with probability P_j.

In practice we divide all possible processes up into process classes, where each member in a process class has the same rate as any other. Then we determine the probability that any process in one class will be selected. The class probabilities are simply the probability of one process in the class multiplied with the number of processes in the class.

By choosing a random number we select first a process class. In a second step we select one member randomly from this process class.

---

[3] The distinction is not often made.

[4] $\Gamma_{i,j}\Delta$ is the propability that the transition to state X_j occurs in the time interval Δ. The probability that any transition occurs within this interval is $\sum_{k\neq i}\Gamma_{i\rightarrow k}\Delta$. Thus, if we ask, after one transition occurred, for the probability that this event was the transition X_j, we obtain $\frac{\Gamma_{i\rightarrow j}\Delta}{\sum_{k\neq i}\Gamma_{i\rightarrow k}\Delta}$. This conditional probability is independent of Δ.

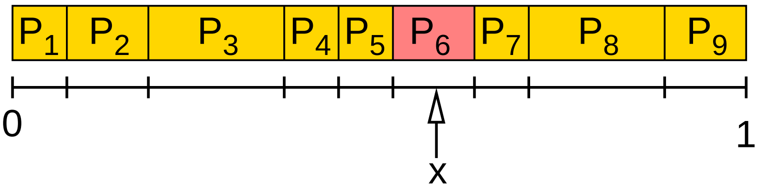


Fig. 3.2: Given the probabilities P_j for events Z_j, one covers the interval $[0,1]$ with intervals of size P_j. Remember that $\sum_j P_j = 1$. A random number between zero and one will fall in the interval for the event Z_j, which extends from $\sum_{k=1}^{j-1} P_j$ to $\sum_{k=1}^{j} P_j$ with probability P_j.

3.5.2 The time delay

Next, we need to determine the physical time interval until this process occurs, the so-called **waiting time**. One possibility would be to calculate the time from the total rate $\Gamma_{tot} = \sum_k \Gamma_k$ for all processes,

$$\Delta = \frac{1}{\sum_k \Gamma_k}$$

However, this choice would discribe a process which occurs precisely after time Δ. In reality, however, there will be a spread of waiting times.

A more rigorous choice is obtained with the help of the maximum-entropy principle. Let us assume that we know that a transition has occured. Let us furthermore assume that we know the rate Γ_{tot} for this transition. We would like to know, **when** it occurred. We are interested in the waiting time. Let us introduce the probability density $p(t)$ defined such that $\int_{t_1}^{t_2} dt\, p(t)$ is the probability that the transition occured in the interval $[t_1, t_2]$. Because we know beforehand that the transition occurred, the probability density is normalized, i.e. $\int_0^\infty dt\, p(t) = 1$. The rate Γ_{tot} imposes a further condition for the probability distribution, namely that the average time is the inverse of the rate. This implies $\int_0^\infty dt\, p(t) \cdot t = \frac{1}{\Gamma_{tot}}$.

Now we use the maximum entropy principle to arrive at the least biased probability distribution for our problem.

$$S[p(t)] = -k_B \int_0^\infty dt\, p(t) \ln[p(t)] - \lambda \left(\int_0^\infty dt\, p(t) - 1 \right) - \mu \left(\int_0^\infty dt\, p(t) t - \frac{1}{\Gamma_{tot}} \right)$$

where we introduced as constraint the normalization and the fact that the expectation value of the delay time must be the inverse total rate. The first term is the entropy functional that we know as $S[P_1, \ldots, P_N] = -k_B \sum_i P_i \ln[P_i]$. The only difference to the known form with discrete probabilities P_i is that we use a continuous probability density $p(t)$ and consequently the sum is replaced by an integral. The second and third terms in the expression above are the two constraints, one for the norm and the other for the average rate.

The equilibrium condition $\frac{\delta S}{\delta p(t)} = 0$ yields

$$-k_B \ln[p] - k_B - \lambda - \mu t = 0 \qquad \Rightarrow \qquad p(t) = \mathrm{e}^{-1-\frac{\lambda}{k_B}} \cdot \mathrm{e}^{-\frac{\mu t}{k_B}} \tag{3.5}$$

Now we insert the normalization constraint

$$\begin{aligned} \frac{dS}{d\lambda} = 0 \qquad \Rightarrow \qquad \int_0^\infty dt\, p(t) &\overset{\text{Eq. 3.5}}{=} \mathrm{e}^{-1-\frac{\lambda}{k_B}} \int_0^\infty dt\, \mathrm{e}^{-\frac{\mu t}{k_B}} \overset{!}{=} 1 \\ \Rightarrow \mathrm{e}^{1+\frac{\lambda}{k_B}} &= \int_0^\infty dt\, \mathrm{e}^{-\frac{\mu t}{k_B}} = \frac{k_B}{\mu} \int_0^\infty dx\, \mathrm{e}^{-x} = \frac{k_B}{\mu} \\ \overset{\text{Eq. 3.5}}{\Rightarrow} \qquad p(t) &= \frac{\mu}{k_B} \mathrm{e}^{-\frac{\mu \Delta}{k_B}} \end{aligned} \tag{3.6}$$

The second constraint condition yields

$$\begin{aligned}
\frac{dS}{d\mu} = 0 \qquad \Rightarrow \qquad \int_0^\infty dt\; p(t)t \quad &= \quad \frac{1}{\Gamma_{tot}} \\
\Rightarrow \frac{1}{\Gamma_{tot}} \overset{Eq.\ 3.6}{=} \int_0^\infty dt\; t\frac{\mu}{k_B}\mathrm{e}^{-\frac{\mu t}{k_B}} &\overset{x \overset{\text{def}}{=} \frac{\mu}{k_B}t}{=} \frac{k_B}{\mu}\int_0^\infty dx\; x\mathrm{e}^{-x} \\
&= \quad \frac{k_B}{\mu}\int_0^\infty dx\; \left[-\partial_x\left(x\mathrm{e}^{-x} + \mathrm{e}^{-x}\right)\right] = \frac{k_B}{\mu} \\
\Rightarrow \mu \quad &= \quad k_B\Gamma_{tot}
\end{aligned}$$

After inserting this result into Eq. 3.6, we obtain the final expression for the probability density of the waiting time.

$$p(t) = \Gamma_{tot}\mathrm{e}^{-\Gamma_{tot}t} \tag{3.7}$$

Our next challenge is to construct a random number that picks out a waiting time in the interval $[t, t+dt]$ is obtained with probability $p(t)dt$. We start out with our standard random variable x which has an equal probability density in the interval $[0, 1]$. Then we introduce a transformation $t = f(x)$ from the variable x in the interval $[0, 1]$ to the variable t in the interval $[0, \infty[$, The transformation is chosen such the probability for $t = f(x)$ is equal to $p(t)$ of x is equally distributed in $[0, 1]$.

The probability for a value of x in the interval $[x_0, x_0 + \epsilon[$ is simply ϵ. If x falls into the interval $[x_0, x_0 + \epsilon[$, then t falls into the interval $[f(x_0), f(x_0 + \epsilon) = [f(x_0), f(x_0) + \frac{df}{dx}\big|_{x_0}\epsilon + O(\epsilon^2)[= [t_0, t_0\ \frac{df}{dx}\big|_{x_0}\epsilon + O(\epsilon^2)[$. The probability for a value of t in this interval is $p(t_0)\frac{df}{dx}\epsilon + O(\epsilon^2)$. On the other hand, this probability is also simply ϵ. Thus

$$p(f(x))\frac{df}{dx}\epsilon = \epsilon \qquad \Rightarrow \qquad \frac{df}{dx} = \frac{1}{p(f(x))}$$

This is a differential equation, which we rearrange using $t = f(x)$ to

$$\begin{aligned}
&\frac{dx}{dt} = p(t) \overset{\text{Eq. 3.7}}{=} \Gamma_{tot}\mathrm{e}^{-\Gamma_{tot}t} \\
\Rightarrow \qquad &x(t) = 1 - \mathrm{e}^{-\Gamma_{tot}t}
\end{aligned}$$

The number one is simply the integration constant that has been fixed so that the intervals are mapped onto each other. Finally we invert the functional dependence and obtain

$$t(x) = -\frac{1}{\Gamma_{tot}}\ln[1 - x]$$

$t(x)$ is nothing but our transformation $f(x)$, that is

$$f(x) = -\frac{1}{\Gamma_{tot}}\ln[1 - x]$$

Thus we produce the correct probability distribution for the time delay Δ if we choose a random number x between zero and one and determine the time delay from

$$\Delta = -\frac{\ln[x]}{\sum_k \Gamma_k}$$

Note that the replacement of $(1 - x)$ by x does not change the probabilities.

3.5.3 Machinery of the kinetic Monte Carlo

1. Divide the possible transitions into classes. All transitions in a class have the same transition probability. In the 2d square Ising model without an external magnetic field, the 5 classes would be

C1 flip a spin with all neighbors aligned parallel

C2 flip a spin with three neighbors aligned parallel and one antiparallel

C3 flip a spin with two neighbors aligned parallel and two antiparallel

C4 flip a spin with one neighbor aligned parallel and three antiparallel

C5 flip a spin with all neighbors antiparallel

In the presence of a magnetic field, there would be 10 classes, because, within each of the classes listed above, one would need to distinguish, if the spin is initially parallel or antiparallel to the external field.

2. Determine the probability for each class of transitions in a given time interval.

$$W_{i,j} = \Gamma_{i\to j}\Delta t$$

The rates can, in principle, be calculated using transition-state theory, i.e. by Eq. 1.19. A simple estimate can be obtained from Eq. 1.13.

If dynamical information is secondary, and if the activation energies are unknown, we may choose the probabilities artificially as in the Metropolis algorithm with the assumption Eq. 3.4 as

$$W_{i,j} = \min\left(1, \mathrm{e}^{-\frac{1}{k_BT}(F_j-F_i)}\right)$$

which we will use in the present example for reasons of simplicity. Note however that this approximation will scramble time scales!

For the example we obtain the probabilities

$$W_{C1} = \mathrm{e}^{-\frac{8J}{k_BT}}; \qquad W_{C2} = \mathrm{e}^{-\frac{4J}{k_BT}}; \qquad W_{C3} = 1; \qquad W_{C4} = 1; \qquad W_{C5} = 1$$

3. Set up a process list, which includes all transitions and attributes a class to each of them. Enumerate the number of transitions in each class for the current state of the system. The number of transitions in class Ci is M_{Ci}.

4. Select one of the classes according to its aggregate probability

$$X_{Ci} = \frac{W_{Ci}M_{Ci}}{\sum_i W_{Ci}M_{Ci}}$$

Note that we can replace W_{Ci} with the real jump rates, because the time interval Δt drops out. In practice we draw a random number r between zero and one. If the random number lies in the interval

$$\sum_{i=1}^{n-1} X_{Ci} < r < \sum_{i=1}^{n} X_{Ci}$$

we select the process class Cn.

5. Select one particular transition in this class at random.

6. Perform the move and update the process list.

7. Estimate the time delay $\Delta = -\frac{\ln[r_t]}{\Gamma_{tot}}$ from a a random number r_t from [0,1].

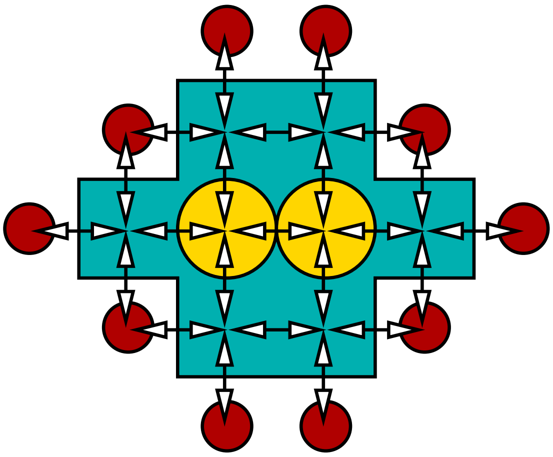
8. Continue with step 4.

3.6 Diffusion processes

We have done a long detour from the diffusion processes we wanted to simulate initially. What we have done so far will be useful when we investigate phase transitions and phase stability.

Now it is time to introduce the next complication. The difference is not one of principle but one of implementation. Instead of flipping spins, we now exchange spins, respectively, we move atoms from occupied sites to unoccupied ones. This makes the process list considerably more complex, because the energy of a jump depends on the environment of two atoms. When updating the process list we need to consider not only the two sites and their neighborhood, but also all neighbors of atoms whose neighborhood has changed, that is up to second nearest neighbors of the two central sites.

In the following figure we represent the updating procedure of the process list. The yellow circles indicate the two sites, on which the spins are exchanged. The double arrows indicate all the possible processes that are affected by the exchange of spins on the two central sites.



3.7 Continuous Monte Carlo simulations

Sofar we discussed Monte Carlo simulations on a lattice. Here we shall discuss how to describe a continuous process such as the Brownian motion. Brownian motion is based on the observation of the british botanist Robert Brown (1773-1858) who observed the motion of particles suspended in a fluid. The motion was due to thermal fluctuations.

The mathematical model for the observed trajectories is the Wiener process[5]

One way to implement such a stochastic process is to determine in each time step of the simulation a random displacement vector. The displacement vector is a random variable which has itself a probability distribution, which is the so-called **transition function** $t(\vec{x} \rightarrow \vec{x}')$. Then one accepts this move with probability

$$W_{\vec{x}\rightarrow\vec{x}'} = t(\vec{x} - \vec{x}')min\left\{1, \frac{P^{eq}(\vec{x}')}{P^{eq}(\vec{x})}\right\}$$

where $P^{eq}(\vec{x})$ is the probability density in thermal equilibrium. If we wish to create a canonical ensemble of a system with potential energy $V(\vec{x})$, the equilibrium distribution would be $P^{eq}(\vec{x}) = \frac{1}{Z}\mathrm{e}^{-\beta V(\vec{x})}$.

---

[5] Norbert Wiener (1894-1964).American mathematician. Pioneer of stochastic and noise processes.

Choice of the random displacement vector

A common choice for the transition function is a constant within a 3N-dimensional hypercube, where N is the number of particles.

$$t(\vec{q}) = \begin{cases} \frac{1}{a^{3N}} \text{ if } & |q_i| < \frac{a}{2} \\ 0 \text{ else} & \end{cases}$$

a is the side length of the hypercube.

Proof

Let us consider the time evolution of the probability distribution for the random walkers

$$P(\vec{x}, t + \Delta) = P(\vec{x}, t) + \int d^{3N}x \; \left[P(\vec{x}', t)W_{\vec{x}' \to \vec{x}} - P(\vec{x}, t)W_{\vec{x} \to \vec{x}'}\right]$$

This equation says that the distribution at a given point $\vec{x}$ increases when particles hop to this site and it decreases if particles hop from this point to other sites.

The stationary solution fulfills the law of detailed balance, namely

$$P(\vec{x}')W_{\vec{x}' \to \vec{x}} = P(\vec{x})W_{\vec{x} \to \vec{x}'}$$

Thus if we wish to determine a random process that produces a given equilibrium distribution $P^{eq}(\vec{x})$ the transition probabilities must fulfill.

$$\frac{W_{\vec{x} \to \vec{x}'}}{W_{\vec{x}' \to \vec{x}}} = \frac{P^{eq}(\vec{x}')}{P^{eq}(\vec{x})}$$

Thus we can choose transition probabilities

$$W_{\vec{x} \to \vec{x}'} = t(\vec{x} - \vec{x}') \min \left\{1, \frac{P^{eq}(\vec{x}')}{P^{eq}(\vec{x})}\right\}$$

with an inversion symmetric transition function $t(\vec{q})$, that is $t(\vec{q}) = t(-\vec{q})$

Implementation

The random process is implemented as follows.

1. construct a starting vector $\vec{x}$
2. choose a random atom
3. create a random 3-dimensional displacement vector from three random numbers in the interval $[-\frac{a}{2}, \frac{a}{2}]$.
4. determine the equilibrium probability $P^{eq}(\vec{x}')$ in the displaced configuration.
5. accept the move with probability $\min[1, \frac{P^{eq}(\vec{x}')}{P^{eq}(\vec{x})}]$.
6. increment the time step number and the add the current value of the observables, that is $\vec{x}$ or $\vec{x}$, to the sum.
7. proceed with step 2.

Chapter 4

Quantum Monte Carlo

4.1 Variational Quantum Monte Carlo

Variational Monte Carlo focusses on the evaluation of the energy

$$E = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

for a given many particle wave function. Doing the integration directly is not feasible because of the high dimensionality of the problem. The wave function is defined on a space with 3N degrees of freedom. Given M points in each direction we would need to determine the wave function M^{3N} times. As mentioned earlier the Monte Carlo method provides a much more economical way to do the integration.

In the Variational Quantum Monte Carlo method one first rewrites the integrals as

$$\begin{aligned}\langle\Psi|\hat{H}|\Psi\rangle &= \int d^{3N}r\ |\Psi(\vec{r})|^2 \cdot \frac{\langle\vec{r}|\hat{H}|\Psi\rangle}{\langle r|\Psi\rangle} \\ \langle\Psi|\Psi\rangle &= \int d^{3N}r\ |\Psi(\vec{r})|^2\end{aligned}$$

Note that the vector $\vec{r}$ encompasses all $3N$ coordinates.

If we find a stochastic process which produces a probability density $P(\vec{r})$ equal to the absolute square of the wave function the expectation value can directly be evaluated as time average for that stochastic process.

$$E = \lim_{n\to\infty} \frac{1}{n} \sum_{i=1}^{n} \frac{\langle\vec{r}|\hat{H}|\Psi\rangle}{\langle\vec{r}|\Psi\rangle}$$

What is left, is to find a stochastic process that fulfills the requirement that its probability density is identical to the absolute square of the wave function. That is we choose a random inversion-symmetric displacement vector and accept the move if the density at the new position is larger and, if it is smaller, we accept with probability $|\Psi_{new}|^2/|\Psi_{old}|^2$.

The variational quantum Monte Carlo method is at best as good as the trial wave function. The advantage over other methods using direct integration is that rather complex wave functions can be used.

4.2 Diffusion quantum Monte Carlo

The diffusion Quantum Monte Carlo (DQMC) method is fundamentally different from variational Quantum Monte Carlo. The Diffusion Monte Carlo method exploits the similarity of the Schrödinger equation with the Fokker-Planck equation.

We start out with the time-independent many-particle Schrödinger equation

$$-\frac{\hbar^2}{2m_e}\vec{\nabla}^2_{\vec{x}}\Psi(x)+V(\vec{x})\Psi(\vec{x})=E\Psi(\vec{x})$$

If we simply invert the sign we obtain an equation with a diffusion term

$$\frac{\hbar^2}{2m_e}\vec{\nabla}^2_{\vec{x}}\Psi(x)-V(\vec{x})\Psi(\vec{x})=-E\Psi(\vec{x})$$

where we interpret the term $D=\hbar^2/(2m_e)$ as diffusion constant.

The terms $(E-V(\vec{x}))\Psi(\vec{x})$ act as sources and sinks.

We start with a set of random walkers. Each random walker is a set of positions in the coordinate space. The walkers perform a random walk. If they are in a region where $(E-V(\vec{x})$ is positive, the random walker is split into two with a certain probability and if it is negative, it is deleted with a certain probability. Thus the number of random walker changes from time step to time step.

Before we discuss the details of the simulation, let us investigate the time evolution of a probability density. Let us consider the eigenvalue spectrum of the Schrödinger equation, which has eigenstates $|\Psi_n\rangle$ with eigenvalues E_n. The time dependent Fokker-Planck equation has the form

$$\partial_\tau|\Psi(t)\rangle=\underbrace{\frac{\hbar^2}{2m_e}\vec{\nabla}^2_{\vec{x}}\Psi(x)-\left(V(\vec{x})-E_{ref}\right)\Psi(\vec{x})}_{E_{ref}-\hat{H}}$$

The solution can be written as

$$|\Psi(\tau)\rangle=\sum_n|\Psi_n\rangle\mathrm{e}^{(E_{ref}-E_n)\tau}c_n$$

which is confirmed by insertion

$$\begin{aligned}
\partial_\tau|\Psi(\tau)\rangle &= \sum_n(E_{ref}-E_n)|\Psi_n\rangle\mathrm{e}^{-(E_{ref}-E_n)\tau}c_n\\
(E_{ref}-\hat{H})|\Psi\rangle &= \sum_n\left(E_{ref}-\hat{H}\right)|\Psi_n\rangle\mathrm{e}^{-(E_{ref}-E_n)t}c_n\\
&\overset{(\hat{H}-E_n)|\Psi_n\rangle=0}{=} \sum_n\left(E_{ref}-E_n\right)|\Psi_n\rangle\mathrm{e}^{-(E_{ref}-E_n)\tau}c_n
\end{aligned}$$

For long simulation times, only the component with the slowest decay constant, or the largest growth factor, survives, that is the one with the smallest energy eigenvalue E_n, the ground state energy E_0. Thus the probability distribution after a long simulation will reflect the ground state.

$$|\Psi(\tau)\rangle\rightarrow|\Psi_0\rangle\mathrm{e}^{-(E_{ref}-E_0)\tau} \tag{4.1}$$

If E_{ref} is larger than E_0, the random walkers will die out and need to be replenished and if it us smaller, the number of random walkers will grow exponentially. The population of random walkers is held constant by adjusting E_{ref} adiabatically.

The ground state energy can be obtained from Eq. 4.1 as

$$E_0=E_{ref}-\partial_\tau\Psi(\tau)$$

is then equal to E_{ref}, that is $E_0=E_{ref}$.

Nodal structure

The method described above can be used if the wave function is real valued and if it is always positive. For Fermions nodes must be present to reflect the anti symmetry of the wave function.

This problem is dealt with in the following way: In the so-called fixed-node approximation, the nodes are defined by an ansatz for the wave function. If the wave function at the position of the random walker changes sign, the random walker is deleted from the set. Thus one performs simulations in a pocket where the wave function has the same sign. Due to the anti-symmetry the other pockets are obtained by particle exchange and therefore contribute the same result as any other pocket. Thus it one only needs to sample one pocket of the coordinate space.

The result of the fixed node calculation is only as good as the nodal structure of the trial wave function. However the trial wave function only defines the position of the node-hypersurface, but not the shape of the wave function within one pocket.

It is also possible to go beyond the fixed node approximation and to optimize the trial wave function for an optimum node structure. Depending on the flexibility of the trial wave function, the result can be exact.

Importance sampling

As described above the Monte Carlo method is still inefficient. However the random process can be tuned by a trial wave function $|\Psi_{trial}\rangle$ to sample the important regions more effectively than the unimportant regions.

Using the trial wave function we determine

$$f(\vec{x},\tau)=\Psi(\vec{x},\tau)\Phi_{trial}(\vec{x})$$

which is approximately equal to the probability density for the particle distribution.

We obtain

$$\begin{aligned}
\partial_\tau f(\vec{x},\tau)&=\left(\partial_\tau\Psi(\vec{x},\tau)\right)\Phi_{trial}(\vec{x})\\
&=\Phi_{trial}(\vec{x})\left[\frac{\hbar^2}{2m_e}\vec{\nabla}^2+\left(E_{ref}-V(\vec{x})\right)\right]\Psi(\vec{x},\tau)\\
&=\frac{\hbar^2}{2m_e}\Phi_{trial}(\vec{x})\vec{\nabla}^2+\left(E_{ref}-V(\vec{x})\right)\Psi(\vec{x},\tau)\Phi_{trial}(\vec{x})\\
&=\frac{\hbar^2}{2m_e}\Phi_{trial}(\vec{x})\vec{\nabla}^2\Psi(\vec{x},\tau)+\left(E_{ref}-V(\vec{x})\right)\Psi(\vec{x},\tau)\Phi_{trial}(\vec{x})
\end{aligned}$$

Using the equation

$$\begin{aligned}
\vec{\nabla}^2 f&=\Phi_{trial}\vec{\nabla}^2\Psi+2\left(\vec{\nabla}\Psi\right)\left(\vec{\nabla}\Phi_{trial}\right)+\Psi\left(\vec{\nabla}^2\Phi_{trial}\right)\\
\Phi_{trial}\vec{\nabla}^2\Psi&=\vec{\nabla}^2 f-2\left(\vec{\nabla}\Psi\right)\left(\vec{\nabla}\Phi_{trial}\right)-\Psi\left(\vec{\nabla}^2\Phi_{trial}\right)\\
&=\vec{\nabla}^2 f-2\left[\left(\vec{\nabla}\Psi\right)\left(\vec{\nabla}\Phi_{trial}\right)+\Psi\left(\vec{\nabla}^2\Phi_{trial}\right)\right]+\Psi\left(\vec{\nabla}^2\Phi_{trial}\right)\\
&=\vec{\nabla}^2 f-2\vec{\nabla}\left[\Psi\left(\vec{\nabla}\Phi_{trial}\right)\right]+\Psi\left(\vec{\nabla}^2\Phi_{trial}\right)\\
&=\vec{\nabla}^2 f-2\vec{\nabla}\left[\underbrace{\Psi\Phi_{trial}}_{f}\underbrace{\frac{\vec{\nabla}\Phi_{trial}}{\Phi_{trial}}}_{\vec{\nabla}\ln[\Phi_{trial}]}\right]+\underbrace{\Psi\Phi_{trial}}_{f}\frac{\vec{\nabla}^2\Phi_{trial}}{\Phi_{trial}}
\end{aligned}$$

we obtain

Diffusion Monte Carlo with importance sampling

$$\begin{aligned}
\partial_\tau f(\vec{x},\tau) &= \frac{\hbar^2}{2m_e}\vec{\nabla}^2 f(\vec{x},\tau) - \vec{\nabla}\left[f(\vec{x},\tau)\underbrace{\frac{\hbar}{m_e}\vec{\nabla}\ln[\Phi_{trial}]}_{\vec{v}_{drift}(\vec{x})}\right] \\
&\quad - \left[\frac{1}{\Phi_{trial}(\vec{x})}\left(-\frac{\hbar^2}{2m_e}\vec{\nabla}^2 + V(\vec{x}) - E_{ref}\right)\Phi_{trial}(\vec{x})\right] f(\vec{x},\tau) \\
\Psi(\vec{x}), t) &= \frac{f(\vec{x},\tau)}{\Phi_{trial}(\vec{x})}
\end{aligned}$$

Thus the walkers have the same diffusion term as before, resulting in a diffusion current away from the maxima of $f(\vec{x}, t)$. The latter is approximately the particle density. With importance sampling the walkers also experience a drift term, that pushes the walkers towards the maximum of the probability density. If the trial wave function is a reasonably good solution of the Schrödinger equation, the source term is proportional to the distribution $f(\vec{x},\tau)$, so that the walkers have a nearly spatially constant branching ratio, which furthermore is on average zero, if the reference energy is equal to the ground state energy.

Chapter 5

Decoherence

A very good introductory text has been written by Zurek in Physics Today[13, 14].

The following books may be of interest:

- Kurt Baumann und Roman U. Sexl, *Die Deutungen der Quantentheorie*, Vieweg Verlag.
- Jürgen Audretsch, *Verschänkte Welt*, Faszination der Quanten, Wiley-VCH
- E. Joos, H.D. Zeh, C. Kiefer, D. Giulini, J. Kupsch and I.O. Stamatescu, *Decoherence and the appearance of the classical world*, Springer Verlag

Papers that I did not yet read are Kiefer and Joos[**?**] and the article by Zeh[**?**].

I believe the paper of van Hove[15] is a key paper regarding the onset of reversibility and the Boltzmann equation.

Check also Redfield theory (See Neufeld, J. Chem Phys. 119, 2488 (2003))

5.1 Schrödinger's cat

One of the major conceptual problems of quantum mechanics is the description of the measurement process. The problem is very well described by the thought experiment with "Schrödinger's cat".

A cat is in a container together with a device that can release poison that kills the cat. The release of the poison is triggered by the decay of a radioactive nucleus. The nucleus, being a quantum system, will end up in a superposition of the intact and the decayed state. Because the intact nucleus is linked (entangled)[1] with the live cat and the decayed nucleus is linked to a dead cat, a quantum description of the whole system describes a superposition of a live and a dead cat. The observation of a cat being simultaneously in a live and dead state contradicts our experience. In the measurement, one assumes that the the state collapes into one of the two states. This collapse, however, cannot be described by a Schrödinger equation, because it corresponds to a non-unitary dynamics.

There are two main questions to this problem:

1. How does the system develop from a superposition of states into an ensemble of two classical possibilities, live and dead cat?
2. How does the system select one of the two choices?

The second question is present also in a classical description if we describe a system via probability distributions. Two states are possible, but when we look, we find that only one of the choices

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[1] entangled=verschränkt

represents reality. The probability distribution can be characterized as a state of our mind, describing our expecations. Any information gain, will alter these expectations.

The first question, however, is the truly puzzling one: starting from a wave function, how do we arrive at classical choices with classical probabilities. One answer is given by the theory of decoherence.

The following is based on the article by Zurek in Physics Today.[13].

5.2 Entanglement and Ensembles

The meaning of the terms "entanglement" and "ensembles" is not grasped easily. However, they pervade the entire discussion of decoherence. Therefore let us take some time to explore their meaning.

This description is taken from P. Blöchl, ΦSX:Quantum theory.

5.2.1 Mixture of states: Ensembles

Imagine that we do not know the state of the system. In order to describe the situation, we may provide several guesses for the state and attribute a probability to each of them. Thus we obtain a set of states $|\Psi_j\rangle$ paired with corresponding probabilities P_j. Such a set of pairs, namely $\{|\Psi_j\rangle, P_j\}$ is an **ensemble** or a **mixture of states**. In use is also the term **macrostate**, which is the ensemble, while the term **microstate** refers to one of the states $|\Psi_j\rangle$ in the ensemble.

We obtain the statistical expectation value of an observable $\hat{A}$ from an ensemble as

$$\langle A\rangle = \sum_j P_j\langle\Psi_j|\hat{A}|\Psi_j\rangle = Tr[\hat{\rho}\hat{A}]$$

where

$$\hat{\rho} = \sum_j |\Psi_j\rangle P_j\langle\Psi_j|$$

is the density operator, that contains the complete measurable information of an ensemble. Note, that there is no requirement of orthogonality for the states $|\Psi_j\rangle$ in the ensemble. The states are normalized and the sum of probabilities add up to one.

We may form a special ensemble from the eigenstates $|a_i\rangle$ of an observable $\hat{A}$, for which the density operator has the form

$$\rho = \sum_i |a_i\rangle P_i\langle a_i|$$

In order to obtain the expectation value of the observable $\hat{A}$ we can weight the expectation value of each state with the probability of the state, i.e.

$$\langle A\rangle = \sum_i P_i\langle a_i|\hat{A}|a_i\rangle = \sum_i P_i a_i$$

We obtain the weighted average of the eigenvalues a_i of the observable $\hat{A}$.

For another observable $\hat{B}$, we obtain

$$\langle B\rangle = \sum_i P_i\langle a_i|\hat{B}|a_i\rangle$$

The result looks similar. However, instead of the eigenvalues of B we have to use the expectation values of $\hat{B}$ with the set of states from our mixture. The probabilities are the same as those that we used to determine the expectation value of the observable $\hat{A}$.

Let us keep these results in mind, because we will compare them below with similar results from a superposition of states.

5.2.2 Superposition of states: Entanglement

Let us now compare these equations for the expectation value with those from a superposition of states.

A superposition $|\Phi\rangle$ of states $|\Psi_j\rangle$ is

$$|\Phi\rangle = \sum_j |\Psi_j\rangle c_j$$

Like in the ensemble, a superposition consists of pairs of states and numbers. The superposition is, however, just another state, whereas an ensemble is characterized by an operator ρ.

We start with a quantum-mechanical state $|\Psi\rangle$. If we want to measure a certain observable $\hat{A}$ it is convenient to expand this state into (orthonormal) eigenstates $|a_i\rangle$ of the operator $\hat{A}$, i.e.

$$|\psi\rangle = \underbrace{\sum_i |a_i\rangle\langle a_i|}_{\hat{1}} \psi\rangle = \sum_i |a_i\rangle \underbrace{c_i}_{\langle a_i|\psi\rangle}$$

This is a superposition of states $|a_i\rangle$. The components of the wave function are **coherent**.

The expectation value of the observable $\hat{A}$ for such a superposition is

$$\langle\psi|\hat{A}|\psi\rangle = \sum_{i,j} c_i^* c_j \langle a_i|\hat{A}|a_j\rangle = \sum_{i,j} c_i^* c_j \langle a_i|a_j\rangle a_j = \sum_i c_i^* c_i a_i = \sum_i P_i^{(A)} a_i$$

Thus the expectation value can be expressed as a sum over the eigenvalues of A with probabilities $P_i = c_i^\dagger c_i = \langle\psi|a_i\rangle\langle a_i|\psi\rangle$ for each eigenvalue.

This equation is basically identical to the one obtained for a mixture of states. However, let us now look at the expectation value of some other operator $\hat{B}$.

$$\langle\psi|\hat{B}|\psi\rangle = \sum_{i,j} c_i^* c_j \langle a_i|\hat{B}|a_j\rangle = \sum_i c_i^* c_i \langle a_i|\hat{B}|a_i\rangle + \sum_{i\neq j} c_i^* c_j \langle a_i|\hat{B}|a_j\rangle$$

This expression differs from the expression for the mixture by the presence of the off-diagonal terms of the double sum. These off-diagonal terms are a sign of a **coherent** superposition of states. Coherent means the following: For a given set of probabilities $P_i^{(A)}$, we can determine the coefficients

$$c_i = \sqrt{P}_i e^{i\varphi_i}$$

only if we also specify the relative phases φ_i of the states.

While a mixture of states is uniquely defined by a set of states, say $\{|a_i\rangle\}$ and their probabilities P_i, a superposition carries additional information, namely the phase information.

If we average the expectation value for $\hat{B}$ over all states that only differ by the relative phases, the off-diagonal terms cancel out, and we are left with an expression for expectation values that is identical to that for a mixture. This is the essence of the so-called **random-phase approximation**. The random phase approximation converts a superposition of states into a mixture of states.

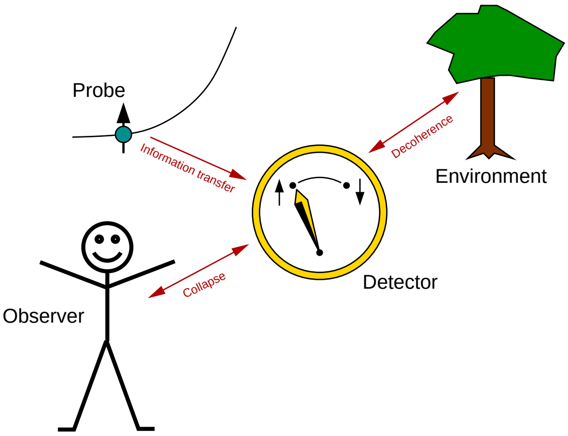
It may be instructive to consider the expectation value for a superposition of states in terms of eigenvalues of the observable B. Let us simply introduce the eigenstates $|b_i\rangle$ and the corresponding eigenvalues b_i.

$$\langle\psi|\hat{B}|\psi\rangle = \sum_{i,j} \langle\psi|b_i\rangle\langle b_i|\hat{B}|b_j\rangle\langle b_j|\psi\rangle = \sum_i |\langle\psi|b_i\rangle|^2 b_i = \sum_i P_i^{(B)} b_i$$

While we can express the expectation value of B as a weighted sum of eigenvalues, the probabilities $P_i^{(B)}$ differ from the probabilities $P_i^{(A)}$, we have used before to obtain the expectation value of A.

5.3 Overview of the measurement process

In the following I will describe in detail the individual steps that take place during a measurement process.



We will see in the following that three steps are required for a measurment

1. **Information transfer:** In a first step information of the measured property is transferred to the detector. The measured property and the detector end up in an entangled state.

2. **Decoherence:** a non-unitary evolution transforms a pure, state into an appropriate mixture. During this step, the off-diagonal elements of the density matrix, expressed in the basis of the observable to be measured, vanish. This step increases the entropy of the state and is thus irreversible.

3. **Collapse:** One of the possible eigenstates of the observable is selected. This step is analogous to the collapse of a classical probability density upon measurement. During this step the entropy is reduced again, usually to zero.

In our analysis we need to consider three parts for the description of the measurement process.

1. **Probe:** The probe is the system whose properties we want to measure. We may refer to it as a magnetic particle with two spin directions $\sigma \in \{|\uparrow\rangle, |\downarrow\rangle\}$. The probe is initially in the state $|\uparrow\rangle\alpha + |\downarrow\rangle\beta$, that is, in a superposition of both magnetic orientations. In the Schrödinger's cat experiment, the probe is the radioactive nucleus, that may be in a superposition of an original state $|\uparrow\rangle$ and a decayed state $|\downarrow\rangle$.

2. **Detector:** The detector is something like a scale. After coming into contact with the probe the detector shows the reading "$\uparrow$" if the probe is in state "$|\uparrow\rangle$" and it shows the reading $\downarrow$ if the probe is in state $\downarrow$. The corresponding two states of the detector are $|d_\uparrow\rangle$ and $|d_\downarrow\rangle$. In the Schrödinger's cat experiment the cat itself plays the role of the detector.

3. **Environment:** The environment strictly describes the rest of the universe. It is per definition a macroscopic system. The relevant states of the environment are likely part of the measurement apparatus itself. This is because the way the detector couples to the environment is vital for the function of the measurement apparatus.

4. **Observer:** The observer only plays a minor part in the measurement process. Its role is limited to the collapse of the wave function, which is considered a mental process and not a physical one.

5.4 Transfer of information to the detector

Consider the following arrangement: A system has two quantum states, namely $|\uparrow\rangle$ and $|\downarrow\rangle$. That is the initial state can be represented by

$$|\psi_i\rangle = |\uparrow\rangle\alpha + |\downarrow\rangle\beta \tag{5.1}$$

We will refer to these states as spins, even though we do not necessarily consider angular momenta. Rather, we may equally well describe the nucleus in the Schrödinger's cat example by the two spin directions, one for the initial and one for the final, decayed state.

Our goal is to measure the spin of the system. This measurement can produce two possible outcomes, namely “spin has the value ↑" or “spin has the value ↓”.

During the measurement we bring the system into contact with a detector. The detector also has two quantum states, namely $|d_\uparrow\rangle$ and $|d_\downarrow\rangle$. The Hilbert space of system and detector has the following quantum states.

$$\left(|\uparrow, d_\uparrow\rangle, |\downarrow, d_\uparrow\rangle, |\uparrow, d_\downarrow\rangle, |\downarrow, d_\downarrow\rangle\right) \tag{5.2}$$

Before the measurement, the detector is prepared in state $|d_\downarrow\rangle$. Hence system and detector are described by the wave function

$$|\psi^{(i)}_{SD}\rangle = |\uparrow, d_\downarrow\rangle\alpha + |\downarrow, d_\downarrow\rangle\beta \tag{5.3}$$

The detector is designed in such a way, that its $|d_\downarrow\rangle$ is flipped if the measured spin σ is in state $|\uparrow\rangle$ and the detector remains in its $|d_\downarrow\rangle$ state, when the measured spin is in its $|\downarrow\rangle$ state.

The propagator has the form

$$\boldsymbol{U} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{5.4}$$

where the representation refers to the basis specified in Eq. 5.2. The matrix $\boldsymbol{U}$ is unitary, that is $\boldsymbol{U}\boldsymbol{U}^\dagger = \mathbf{1}$. Hence it can be derived from a Hamiltonian as shown in section 5.4.1.

The propagator transforms the initial state Eq. 5.3 into

$$\hat{U}\Bigg(|\uparrow, d_\downarrow\rangle\alpha + |\downarrow, d_\downarrow\rangle\beta\Bigg) = |\uparrow, d_\uparrow\rangle\alpha + |\downarrow, d_\downarrow\rangle\beta$$

The spin and the detector are in and entangled state.

5.4.1 Hamiltonian for the coupling between detector and measured system

One may wonder, if the transformation $\boldsymbol{U}$ from Eq. 5.4 can be expressed by a physical process. To answer this question, we need to show that $\boldsymbol{U}$ can be obtained as propagator of the time evolution under a hermitean Hamilton operator.

Were we will show, that the Hamiltonian leading to the propagator U of Eq. 5.4 has the form

$$\boldsymbol{H} = \begin{pmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \hbar\omega \cdot \theta(t)\theta(\frac{\pi}{2\omega} - t) \tag{5.5}$$

$\theta(t)$ is the Heaviside function.

The proof that the Hamiltonian has the form Eq. 5.5 is as follows:

We are guided by the observation that the propagator Eq. 5.4 describes a rotation in two dimensions by $\frac{\pi}{2}$. This information can be obtained by inspection of Eq. 5.4 in the relevant two-dimensional subspace.

- Firstly, we determine the Taylor expansions of sine and cosine.

$$\mathrm{e}^{ix}=\cos(x)+i\sin(x)=\sum_{n=0}^{\infty}\frac{1}{n!}(ix)^n=\underbrace{\sum_{k=0}^{\infty}\frac{(-1)^k}{(2k)!}x^{2k}}_{\cos(x)}+i\underbrace{\sum_{k=0}^{\infty}\frac{(-1)^k}{(2k+1)!}x^{2k+1}}_{\sin(x)}$$

- Secondly, we describe a plane rotation by an exponential function. Let is start exploring the powers of $i\boldsymbol{\sigma}_y$, where $\boldsymbol{\sigma}_y$ is a Pauli matrix. We obtain

$$(i\boldsymbol{\sigma}_y)^0=\begin{pmatrix}1&0\\0&1\end{pmatrix}\quad;\quad(i\sigma_y)^1=\begin{pmatrix}0&1\\-1&0\end{pmatrix}\quad;\quad(i\sigma_y)^2=\begin{pmatrix}-1&0\\0&-1\end{pmatrix}\quad;\quad(i\sigma_y)^3=\begin{pmatrix}0&-1\\1&0\end{pmatrix}$$
$$\text{and}\qquad(i\sigma_y)^(n+4)=(i\sigma_y)^n$$

Thus the Taylor expansion of the exponential function $\mathrm{e}^x=\sum_{n=0}^{\infty}\frac{1}{n!}x^n$ yields

$$\exp\begin{pmatrix}0&\phi\\-\phi&0\end{pmatrix}=\begin{pmatrix}1&0\\0&1\end{pmatrix}\underbrace{\sum_{k=0}^{\infty}\frac{(-1)^k}{(2k)!}\phi^{2k}}_{\cos(\phi)}+\begin{pmatrix}0&1\\-1&0\end{pmatrix}\underbrace{\sum_{k=0}^{\infty}\frac{(-1)^k}{(2k+1)!}\phi^{2k+1}}_{\sin(\phi)}=\begin{pmatrix}\cos(\phi)&\sin(\phi)\\-\sin(\phi)&\cos(\phi)\end{pmatrix}$$

- Finally we extract the Hamilton operator.

$$\begin{pmatrix}0&1\\-1&0\end{pmatrix}=\begin{pmatrix}\cos(\frac{\pi}{2})&\sin(\frac{\pi}{2})\\-\sin(\frac{\pi}{2})&\cos(\frac{\pi}{2})\end{pmatrix}=\exp\left[\frac{\pi}{2}\begin{pmatrix}0&1\\-1&0\end{pmatrix}\right]=\exp\left[-\frac{i}{\hbar}\cdot\underbrace{\begin{pmatrix}0&i\hbar\omega\\-i\hbar\omega&0\end{pmatrix}}_{\boldsymbol{H}}\cdot\underbrace{\frac{\pi}{2\omega}}_{\Delta t}\right]$$

Thus, if we switch the Hamilton operator on for the specified period $\Delta t=\frac{\pi}{2\omega}=\frac{1}{4}T$, where $T=2\pi/\omega$ is the period of oscillation, we perform a 90° rotation in the 2-dimensional Hilbert space.

This leads directly given to the form in Eq. 5.5.

5.5 Density matrices

So-far we have clearly transferred all the information from the measured spin to the detector. However, the detector is still in a superposition of the two states. In the decoherence step, we need to find out how the system can evolve from a coherent superposition of two states into an statistical ensemble of two states.

In order to describe pure states and statistical mixtures, we need to introduce the concept of density matrices.

The density matrix of the final, coherent state is

$$\begin{aligned}\hat\rho&=|\Phi^f\rangle\langle\Phi^f|=|\uparrow d_\uparrow\rangle|\alpha|^2\langle\uparrow d_\uparrow|+|\downarrow d_\downarrow\rangle\beta\alpha^*\langle\uparrow d_\uparrow|+|\uparrow d_\uparrow\rangle\alpha\beta^*\langle\downarrow d_\downarrow|+|\downarrow d_\downarrow\rangle|\beta|^2\langle\downarrow d_\downarrow|\\&=\begin{pmatrix}|\uparrow d_\uparrow\rangle\\|\downarrow d_\downarrow\rangle\end{pmatrix}\begin{pmatrix}|\alpha|^2&\alpha\beta^*\\\beta\alpha^*&|\beta|^2\end{pmatrix}\begin{pmatrix}\langle\uparrow d_\uparrow|\\\langle\downarrow d_\downarrow|\end{pmatrix}\end{aligned}$$

As shown below, this state is idempotent, i.e. $\hat{\rho}^2 = \hat{\rho}$, and therefore describes a pure state.

$$\begin{aligned}
\hat{\rho}^2 &= \begin{pmatrix} |\uparrow d_\uparrow\rangle \\ |\downarrow d_\downarrow\rangle \end{pmatrix} \begin{pmatrix} |\alpha|^2 & \alpha\beta^* \\ \beta\alpha^* & |\beta|^2 \end{pmatrix} \begin{pmatrix} |\alpha|^2 & \alpha\beta^* \\ \beta\alpha^* & |\beta|^2 \end{pmatrix} \begin{pmatrix} \langle\uparrow d_\uparrow| \\ \langle\downarrow d_\downarrow| \end{pmatrix} \\
&= \begin{pmatrix} |\uparrow d_\uparrow\rangle \\ |\downarrow d_\downarrow\rangle \end{pmatrix} \begin{pmatrix} |\alpha|^2|\alpha|^2 + \alpha\beta^*\beta\alpha^* & |\alpha|^2\alpha\beta^* + \alpha\beta^*|\beta|^2 \\ \beta\alpha^*|\alpha|^2 + |\beta|^2\beta\alpha^* & \beta\alpha^*\alpha\beta^* + |\beta|^2|\beta|^2 \end{pmatrix} \begin{pmatrix} \langle\uparrow d_\uparrow| \\ \langle\downarrow d_\downarrow| \end{pmatrix} \\
&= \begin{pmatrix} |\uparrow d_\uparrow\rangle \\ |\downarrow d_\downarrow\rangle \end{pmatrix} \begin{pmatrix} |\alpha|^2(|\alpha|^2 + |\beta|^2) & \alpha\beta^*(|\alpha|^2 + |\beta|^2 \\ \beta\alpha^*(|\alpha|^2 + |\beta|^2) & |\beta|^2(|\alpha|^2 + |\beta|^2|) \end{pmatrix} \begin{pmatrix} \langle\uparrow d_\uparrow| \\ \langle\downarrow d_\downarrow| \end{pmatrix} \\
&\overset{|\alpha|^2+|\beta|^2=1}{=} \begin{pmatrix} |\uparrow d_\uparrow\rangle \\ |\downarrow d_\downarrow\rangle \end{pmatrix} \begin{pmatrix} |\alpha|^2 & \alpha\beta^* \\ \beta\alpha^* & |\beta|^2 \end{pmatrix} \begin{pmatrix} \langle\uparrow d_\uparrow| \\ \langle\downarrow d_\downarrow| \end{pmatrix} = \hat{\rho}
\end{aligned}$$

A statistical interpretation would evolve, if the off-diagonal elements of the density matrix disappear, so that we can identify $P_\alpha = |\alpha|^2$ and $P_\beta = |\beta|^2$ as probabilities for the two possible outcomes of the measurement.

In terms of a density matrices the decoherence step maps the density matrix onto a diagonal matrix

$$\begin{pmatrix} |\alpha|^2 & \alpha\beta^* \\ \beta\alpha^* & |\beta|^2 \end{pmatrix} \longrightarrow \begin{pmatrix} |\alpha|^2 & 0 \\ 0 & |\beta|^2 \end{pmatrix}$$

Dynamics: von Neumann equation

If the dynamics is governed by the Schrödinger equation, the density matrix propagates according to the von-Neumann equation

$$i\hbar\partial_t\hat{\rho} = [\hat{H}, \hat{\rho}] \tag{5.6}$$

5.6 Entropy

The entropy of a state or a mixture of a state provides us with a measure of the information about the system. The entropy of a pure state is zero. The entropy of a mixture is positive.

We can attribute an entropy to a density matrix, the so-called von-Neumann entropy. The von Neumann entropy is defined as

$$S = -k_B \mathrm{Tr}\left[\hat{\rho}\ln(\hat{\rho})\right]$$

It can be shown(see ΦSX:Statistical Physics, Discussion of the H-theorem) that this entropy remains conserved under a unitary dynamics, i.e. if it is propagated by a Schrödinger equation. A statistical mixture, however, always has a positive entropy, unless $|\alpha|^2$ is either zero or one. In our example the entropy, after dropping the off-diagonal terms of the density matrix, has the value

$$S = -k_B\left[|\alpha|^2\ln(|\alpha|^2) + |\beta|^2\ln(|\beta|^2)\right] > 0$$

which is positive.

Thus the decoherence step, which increases the entropy, cannot be explained by a reversible Schrödinger dynamics: The measurement process is irreversible.

Reduced density matrix

We will see that in order to remove the off-diagonal elements from the density matrix, we need the coupling to an environment. That is, we describe an open system.

Now we form the reduced density matrix for a system that consists of two sub-Hilbert spaces A and B. A may contain the probe and the detector, while B contains the environment.

$$\hat{\rho}^{\text{red(A)}} = \sum_{i,j,k} |a_i\rangle\langle a_i b_k| \underbrace{\left(\sum_n |\psi_n\rangle P_n \langle\psi_n|\right)}_{\hat{\rho}} |a_j b_k\rangle\langle a_j|$$

The reduced density matrix is sufficient to evaluate the expectation value of any observable that acts only on the subsystem A. The expectation value of an operator in A evaluated as trace with the reduced density matrix is the same as the expectation value of $\hat{A}\otimes\hat{1}_{\mathcal{E}}$ acting on the complete system.

The process of forming a reduced density matrix can be demonstrated as follows. First we divide the density matrix in blocks, which are characterized by a pair of eigenvalues of the system B. Then all the off-diagonal blocks are dropped. Finally the diagonal sub-blocks are summed up forming a smaller density matrix referring only to system A.

$$\left(\begin{array}{c|c|c|c}
\langle a_i b_1|\hat{\rho}|a_j b_1\rangle & \langle a_i b_1|\hat{\rho}|a_j b_2\rangle & \langle a_i b_1|\hat{\rho}|a_j b_3\rangle & \cdots \\ \hline
\langle a_i b_2|\hat{\rho}|a_j b_1\rangle & \langle a_i b_2|\hat{\rho}|a_j b_2\rangle & \langle a_i b_2|\hat{\rho}|a_j b_3\rangle & \cdots \\ \hline
\langle a_i b_3|\hat{\rho}|a_j b_1\rangle & \langle a_i b_3|\hat{\rho}|a_j b_2\rangle & \langle a_i b_3|\hat{\rho}|a_j b_3\rangle & \cdots \\ \hline
\vdots & \vdots & \vdots & \vdots
\end{array}\right)
\longrightarrow
\left(\begin{array}{c|c|c|c}
\langle a_i b_1|\hat{\rho}|a_j b_1\rangle & 0 & 0 & \cdots \\ \hline
0 & \langle a_i b_2|\hat{\rho}|a_j b_2\rangle & 0 & \cdots \\ \hline
0 & 0 & \langle a_i b_3|\hat{\rho}|a_j b_3\rangle & \cdots \\ \hline
\vdots & \vdots & \vdots & \vdots
\end{array}\right)$$

$$\longrightarrow \Big(\langle a_i b_1|\hat{\rho}|a_j b_1\rangle + \langle a_i b_2|\hat{\rho}|a_j b_2\rangle + \langle a_i b_3|\hat{\rho}|a_j b_3\rangle + \cdots \Big)$$

In our problem we would like to obtain the reduced density matrix for the measurement apparatus by tracing out the degrees of freedom of the environment.

$$\hat{\rho}^{\text{red(SD)}} = \sum_i |\uparrow, d_\uparrow\rangle\langle\uparrow, d_\uparrow, \mathcal{E}_j|\hat{\rho}|\uparrow, d_\uparrow, \mathcal{E}_j\rangle\langle\uparrow, d_\uparrow| \ldots$$

5.7 Tracing out the environment: decoherence

Hilbert space with environment

Let us describe the environment by a set of states $|\mathcal{E}_i\rangle$. A complete basis would be

$$\Big\{ |\uparrow, d_\uparrow, \mathcal{E}_i\rangle; |\uparrow, d_\downarrow, \mathcal{E}_i\rangle; |\downarrow, d_\uparrow, \mathcal{E}_i\rangle; |\downarrow, d_\downarrow, \mathcal{E}_i\rangle \qquad \text{for} \qquad i = 0, \ldots \Big\}$$

Observable

The observable for the pointer reading of the measurement device shall be $\hat{O}$.

$$\hat{O} = |d_\uparrow\rangle\langle d_\uparrow| - |d_\downarrow\rangle\langle d_\downarrow| = \sum_\sigma |d_\sigma\rangle\sigma\langle d_\sigma|$$

where $\sigma = 1$ for $\sigma =\uparrow$ and $\sigma = -1$ for $\sigma =\downarrow$.

Let us now extend the operator to the complete basisset.

$$\hat{O} = \sum_{i,\sigma} \Big(|\sigma, d_\uparrow, \mathcal{E}_i\rangle\langle\sigma, d_\uparrow, \mathcal{E}_i| - |\sigma, d_\downarrow, \mathcal{E}_i\rangle\langle\sigma, d_\downarrow, \mathcal{E}_i| \Big) = \sum_{i,\sigma,\sigma'} |\sigma, d_{\sigma'}, \mathcal{E}_i\rangle\sigma'\langle\sigma, d_{\sigma'}, \mathcal{E}_i|$$

It may be surprising that we discuss the observable of the pointer-reading rather than that of the spin. The motivation is that the pointer reading is independent of the measured spin, once the interaction has been switched off. The goal is now to investigate the pointer reading, that reflects the state of the measured spin at the time of the interaction with the detector. The future of this measured spin after the information transfer to the detector is of no concern.

Our measurement aparatus must be constructed such that its interaction with the environment commutates with the observable $\hat{O}$ to be measured. This requirement ensures that the environment does not change the reading of the device for the quantity to be measured.

The observable to be measured is the reading, $d_\uparrow$ or $d_\downarrow$ of the measurement device, not the spin to be determined $\uparrow$ or $\downarrow$. The identification of the spin is obtained indirectly from the reading of the measurement device, because the correlation between spin and pointer reading has already been established. The latter shall be macroscopic, which in our case implies that it may interact with the environment.

We assume that the total Hamiltonian consists only of two parts, of which one is the interaction between the spin and the measurement device on the one hand and the interaction between the measurement apparatus with the environment on the other. The former is switched off before the reading of the measurement apparatus takes place.

Interaction of the detector with the environment

The most general interaction operator between the measurement device and the environment has the form

$$\hat{H}_{int}=\sum_{i,j}\sum_{\sigma}\sum_{\bar\sigma,\bar\sigma'}|\sigma,d_{\bar\sigma}\mathcal{E}_i\rangle A^{(\bar\sigma,\bar\sigma')}_{i,j}\langle\sigma,d_{\bar\sigma'}\mathcal{E}_j|$$

where

$$A^{\bar\sigma,\bar\sigma'}_{i,j}=\langle d_{\bar\sigma},\mathcal{E}_i|\hat{H}_{int}|d_{\bar\sigma'},\mathcal{E}_j\rangle$$

On the subspace of the spin to be determined, the interaction operator is the unity operator[2]. The states of the measurement device and the environment may be scrambled by the interaction.

The commutator has the form

$$[\hat{O},\hat{H}_{int}]_-=\sum_{i,j}\sum_{\sigma}\sum_{\bar\sigma,\bar\sigma'}|\sigma,d_{\bar\sigma}\mathcal{E}_i\rangle\Big(\bar\sigma A^{(\bar\sigma,\bar\sigma')}_{i,j}-A^{(\bar\sigma,\bar\sigma')}_{i,j}\bar\sigma'\Big)\langle\sigma,d_{\bar\sigma'}\mathcal{E}_j| \tag{5.8}$$

The commutator vanishes, if $A^{(\bar\sigma,\bar\sigma')}_{i,j}(\bar\sigma-\bar\sigma')=0$, that is for

$$A^{(\bar\sigma,\bar\sigma')}_{i,j}=0 \qquad \text{for} \qquad \bar\sigma\neq\bar\sigma' \tag{5.9}$$

Thus, an interaction that leaves the observable invariant has the form

$$\hat{H}_{int}=\sum_{i,j}\sum_{\sigma}\sum_{\bar\sigma}|\sigma,d_{\bar\sigma},\mathcal{E}_i\rangle A^{(\bar\sigma,\bar\sigma)}_{i,j}\langle\sigma,d_{\bar\sigma},\mathcal{E}_j| \tag{5.10}$$

The interaction is diagonal in the observable, which does not imply that there is no interaction with the environment. The matrix $A^{(\uparrow,\uparrow)}_{i,j}\neq A^{(\downarrow,\downarrow)}_{i,j}$ explicitly depends on the value of the observable $\bar\sigma$.

Without limitation of generality, we may diagonalize the operator $\sum_{i,j}|\mathcal{E}_i\rangle A^{(\bar\sigma,\bar\sigma)}_{i,j}\langle\mathcal{E}_j|$, which acts on the environment and depends parametrically on the state of the detector. Thus we obtain two different sets of eigenvalues and eigenstates, one for each value of $\bar\sigma$, leading to two linear dependent basis sets for the environment.

$$\Big[\sum_{i,j}|\mathcal{E}_i\rangle A^{(\bar\sigma,\bar\sigma)}_{i,j}\langle\mathcal{E}_j|\Big]|e^{\bar\sigma}_n\rangle=|e^{\bar\sigma}_n\rangle\epsilon^{\bar\sigma}_n \tag{5.11}$$

---

[2] This means the following: for an arbitrary, but specific set of $\bar\sigma,\bar\sigma',i,j$, that matrix elements

$$\langle\sigma,d_{\bar\sigma},\mathcal{E}_i|\hat{H}_{int}|\sigma,d_{\bar\sigma},\mathcal{E}_i\rangle=\delta_{\sigma,\sigma'}A^{(\bar\sigma,\bar\sigma)}_{i,j} \tag{5.7}$$

are proportional to the unit matrix in the σ,σ' subspace.

where

$$\langle e_i^{\bar\sigma}|e_j^{\bar\sigma}\rangle = \delta_{i,j} \qquad \text{and} \qquad \langle e_i^{\uparrow}|e_j^{\downarrow}\rangle \qquad \text{is unitary}$$

Thus with the restriction that the the observable $\mathcal{O}$ and the interaction Hamiltonian commutate, in interaction of the detector with the environment can be written in the form

$$\hat{H}_{int} = \sum_i \sum_\sigma \sum_{\bar\sigma} |\sigma, d_{\bar\sigma}, e_i^{\bar\sigma}\rangle \epsilon_i^{\bar\sigma} \langle \sigma, d_{\bar\sigma}, e_i^{\bar\sigma}| \tag{5.12}$$

Propagators

The interaction Hamiltonian of the detector with the environment has the form of one Hamiltonian $\hat{H}_{\mathcal{E}}^{\uparrow}$ acting on the environment, if the detector is in its $|d_\uparrow\rangle$ state and another Hamiltonian $H_{\mathcal{E}}^{\downarrow}$ acting on the environment if the detector is in its $|d_\downarrow\rangle$ state.

$$\hat{H}_{\mathcal{E}}^{\bar\sigma} = \sum_i |e_i^{\bar\sigma}\rangle \epsilon_i^{\bar\sigma} \langle e_i^{\bar\sigma}|$$

For each setting of the detector we can now define a propagator for the environment.

$$\begin{aligned} i\hbar\partial_t |\mathcal{E}^{\bar\sigma}(t)\rangle &= \hat{H}_{\mathcal{E}}^{\bar\sigma} |\mathcal{E}^{\bar\sigma}(t)\rangle \\ \Rightarrow |\mathcal{E}^{\bar\sigma}(t)\rangle &= \hat{U}_{\mathcal{E}}^{\bar\sigma}(t)|\mathcal{E}_0\rangle \qquad \text{with} \qquad \hat{U}_{\mathcal{E}}^{\bar\sigma}(t) = \sum_i |e_i^{\bar\sigma}\rangle \mathrm{e}^{-\frac{i}{\hbar}\epsilon_i^{\bar\sigma} t} \langle e_i^{\bar\sigma}| \end{aligned} \tag{5.13}$$

The propagator for the complete system has the form

$$\hat{U}(t) = \exp\left(\frac{i}{\hbar}\hat{H}_{int} t\right) = \sum_i \sum_\sigma \sum_{\bar\sigma} |\sigma, d_{\bar\sigma}, e_i^{\bar\sigma}\rangle \mathrm{e}^{-\frac{i}{\hbar}\epsilon_i^{\bar\sigma} t} \langle \sigma, d_{\bar\sigma}, e_i^{\bar\sigma}| = \sum_{\bar\sigma} \hat{U}^{\bar\sigma}(t)$$

where

$$\hat{U}^{\bar\sigma}(t) = \sum_{\sigma,i} |\sigma, d_{\bar\sigma}, \epsilon_i^{\bar\sigma}\rangle \mathrm{e}^{-\frac{i}{\hbar}\epsilon_i^{\bar\sigma} t} \langle \sigma, d_{\bar\sigma}, \epsilon_i^{\bar\sigma}| \tag{5.14}$$

is the propagator defined above in Eq. 5.13, but extended for the complete system.

The propagator $\hat{U}^{\bar\sigma}(t)$ is the product of a unity operator $\hat{1} = \sum_\sigma |\sigma\rangle\langle\sigma|$ on the Hilbert space of the spin, a projection operator $P_{\bar\sigma} = |d_{\bar\sigma}\rangle\langle d_{\bar\sigma}|$ onto a specific detector state, and a $\bar\sigma$-dependent propagator $\hat{U}_{\mathcal{E}}^{\bar\sigma}(t) = \sum_i |\epsilon_i^{\bar\sigma}\rangle \mathrm{e}^{-\frac{i}{\hbar}\epsilon_i^{\bar\sigma} t} \langle \epsilon_i^{\bar\sigma}|$ for the states of the environment. All these three operators act in orthogonal sub-Hilbert spaces of the complete system.

$$\begin{aligned} \langle \sigma', d_{\bar\sigma'}, e_m^{\bar\sigma'}|\hat{U}(t)|\sigma'', d_{\bar\sigma''}, e_n^{\bar\sigma''}\rangle &= \sum_i \sum_\sigma \sum_{\bar\sigma} \langle \sigma', d_{\bar\sigma'}, e_m^{\bar\sigma'}|\sigma, d_{\bar\sigma}, e_i^{\bar\sigma}\rangle \mathrm{e}^{-\frac{i}{\hbar}\epsilon_i^{\bar\sigma} t} \langle \sigma, d_{\bar\sigma}, e_i^{\bar\sigma}|\sigma'', d_{\bar\sigma''}, e_n^{\bar\sigma''}\rangle \\ &= \sum_i \sum_\sigma \sum_{\bar\sigma} \langle \sigma'|\sigma\rangle \langle d_{\bar\sigma'}|d_{\bar\sigma}\rangle \langle e_m^{\bar\sigma'}|e_i^{\bar\sigma}\rangle \mathrm{e}^{-\frac{i}{\hbar}\epsilon_i^{\bar\sigma} t} \langle \sigma|\sigma''\rangle \langle d_{\bar\sigma}|d_{\bar\sigma''}\rangle \langle e_i^{\bar\sigma}|e_n^{\bar\sigma''}\rangle \\ &= \sum_i \langle \sigma'|\sigma''\rangle \langle d_{\bar\sigma'}|d_{\bar\sigma''}\rangle \langle e_m^{\bar\sigma'}|e_i^{\bar\sigma'}\rangle \mathrm{e}^{-\frac{i}{\hbar}\epsilon_i^{\bar\sigma'} t} \langle e_i^{\bar\sigma'}|e_n^{\bar\sigma''}\rangle \\ &= \langle \sigma'|\sigma''\rangle \langle d_{\bar\sigma'}|d_{\bar\sigma''}\rangle \langle e_m^{\bar\sigma'}| \left(\sum_i |e_i^{\bar\sigma'}\rangle \mathrm{e}^{-\frac{i}{\hbar}\epsilon_i^{\bar\sigma'} t} \langle e_i^{\bar\sigma'}| \right) |e_n^{\bar\sigma''}\rangle \\ &= \delta_{\sigma',\sigma''} \delta_{\bar\sigma',\bar\sigma''} \langle e_m^{\bar\sigma'}|\hat{U}_{\mathcal{E}}^{\bar\sigma'}(t)|e_n^{\bar\sigma'}\rangle \end{aligned}$$

Propagating the density matrix

Now we apply it to an initial state, which obtained right after the spin has interacted with the measurement device.

$$|\psi(0) = |\uparrow, d_{\uparrow}, \mathcal{E}_0\rangle\alpha + |\downarrow, d_{\downarrow}, \mathcal{E}_0\rangle\beta \tag{5.15}$$

Thus, at time t we obtain

$$\begin{aligned}|\psi(t) &= \sum_{\bar\sigma} \hat U^{\bar\sigma}|\psi(0)\rangle = \sum_{\bar\sigma} \hat U^{\bar\sigma}(t)|\uparrow, d_{\uparrow}, \mathcal{E}_0\rangle\alpha + \sum_{\bar\sigma} \hat U^{\bar\sigma}(t)|\downarrow, d_{\downarrow}, \mathcal{E}_0\rangle\beta \\ &= \hat U^{\uparrow}(t)|\uparrow, d_{\uparrow}, \mathcal{E}_0\rangle\alpha + \hat U^{\downarrow}(t)|\downarrow, d_{\downarrow}, \mathcal{E}_0\rangle\beta \\ &= \sum_{\sigma} \hat U^{\sigma}(t)|\sigma, d_{\sigma}, \mathcal{E}_0\rangle\alpha_{\sigma} \end{aligned} \tag{5.16}$$

Here we introduced the symbol $\alpha_{\uparrow} = \alpha$ and $\alpha_{\downarrow} = \beta$ and

The resulting density matrix has the form

$$|\psi(t)\rangle\langle\psi(t)| = \sum_{\sigma,\sigma'} \hat U^{\sigma}(t)|\sigma, d_{\sigma}, \mathcal{E}_0\rangle\alpha_{\sigma}\alpha^*_{\sigma'}\langle\sigma', d_{\sigma'}, \mathcal{E}_0| \left(\hat U^{\sigma'}(t)\right)^{\dagger}$$

Tracing out the environment

Now we form the trace over the environment. We perform the trace in the basisset $\{|e_k^{\uparrow}\rangle\}$, which is a complete orthonormal basis set for the bath.

$$\begin{aligned} Tr_{\mathcal{E}}\left[|\psi(t)\rangle\langle\psi(t)|\right] &= \sum_{\sigma,\sigma'}\sum_{\bar\sigma,\bar\sigma'} |\sigma, d_{\bar\sigma}\rangle \left[\sum_k \langle\sigma, d_{\bar\sigma}, e_k^{\uparrow}|\psi(t)\rangle\langle\psi(t)|\sigma', d_{\bar\sigma'}, e_k^{\uparrow}\rangle\right] \langle\sigma', d_{\bar\sigma'}| \\ &\overset{\text{Eq. 5.16}}{=} \sum_{\sigma,\sigma'}\sum_{\bar\sigma,\bar\sigma'} |\sigma, d_{\bar\sigma}\rangle \Bigg(\sum_k \langle\sigma, d_{\bar\sigma}, e_k^{\uparrow}| \Bigg[\underbrace{\sum_{\sigma'',\sigma'''} \hat U^{\sigma''}(t)|\sigma'', d_{\sigma''}, \mathcal{E}_0\rangle\alpha_{\sigma''}}_{|\Psi(t)\rangle} \\ &\qquad\qquad \times \underbrace{\alpha^*_{\sigma'''}\langle\sigma''', d_{\sigma'''}, \mathcal{E}_0| \left(\hat U^{\sigma'''}(t)\right)^{\dagger}}_{\langle\Psi(t)|}\Bigg] |\sigma', d_{\bar\sigma'}, e_k^{\uparrow}\rangle\Bigg) \langle\sigma', d_{\bar\sigma'}| \\ &= \sum_{\sigma,\sigma'}\sum_{\bar\sigma,\bar\sigma'} |\sigma, d_{\bar\sigma}\rangle \Bigg(\sum_k \sum_{\sigma'',\sigma'''} \underbrace{\langle\sigma, d_{\bar\sigma}, e_k^{\uparrow}|\hat U^{\sigma''}(t)|\sigma'', d_{\sigma''}, \mathcal{E}_0\rangle}_{\langle\sigma|\sigma''\rangle\langle d_{\bar\sigma}|d_{\sigma''}\rangle\langle e_k^{\uparrow}|\hat U^{\sigma''}(t)|\mathcal{E}_0\rangle \rightsquigarrow \quad \sigma=\sigma''=\bar\sigma} \quad \alpha_{\sigma''} \\ &\qquad\qquad \times\alpha^*_{\sigma'''} \quad \underbrace{\langle\sigma''', d_{\sigma'''}, \mathcal{E}_0| \left(\hat U^{\sigma'''}(t)\right)^{\dagger} |\sigma', d_{\bar\sigma'}, e_k^{\uparrow}\rangle}_{\langle\sigma'''|\sigma'\rangle\langle d_{\sigma'''}|d_{\bar\sigma'}\rangle\langle\mathcal{E}_0|\left(\hat U^{\sigma'''}(t)\right)^{\dagger}|e_k^{\uparrow}\rangle \rightsquigarrow \quad \sigma'=\sigma'''=\bar\sigma'} \quad \Bigg)\langle\sigma', d_{\bar\sigma'}| \\ &= \sum_{\sigma,\sigma'} |\sigma, d_{\sigma}\rangle \Bigg(\sum_k \langle e_k^{\uparrow}|\hat U^{\sigma}(t)|\mathcal{E}_0\rangle\alpha_{\sigma} \quad \alpha^*_{\sigma'}\langle\mathcal{E}_0| \left(\hat U^{\sigma'}(t)\right)^{\dagger} |e_k^{\uparrow}\rangle\Bigg)\langle\sigma', d_{\sigma'}| \end{aligned} \tag{5.17}$$

We exploit that $\hat U^{\sigma}(t)$ contains a projector on $|d_{\sigma}\rangle$, which is evident from the form in Eq. 5.13, and that is diagonal in the spin variable.

In the following we will use the states $|\mathcal{E}^{\sigma}(t)\rangle$ defined in Eq. 5.13 that is obtained from the environment state $|\mathcal{E}_0\rangle$ by propagating with one or the other propagators, that depend on the detector state variable.

Thus one obtains

$$
\begin{aligned}
Tr_{\mathcal{E}}\left[|\psi(t)\rangle\langle\psi(t)|\right] &= \sum_{\sigma,\sigma'} |\sigma, d_\sigma\rangle \left(\alpha^*_{\sigma'} \underbrace{\langle\mathcal{E}_0| \left(\hat{U}^{\sigma'}(t)\right)^\dagger}_{\langle\mathcal{E}^{\sigma'}(t)|} \underbrace{\left(\sum_k |e_k^\uparrow\rangle\langle e_k^\uparrow|\right)}_{\hat{1}} \underbrace{\hat{U}^{\sigma}(t)|\mathcal{E}_0\rangle}_{|\mathcal{E}^{\sigma}(t)\rangle} \alpha_\sigma \right) \langle\sigma', d_{\sigma'}| \\
&= \sum_{\sigma,\sigma'} |\sigma, d_\sigma\rangle \left(\alpha^*_{\sigma'} \langle\mathcal{E}^{\sigma'}(t)|\mathcal{E}^{\sigma}(t)\rangle \alpha_\sigma \right) \langle\sigma', d_{\sigma'}|
\end{aligned}
$$

Now we can rewrite the reduced density matrix

DECOHERENCE

$$
Tr_{\mathcal{E}}\left[|\psi(t)\rangle\langle\psi(t)|\right] = \begin{pmatrix} |\uparrow, d_\uparrow\rangle \\ |\downarrow, d_\downarrow\rangle \end{pmatrix} \begin{pmatrix} |\alpha|^2 & \alpha\beta^*\langle\mathcal{E}^\downarrow(t)|\mathcal{E}^\uparrow(t)\rangle \\ \beta\alpha^*\langle\mathcal{E}^\uparrow(t)|\mathcal{E}^\downarrow(t)\rangle & |\beta|^2 \end{pmatrix} \begin{pmatrix} \langle\uparrow, d_\uparrow| \\ \langle\uparrow, d_\uparrow| \end{pmatrix} \tag{5.18}
$$

Decoherence results when the overlap $\langle\mathcal{E}^\uparrow(t)|\mathcal{E}^\downarrow(t)\rangle$ of the environment states $|\mathcal{E}_\uparrow(t)\rangle$ and $|\mathcal{E}_\downarrow(t)\rangle$ vanishes. The environment states are experience a Hamiltonian that depends parametrically on the state of the detector. The most general form for the Hamiltonian is given by Eq. 5.12

The overlap $\langle\mathcal{E}^\uparrow(t)|\mathcal{E}^\downarrow(t)\rangle$ remains sizeable only under special conditions. With this I mean that the probability that two random vectors have a non zero angle between each other becomes increasingly smaller with the dimension of the space.

Thus we see that there are two conditions for the interaction between the detector and the environment:

- it must commutate with the observable, i.e. $[\hat{H}_{int}, \hat{O}]_- = 0$.
- The setting of the detector must affect the environment sufficiently, so that the overlap $\langle\mathcal{E}^\uparrow(t)|\mathcal{E}^\downarrow(t)\rangle$ between environment states propagated with different settings d_σ of the detector become orthogonal.

The second condition is not very stringent, because the probability that two states have a overlap matrix element beyond a given size is very small.

This finding also shows that there is no decoherence without coupling to an environment.

The different interaction probably describes the transport of entropy from the environment into the system as the coherence is destroyed.

In the remainder of this section we will try to shed some light on when and how the matrix elements $\langle\mathcal{E}^\downarrow(t)|\mathcal{E}^\uparrow(t)\rangle$ disappear. I will give some argument that it is very unlikely that it does not desappear and I will analyze some examples for an interaction and see how the matrix elements vanish. It should be clear that this is not an attempt to proove that this matrix element always disappears. Such a proof can not succeed. This proof must be done for any potential measurement device individually. If the proof fails, the device is simply not regarded as a measurement devide for the observable $\hat{O}$.

Orthogonality of random vectors in infinite dimensions

We consider two random, but normalized vectors, $\vec{a}, \vec{b}$ in dimension N. The cartesian coordinate system is chosen that the first unit vector points along $\vec{a}$, i.e.

$$
\vec{a} \widehat{=} (1, 0, 0, \dots)
$$

The scalar product is $\vec{a}\vec{b} = b_1$, that is proportional to the first component of vector b. Because the second vector is normalized we have

$$\langle b_1^2 \rangle = \langle b_i^2 \rangle = \langle \frac{1}{N} \underbrace{\sum_i b_i^2}_{=1} \rangle = \frac{1}{N}$$

Thus the scalar product between any two normalized vectors is

$$\langle \vec{a}\vec{b} \rangle = \langle \cos(\angle(\vec{a}, \vec{b})) \rangle = N^{-\frac{1}{2}}$$

For $N \to \infty$ the scalar product vanishes.

Special case: eigenstates of the environment independent of the observable

In order to obtain a feeling for the decay of the overlap matrix element let us make the simplifying assumption that the eigenstates of the Hamiltonian $\hat{H}^{\sigma}_{\mathcal{E}}$ are independent of σ. That is $|e_i^{\uparrow}\rangle = |e_i^{\downarrow}\rangle =: |e_i\rangle$. Let us furthermore introduce $\Delta_i := \epsilon_i^{\uparrow} - \epsilon_i^{\downarrow}$.

$$\begin{aligned}
\langle \mathcal{E}^{\uparrow}(t)|\mathcal{E}^{\downarrow}(t)\rangle &= \sum_{i,j} \langle \mathcal{E}_0|e_i\rangle \mathrm{e}^{\frac{i}{\hbar}\epsilon_i^{\uparrow} t} \underbrace{\langle e_i|e_j\rangle}_{\delta_{i,j}} \mathrm{e}^{\frac{i}{\hbar}\epsilon_j^{\uparrow} t} \langle e_j|\mathcal{E}_0\rangle = \sum_i \langle \mathcal{E}_0|e_i\rangle \mathrm{e}^{\frac{i}{\hbar}(\epsilon_i^{\uparrow}-\epsilon_i^{\downarrow})t} \langle e_i|\mathcal{E}_0\rangle \\
&= \sum_i |\langle e_i|\mathcal{E}_0\rangle|^2 \, \mathrm{e}^{\frac{i}{\hbar}\Delta_i t} \\
&= \int d(\hbar\omega) \, \underbrace{\left[\sum_i |\langle e_i|\mathcal{E}_0\rangle|^2 \, \delta(\hbar\omega - \Delta_i) \right]}_{\Gamma(\hbar\omega)} \mathrm{e}^{i\omega t}
\end{aligned}$$

The function $\Gamma(\hbar\omega)$ plays a role of a density of states. It is probably a measure of the excitation spectrum as obtained by a time dependent perturbation that couples to the detector setting d_σ.

Because the initial environment state is normalized,i.e.$\sum_i |\langle e_i|\mathcal{E}_0\rangle|^2 = 1$, it follows

$$\int d(\hbar\omega) \, \Gamma(\hbar\omega) = 1$$

This reflects that the matrix element initially is equal to one.

If $\Gamma(\hbar\omega)$ function is a sufficently smooth function of ω, the Fourier transform, which is the scalar product $\langle \mathcal{E}^{\uparrow}(t)|\mathcal{E}^{\downarrow}(t)\rangle$ is localized in real time.

Let us consider a few special cases and the corresponding $\Gamma(\hbar\omega)$.

- In the first example the environment has only a single frequency, which however, differs for the two detector states. $\Gamma(\hbar\omega) = \frac{1}{2}\left(\delta(\hbar\omega - \hbar\omega_0) + \delta(\hbar\omega + \hbar\omega_0)\right)$

  $$\langle \mathcal{E}^{\uparrow}(t)|\mathcal{E}^{\downarrow}(t)\rangle = \cos(\omega_0 t)$$

  This implies that there is no decoherence.

- In the second example the spectrum of Δ_i is continous but has a maximum value. $\Gamma(\omega) = \frac{1}{2\hbar\omega_0}\theta(\hbar\omega - \hbar\omega_0)\theta(\hbar\omega_0 - \hbar\omega)$

  $$\langle \mathcal{E}^{\uparrow}(t)|\mathcal{E}^{\downarrow}(t)\rangle = \frac{\sin(\hbar\omega_0 t)}{\hbar\omega_0 t}$$

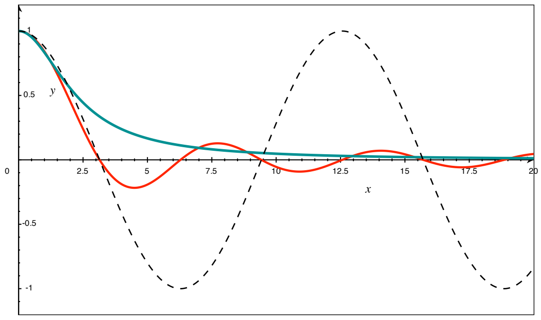
  There are oscillations, which however die out in time. Thus the system will be dcoherent.

- The final example considers continuous spectrum of Δ-values, that smoothly falls off to zero. $\Gamma(\omega)=\frac{a\hbar}{2}\mathrm{e}^{-a|\hbar\omega|}$

  $$\langle\mathcal{E}^{\uparrow}(t)|\mathcal{E}^{\downarrow}(t)\rangle=\frac{\hbar^2a^2}{\hbar^2a^2+t^2}$$

  In example the overlap of the environment states fall of rapidly without any oscillations.

The following figure shows the decay of the matrix element $\langle\mathcal{E}^{\uparrow}(t)|\mathcal{E}^{\downarrow}(t)\rangle$ with time for the three examples discussed above, namely $cos(\frac{1}{2}t)$ (dashed, black), $\frac{sin(t)}{t}$ (red), and $(1+(t/5))^{-1}$.



Temperature of the environment

Up to now we have assumed that there is a single initial state in order to show that decoherence is not the result of any ensemble averaging.

We can, however, also extend our expressions to a thermal ensemble. We make the same assumption as before, that the eigenstates of the environment are independent of the observable, while the energy spectrum $\{e_n^{\bar\sigma}\}$ of the environment does depend on it.

Then we consider an ensemble of environment states, which are eigenstates of the environment Hamiltonian $|e_j\rangle$ and which have probabilities $P_j=\frac{1}{Z(\beta)}\mathrm{e}^{-\beta\epsilon_j}$. The energies shall be independent of the observable, i.e. $\epsilon_j=\frac{1}{2}(\epsilon_j^{\uparrow}+\epsilon_j^{\downarrow})$.

$$\begin{aligned}\langle\mathcal{E}^{\uparrow}(t)|\mathcal{E}^{\downarrow}(t)\rangle_T&=\int d(\hbar\omega)\,\underbrace{\left[\sum_j P_j\sum_i|\langle e_i|e_j\rangle|^2\,\delta(\hbar\omega-\Delta_i)\right]}_{\Gamma(\hbar\omega,T)}\mathrm{e}^{i\omega t}\\&=\int d(\hbar\omega)\,\underbrace{\left[\frac{1}{\sum_j\mathrm{e}^{-\beta\epsilon_j}}\sum_j\mathrm{e}^{-\beta\epsilon_j}\delta(\hbar\omega-\Delta_j)\right]}_{\Gamma(\hbar\omega,T)}\mathrm{e}^{i\omega t}\end{aligned}$$

If the excitation energies $\epsilon_j-\epsilon_0$ are larger than k_BT, decoherence is likely to disappear, because only a single state of the environment contributes.

5.7.1 Decoherence time

The decoherence time itself can be calculated by propagating the environment state with one or the other setting of the detector, and to monitor the overlap matrix element of the two states. The result should be averaged over an appropriate ensemble for the environment.

$$|\sum_j P_j \langle \mathcal{E}_j | \hat{U}^{\uparrow}(-t)\hat{U}^{\downarrow}(t)|\mathcal{E}_j\rangle| = \mathrm{e}^{-\frac{t}{\tau}}$$

$$\frac{1}{\tau} = -\frac{1}{t}\ln\left|\sum_j P_j \langle \mathcal{E}_j | \hat{U}^{\uparrow}(-t)\hat{U}^{\downarrow}(t)|\mathcal{E}_j\rangle\right|$$

This is not a complete definition, but this reflects that there is not necessarily a single decoherence time-scale.

5.8 Phase average

The average of the phases of the components of the wave functions deletes the non-diagonal elements. We define the coefficient β of the initial wave function to be variable by a phase $\mathrm{e}^{i\phi}$, i.e.

$$\beta(\phi) = \beta_0 \mathrm{e}^{i\phi} \tag{5.19}$$

The corresponding phase averaged density matrix is

$$\hat{\rho}_{\text{phaseaveraged}} = \frac{1}{2\pi}\int_0^{2\pi} d\phi\ \rho(\phi) = |\uparrow d_{\uparrow}\rangle|\alpha|^2\langle\uparrow d_{\uparrow}| + |\downarrow d_{\downarrow}\rangle|\beta|^2\langle\downarrow d_{\downarrow}|$$

Thus the phase averaged is on the same level as a classical probability formulation.

The phase average is dependent on a unitary transformation of the basis. Thus, the phase average singles out certain observables.

A phase shift can be induced by a constant potential

$$\hat{U} = \hat{U}_0 \mathrm{e}^{-\frac{i}{\hbar}V_0 t}$$

where the phase shift is $\delta\phi = -\frac{1}{\hbar}V_0 t$. An overall constant potential does not yet affect the relative shift between different contributions of the wave function. If the potential acts differently on the different parts of the wave function the coherence between them is destroyed.

In order to induce a shift by 2π the potential must be of order $\hbar\frac{2\pi}{T}$, where T is the duration for which the potential is applied. Thus

- a potential of 1 eV induces a phase change of 2π within 1 fs.
- a potential of 1 meV induces a phase change of 2π within 1 ps.

$$\hat{U} = \hat{U}_0 \mathrm{e}^{-\frac{i}{\hbar}[|\uparrow\rangle V_{\uparrow}\langle\uparrow| + |\downarrow\rangle V_{\downarrow}\langle\downarrow|]t}$$

This additional Hamiltonian singles out a particular basis. A detector must be constructed such that the perturbing potential destroyes the coherence between the different eigenstates of the observable the detector wants to measure.

Where or when does the perturbing potential act? The perturbing potential can destroy the coherence before the interaction with the detector, in which the detector does not experience a pure state but a statistical mixture. It can however also act after the measurement on the entangled state of the measured system and the detector! In the latter case a physical interaction with the system to be measured is not required, and the decoherence may be a property entirely of the detector. In this case a coherent state enters the detector, but after the measurement the detector is in a statistical mixture of two possibilities.

This implies that the detector must have two properties

1. a certain interaction between the system to be measured and the detector, which changes the detector into specified states depending on the state of the system and
2. a perturbing external interaction that destroyes the coherence between eigenstates with different eigenvalues of the observable to be measured.

5.9 Collapse

One question, not discussed in detail is the collapse of the probability distribution. I look at this a classical process of information gathering.

Consciousnes as detector

We can can consider our consciousness as the detector $\{d_\uparrow, d_\downarrow\}$ in the sense of the von Neumann chain. Even though our consciousness may be in a superposition of states, we are unable to "detect" it, because in each case our consciousness is tied to the state of the system, if the corresponding correlation has been done in a measurement. Two possibilities exist: either the spin is in the up state and we believe that it is in an up state, or the spin is in the down state and we believe that it is in a down state. In none of the cases would be observe something like a fluctuating, or smeared out reading: Whatever we believe is right, if we gain that information from the measurement. With this argument we might even live well with being in a superposition of states, rather than in one of two classical possibilities. A collapse is not relevant and does not take place.

Classical probabilities

If decoherence has taken place I can stick to the subjective interpretation of probabilities as a means to describe our state of mind, rather than reality. If we do not look at the measurement our probabilities are not affected, and the future is a weighted superposition of possibilities. If we gain information about additional information, the probability distribution collapses and the choice of future developments is restricted.

Chapter 6

Notes on the Interpretation of Quantum Mechanics

by Tom Kirchner (`tomk@yorku.ca`)

In this chapter we attempt to provide an introduction to the problem of interpreting quantum mechanics (QM), which has troubled physicists and philoshophers since the groundwork of the theory was laid in the 1920s. Necessarily, our discussion will be incomplete and the selection of topics subjective. The idea is to focus on some ideas put forward by physicists that solve — at least partially — the so-called measurement problem. The buzzword associated with these ideas is *decoherence*. Decoherence describes a physical process and not a philosophical concept, and this is why we think the topic is well-suited for this course.

Let us first define our goal and ask: what shall interpretation of a physical theory mean?

1st answer: interpretation := understanding the physical content of the theory

This seems to be a rather modest goal. Understanding in this context means to know what the physical laws express and which phenomena they describe. It means to know, *how* things work — but not *why* they work the way they do. In classical mechanics and electrodynamics this kind of understanding is pretty straightforward. The basic laws (e.g. Newton's equation of motion) express how observable quantities such as position or velocity of a particle evolve in space and time[1]. In QM this is not the case. The basic quantities are manifestly abstract quantities — one cannot observe wave functions or hermitian operators, and this why we face an interpretation problem. In order to unravel it, it is useful to formulate a more precise answer to our question.

2nd answer: interpretation := establishing (unique) relationships between the mathematical symbols of the theory and the observable data

In classical physics these relationships are more or less trivial: the basic mathematical symbols such as the position vector of a particle $\boldsymbol{r}(t)$ are directly observable[2]. But we would like to discuss QM! To set the stage for this discussion let us briefly review the mathematical symbols of the theory.

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[1] Actually, things are somewhat less obvious in electrodynamics than in mechanics, since the electromagnetic field is not really an obserable quantity, but a theoretical concept. It is, however, directly related to observable quantities, i.e., to the effects of forces on charged particles.

[2] Again, electrodynamics is somewhat less trivial than mechanics: Maxwell's field equations can be rewritten as differential equations for the scalar and vector potentials, which are not observable. However, their relationships to (almost) observable quantities — the components of the electromagnetic field — are well defined and clear cut.

6.1 Brief Review of the Mathematical Symbols of Quantum Mechanics

The basic quantities of QM are state vectors and operators. Their fundamental properties and relations are usually collected in a set of postulates, which we repeat here without much comment and in a somewhat unusual way that suits our needs.

(i) States are characterized by Hilbert space vectors: $|\Psi\rangle \in \mathcal{H}$.

(ii) A (hermitian) operator $\hat{A}$ mediates a linear map between state vectors: $|\Phi\rangle = \hat{A}|\Psi\rangle \in \mathcal{H}$.

(iii) There are fundamental commutation relations between the fundamental operators, e.g., $[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$.

(iv) The dynamics of a quantum system is governed by the Schrödinger equation

$$
\begin{aligned}
i\hbar\frac{d}{dt}\ |\Psi(t)\rangle &= \hat{H}(t)\ |\Psi(t)\rangle \\
|\Psi(t_0)\rangle &= |\Psi_0\rangle\,.
\end{aligned}
$$

The mathematical structure of QM is determined by (i)-(iv). Apparently, it is a rather abstract theory, and its relation to observations is far from obvious. The theory can be made more explicit by applying representation theory, e.g., we can use the position (real space) representation:

$$
\begin{aligned}
\hat{x}_j &\to x_j \\
\hat{p}_j &\to \frac{\hbar}{i}\frac{\partial}{\partial x_j}
\end{aligned}
$$

$$
|\Psi\rangle \ \to\ \langle \boldsymbol{r}|\Psi\rangle = \Psi(\boldsymbol{r})
$$

The Schrödinger equation for a one-particle system then reads

$$
i\hbar\partial_t\ \Psi(r,t) = (-\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{r}))\ \Psi(\boldsymbol{r},t).
$$

Instead of state vectors and abstract operators we are now dealing with wave functions, differential operators, and partial differential equations. This looks much more familiar and suggests that QM can be interpreted as a classical field theory for matter waves. It was Schrödinger's original hope that this interpretation would prevail, but it did not. In fact, it is untenable for several reasons:

1) Matter waves disperse in the vacuum.

2) The wave concept alone cannot describe the double-slit experiment.

3) It is not clear what kind of matter wave is associated with the wave function of an N-particle state.

6.2 The Standard Interpretation Rules ("Copenhagen")

If the classical wave interpretation is untenable the relationships between the mathematical symbols of QM and the observable quantities must be very different from those of classical physics. A set of rules was introduced by Bohr, Heisenberg, and Pauli soon after QM had been discovered. The three thinkers often met in Copenhagen, which is why this interpretation is called the *Copenhagen interpretation*[3].

(i) The spectrum of real eigenvalues a_n of a hermitian operator $\hat{A}$ is the set of the possible outcomes of measurements of the corresponding observable.

(ii) Expectation values are given by

$$\begin{aligned} < \hat{A} > &= \langle \Psi | \hat{A} | \Psi \rangle \\ &= \sum_{n,n'} \langle \Psi | a_n \rangle \langle a_n | \hat{A} | a_{n'} \rangle \langle a_{n'} | \Psi \rangle \\ &= \sum_n |\langle \Psi | a_n \rangle|^2 \; a_n \end{aligned}$$

if$\langle \Psi | \Psi \rangle = 1$.

(iii) The probability to measure the value a_n is given by

$$w_n = |\langle \Psi | a_n \rangle|^2 .$$

(iv) The result of an individual measurement is not determined.

Statements (iii) and (iv) comprise the probabilistic interpretation of QM, which was first suggested by Max Born in 1926[4]. He was awarded the Nobel prize for it in 1954.

(v) Reduction ("collapse") of the wave function:

$$|\Psi\rangle \xrightarrow[\text{find } a_m]{\text{measure } \hat{A}} |a_m\rangle \xrightarrow{\text{measure } \hat{A}} |a_m\rangle$$

Whereas (iii) and (iv) concern the question what can be known before a measurement takes place, this statement concerns the question what happens in a measurement and what is known about the system afterwards.

These rules have been criticized and challenged in several respects. We mention two areas of concern:

(i) A farewell to determinism or: is QM incomplete?
(e.g. Einstein, Podolsky, Rosen 1935 (EPR) [2])
Rules (i) to (iii) are more or less accepted, but rule (iv) is not. It is claimed that the unpredictability of the outcome of an individual measurement is not a fundamental fact, but a sign of the incompleteness of the theory. It is assumed that so-called hidden variables exist that would eliminate the unpredictabiltiy if they were uncovered.
However, John v. Neumann had presented a proof in 1932 that excluded the existence of

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[3] It was often pointed out later on that Bohr's, Heisenberg's, and Pauli's viewpoints were similar, but not identical and also changed over time. However, we will not dwell on such subleties.

[4] in a footnote of an article entitled *Zur Quantenmechanik der Stoßvorgänge* [1]: "Genauere Überlegung zeigt, dass die Wahrscheinlichkeit dem Quadrat der Größe (...) proportional ist". Born understood very well that this interpretation opened a Pandora's box. In the same article he wrote: "Hier erhebt sich die ganze Problematik des Determinismus. (...) Ich selber neige dazu, die Determiniertheit in der atomaren Welt aufzugeben. Aber das ist eine philosophische Frage, für die physikalische Argumente nicht allein maßgebend sind."

hidden vaiables [3]. Nevertheless, the discussion went on, and new suggestions were made by D. Bohm in 1952 [4]. It was John Bell who showed that v. Neumann's assumptions were too restricted [5]. His investigations led to the celebrated Bell's inequalities [6], which provided a testable criterion for hidden variables versus standard QM. Subsequently, experiments were performed, most notably by A. Aspect et al. in 1982 [7]. All of these experiments have been in favor of standard QM, but have not ended the discussion on hidden variables to the present date.

We will not dwell on this issue, but elaborate on a second critique, whose starting point is the question:

(ii) What is the nature of the collapse?
The problem with the collapse is that it comes as an ad-hoc assumption. It is not properly formulated in terms of a fundamental equation that tells us what causes it and when exactly it takes place. To make it worse, one can show that it contradicts the fundamental dynamical law of QM: the Schrödinger equation! In other words: the rule that pretends to interpret QM violates the theory!

6.3 Elementary Measurement Theory

It is not difficult to see that the collapse postulate contradicts the Schrödinger equation. The latter is a linear map of a state vector

$$|\Psi(t_0)\rangle \xrightarrow{\text{linear}} |\Psi(t)\rangle$$

$$\hookrightarrow \ \alpha|\Psi_1(t_0)\rangle + \beta|\Psi_2(t_0)\rangle \ \longmapsto \ \alpha|\Psi_1(t)\rangle + \beta|\Psi_2(t)\rangle .$$

The collapse is also a map

$$|\Psi\rangle \ \xrightarrow[\text{find } a_m]{\text{measure } \hat{A}} \ |a_m\rangle ,$$

but it is not linear as illustrated by the following example. We assume that measurements of the observable $\hat{A}$ on the the states $|\Psi_1\rangle$ and $|\Psi_2\rangle$ produce different results

$$|\Psi_1\rangle \ \xrightarrow{\text{measure } \hat{A}} \ |a_1\rangle$$

$$|\Psi_2\rangle \ \xrightarrow{\text{measure } \hat{A}} \ |a_2\rangle .$$

Now we consider as a third (legitimate) state a linear combination of $|\Psi_1\rangle$ and $|\Psi_2\rangle$. If the collapse were a linear map a measurement of $\hat{A}$ would proceed according to

$$|\Psi\rangle = \alpha|\Psi_1\rangle + \beta|\Psi_2\rangle \ \overset{\text{measure } \hat{A}}{\rightarrow} \ \alpha|a_1\rangle + \beta|a_2\rangle .$$

But this is not what will be found! Instead of a linear combination of eigenvalues a measurement on $|\Psi\rangle$ will yield one of the eigenvalues of $\hat{A}$, i.e.,

$$|\Psi\rangle = \alpha|\Psi_1\rangle + \beta|\Psi_2\rangle \ \overset{\text{measure } \hat{A}}{\rightarrow} \ |a_\psi\rangle \, .$$

Bohr was — of course — well aware of this problem. His answer went like this: Measurements take place in the macroscopic world even if the objects considered are elements of the microworld. Accordingly, one has to distinguish classical and quantum worlds, for the laws that govern them are different. The reduction of the wave function is the bridge between both worlds and cannot be described with the laws of either one of the two worlds. In other words: it makes no sense to try to reconcile the collapse with the Schrödinger equation.

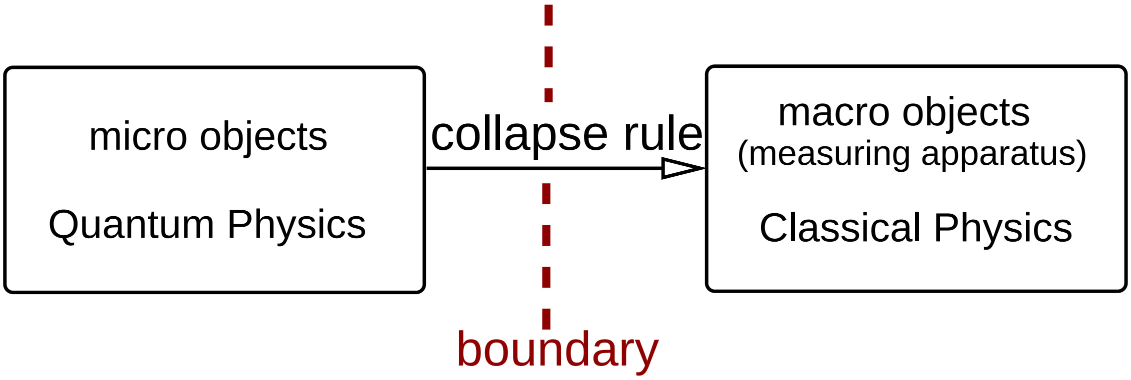

Fig. 6.1: The world according to Bohr

This directive is problematic for several reasons:

- It provokes (but does not answer) the question where the border between both worlds is located. In view of (almost) macroscopic quantum phenomena, such as interfering buckyballs this question has become more pressing in recent years.
- According to Bohr quantum theory is *not* universal. While this was acceptable when it was first introduced most contemporary physicists would insist on its universality.
- One might wonder whether the use of two different languages — one for the quantum system and one for the measuring device and the actual measurement — causes logical problems[5].

We will take a different (i.e., John v. Neumann's) point of view in the following. We will assume that QM is universal and therefore also applicable to the interaction of a (macroscopic) measuring device and a (microscopic) quantum system. This is to say, we will assume that the act of measuring can be expressed by a Schrödinger equation. Due to the linearity of the latter this will lead to a contradiction with the collapse rule. We will analyze this contradiction in some detail, because this leads to new insights.

So, here is our program:

- Investigate the Schrödinger equation for the measurement process
- Learn from the juxtaposition of its result with the collapse.

6.3.1 von Neumann's Model

Let us consider a quantum system Q and a measuring device M. Both are to be described by quantum mechanics. A measurement is therefore an interaction between Q and M. The state that characterizes Q is a Hilbert space vector $|\psi\rangle \in \mathcal{H}_{\mathcal{Q}}$, and the state that characterizes M is a Hilbert space vector $|\phi\rangle \in \mathcal{H}_{\mathcal{M}}$. The state of the composite system QM is an element of the product space $\mathcal{H}_{\mathcal{QM}} = \mathcal{H}_{\mathcal{Q}} \otimes \mathcal{H}_{\mathcal{M}}$.

Before the interaction between Q and M ($t < 0$) the total Hamiltonian consists of two parts

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[5] Bohr countered this concern with the introduction of *complementarity*.

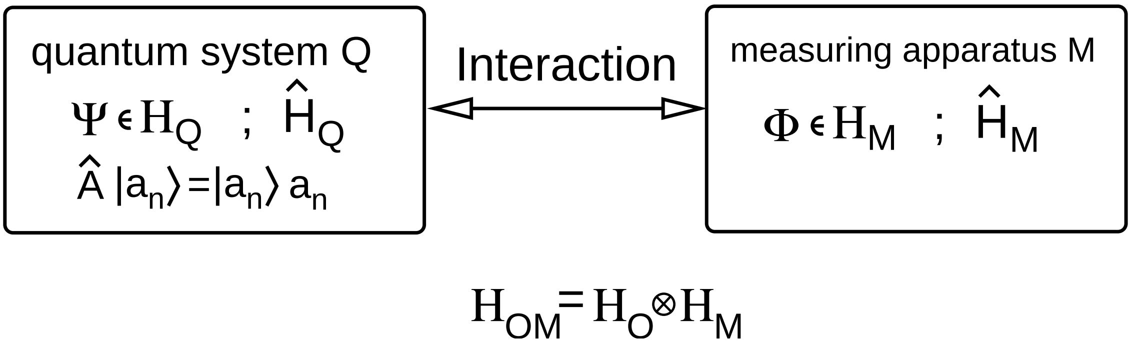

Fig. 6.2: Composite system of a quantum system and a measuring device

$$\hat{H} \equiv \hat{H}_0 = \hat{H}_Q + \hat{H}_M \tag{6.1}$$

associated with both subsystems[6]. The state of the noninteracting system is a product state

$$|\chi_0\rangle = |\psi_0\rangle\ |\phi_0\rangle. \tag{6.2}$$

Let us now consider a few scenarios.

Case 1:

Q

We assume that before the interaction Q is in an eigenstate of the observable $\hat{A}$ we wish to measure

$$|\psi_0\rangle = |a_1\rangle \tag{6.3a}$$
$$\hat{A}|a_1\rangle = a_1|a_1\rangle \tag{6.3b}$$
$$\left[\hat{H}_Q, \hat{A}\right] = 0. \tag{6.3c}$$

Because of the commutator $\hat{A}$ is a constant of motion.

M

The measuring device shall be described by one degree of freedom representing the position of a pointer on a ruler

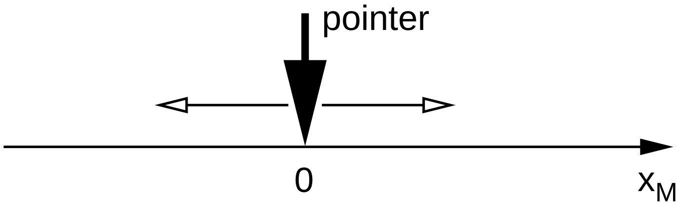

Fig. 6.3: $|\phi_0\rangle\ \leftrightarrow$ pointer position $x_M = 0$

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[6] Actually one should write $\hat{H}_0 = \hat{H}_Q \otimes \hat{1}_M + \hat{1}_Q \otimes \hat{H}_M$.

$$|\phi_0\rangle = |x_M = 0\rangle \tag{6.4}$$
$$\hat{x}_M\,|\phi_0\rangle = 0 \tag{6.5}$$
$$\left[\hat{H}_M, \hat{x}_M\right] = 0. \tag{6.6}$$

The interaction between Q and M is expressed by a (potential) operator in the total Hamiltonian at times $t \geq 0$:

$$\hat{H} = \hat{H}_0 + \hat{V}(t) \tag{6.7}$$

$$\hat{V}(t) \neq 0 \text{ für } \; 0 \leq t \leq \varepsilon\ .$$

The time development of the system QM is described by the Schrödinger equation for the Hamiltonian $\hat{H}$. Equivalently, we can express it by using the evolution operator $\hat{U}$:

$$\begin{aligned} |\chi(t)\rangle &= \hat{U}(t,0)\ |\chi(0)\rangle \\ &= \hat{U}(t,0)\ |\psi_0\rangle\ |\phi_0\rangle \end{aligned} \tag{6.8}$$

$$\text{with} \quad i\hbar\frac{d}{dt}\ \hat{U}(t,0) = \hat{H}(t)\ U(t,0). \tag{6.9}$$

To proceed we need an ansatz for the interaction $\hat{V}$:

$$\hat{V}(t) = g(t)\ \hat{p}_M\ \hat{A} \tag{6.10a}$$
$$\text{with} \quad [\hat{x}_M, \hat{p}_M] = i\hbar. \tag{6.10b}$$

If ε is small and the interaction is strong we can approximate the evolution operator according to

$$\begin{aligned} \hat{U}\,(\varepsilon,0) &\approx \exp\left(-\frac{i}{\hbar}\int_0^\varepsilon \hat{H}(t)dt\right) \\ &= \exp\left[-\frac{i}{\hbar}\left(\hat{H}_0\ \varepsilon + \hat{p}_M\ \hat{A}\int_0^\varepsilon g(t)dt\right)\right] \\ &\approx \exp\left[-\frac{i}{\hbar}\lambda\hat{p}_M\ \hat{A}\right], \end{aligned} \tag{6.11}$$

where we have defined the amplification function λ in the last step

$$\lambda = \int_0^\varepsilon g(t)dt. \tag{6.12}$$

$$\begin{aligned} \hookrightarrow \quad |\chi(t)\rangle &= \exp\left(-\frac{i}{\hbar}\lambda\ \hat{p}_M\hat{A}\right)|a_1\rangle\ |x_M = 0\rangle \\ &= \Big[\underbrace{\exp\left(-\frac{i}{\hbar}\lambda\ a_1\ \hat{p}_M\right)}_{\text{translation by } \lambda\ a_1}\ |x_M = 0\rangle\Big]\,|a_1\rangle \qquad (6.13) \\ &= |x_M = \lambda a_1\rangle\,|a_1\rangle \qquad (6.14) \end{aligned}$$

After the measurement the state is still a product state. The state of Q is unchanged, but the pointer of the apparatus has moved from the position 0 to the position λa_1[7]. For a fixed (and known) amplification function the new pointer position characterizes the measured eigenvalue of Q.

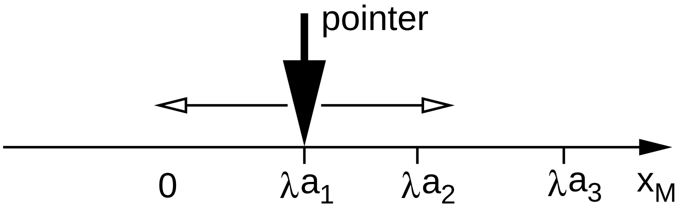

Fig. 6.4: The final state of the apparatus

This is exactly what a measurement should do. There is no problem in this case.

Case 2:
Now we choose a different initial condition for Q

$$|\psi_0\rangle = c_1\ |a_1\rangle + c_2\ |a_2\rangle. \tag{6.15}$$

Applying the same arguments we find

$$\begin{aligned} |\chi(t)\rangle &\approx \exp\left(-\frac{i}{\hbar}\lambda\ \hat{p}_M\hat{A}\right)|\psi_0\rangle|\phi_0\rangle \\ &= c_1\ |a_1\rangle\ \exp\left(-\frac{i}{\hbar}\lambda\ a_1\ \hat{p}_M\right)|x_M=0\rangle + c_2\ |a_2\rangle\ \exp\left(-\frac{i}{\hbar}\lambda\ a_2\ \hat{p}_M\right)|x_M=0\rangle \\ &= \underbrace{c_1\ |a_1\rangle\ |x_M=\lambda\ a_1\rangle + c_2\ |a_2\rangle\ |x_M=\lambda\ a_2\rangle}_{\text{entangled state}} \end{aligned} \tag{6.16}$$

Obviously, this result cannot be associated with a unique pointer position. However, an actual measurement does produce a well-defined pointer position. Hence, we face a problem: a contradiction between the QM description of the measurement process and experience (and the collapse rule).

Discussion

(i) Let us apply the collapse rule to our scenarios.

$$\text{Case 1:}\quad |\psi_0\rangle = |a_1\rangle \xrightarrow{\hat{A}} |a_1\rangle \text{ "certain measurement"}$$

$$\text{Case 2:}\quad |\psi_0\rangle \xrightarrow{\hat{A}} |a_1\rangle \text{ or } |a_2\rangle$$

Case 1 produces the same result, but case 2 does not. The (linear) Schrödinger equation does not yield distinguishable alternatives (simple product states), but a superposition of product states.

(ii) According to the QM description of the measurement the superposition in the initial state of Q is transferred to the apparatus. The final state (6.16) of QM is called an *entangled* state. It is associated with macroscopic interferences of two different pointer positions — an untenable situation!

(iii) One might hope that a further measurement of the system QM conducted by a 'super apparatus' can remedy the situation, but this is not the case. The same scheme applies to further measurements such that the superposition is transferred to the super apparatus and so on and so forth. This hopeless situation is called v. Neumann's chain.

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[7] λ must be large so that the new position of the pointer is macroscopically distinguishable from its initial position.

(iv) To escape from his infinite chain v. Neumann resorted to a rather weird idea: he proposed that it is the consciousness of the observer that breaks the chain, i.e., he transferred the collapse into the human brain. Interestingly enough this idea was developed further by others, but it seems incredible today, because experimental data are now 'read' by computers and not by human beings.

(v) From a more pragmatic point of view one might think that the problem has been overrated and the entangled state (6.16) can be interpreted as signifying unique relations between the eigenvalues of Q and pointer positions. Aren't these relations similar to classical alternatives when one throws a coin? A variation of our case 2 shows that the situation is much more serious.

Case 2'

To be more specific let us assume that Q is a spin $\frac{1}{2}$ particle. Then we can write for the initial (superposition) state

$$|\psi_0\rangle = c_1|\uparrow\rangle + c_2|\downarrow\rangle.$$

If we repeat the argument we find the following:

$$\begin{array}{ccc} t \leq 0 & \text{measurement } t \geq \varepsilon & \\ |\chi_0\rangle = |\psi_0\rangle|\phi_0\rangle & \longrightarrow & |\chi\rangle = c_1 \,|\uparrow\rangle\, |\phi_\uparrow\rangle + c_2 \,|\downarrow\rangle\, |\phi_\downarrow\rangle. \end{array}$$

We pick a special situation: $c_1 = -c_2 = \frac{1}{\sqrt{2}}$

$$\hookrightarrow \quad |\chi\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow\rangle\, |\phi_\uparrow\rangle - |\downarrow\rangle\, |\phi_\downarrow\rangle\right). \tag{6.17}$$

The state of Q can be represented in a different basis. For instance, we can consider the following transformation of basis states

$$\begin{aligned} |0\rangle &= \tfrac{1}{\sqrt{2}} \left(|\uparrow\rangle + |\downarrow\rangle\right) \\ |1\rangle &= \tfrac{1}{\sqrt{2}} \left(|\uparrow\rangle - |\downarrow\rangle\right). \end{aligned} \tag{6.18}$$

Let us also transform the states of the apparatus:

$$\begin{aligned} |\phi^0\rangle &= \tfrac{1}{\sqrt{2}} \left(|\phi_\uparrow\rangle - |\phi_\downarrow\rangle\right) \\ |\phi^1\rangle &= \tfrac{1}{\sqrt{2}} \left(|\phi_\uparrow\rangle + |\phi_\downarrow\rangle\right). \end{aligned} \tag{6.19}$$

It is straightforward to show that the state (6.17) of QM can also be written as

$$|\chi\rangle = \frac{1}{\sqrt{2}} \left(|1\rangle\, |\phi^1\rangle - |0\rangle\, |\phi^0\rangle\right). \tag{6.20}$$

To interpret this result let us assume that $|\uparrow\rangle$, $|\downarrow\rangle$ are eigenstates of $\hat{s}_z$ (for $m_s = \pm\frac{\hbar}{2}$). The well-known matrix representations of different components of the spin operator are

$$\underline{\underline{s}}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\underline{\underline{s}}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

Accordingly

$$\begin{aligned}
\hat{s}_x|0\rangle &\to \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} \to \frac{\hbar}{2}\,|0\rangle \\
\hat{s}_x|1\rangle &\to \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} \to -\frac{\hbar}{2}\,|1\rangle
\end{aligned}$$

This shows that $|0\rangle$, $|1\rangle$ are eigenstates of $\hat{s}_x$ (for $m_s = \pm\frac{\hbar}{2}$), and it indicates that the pragmatic point of view does not lead us out of the dark. If we resort to it we can interpret $|\chi\rangle$ either as the result of a measurement of the z-component of the spin or a measurement of the x-component. In other words: not even the the two sides of the medal (the alternatives) are well-defined. Without collapse we are still in the land of ignorance and uncertainty!

6.3.2 Density Operators

To proceed it is useful to introduce/recall the concept of density operators.

Pure States

Let us consider a quantum system described by a state vector $|\Psi\rangle$ and a Schrödinger equation

$$i\hbar\frac{d}{dt}\,|\Psi(t)\rangle = \hat{H}\,|\Psi(t)\rangle$$

Definition: density operator

$$\hat{\varrho}(t) := |\Psi(t)\rangle\langle\Psi(t)| \tag{6.21}$$

$$\begin{aligned}
\lhd \qquad i\hbar\frac{d}{dt}\hat{\varrho} &= \left(i\hbar\frac{d}{dt}|\Psi(t)\rangle\right)\langle\Psi(t)| - |\Psi(t)\rangle\left(-i\hbar\frac{d}{dt}\langle\Psi(t)|\right) \\
&= \hat{H}|\Psi(t)\rangle\langle\Psi(t)| - |\Psi(t)\rangle\langle\Psi(t)|\hat{H} \\
&= \left[\hat{H},\hat{\varrho}\right] \qquad (6.22)
\end{aligned}$$

(von Neumann equation)

One can formulate QM in terms of the density operator instead of the state vector. For instance:

- Expectation values

$$\begin{aligned}
\langle\hat{A}\rangle &= \langle\Psi|\hat{A}|\Psi\rangle \\
&= \sum_n \langle\Psi|a_n\rangle\; a_n\; \langle a_n|\Psi\rangle \\
&= \sum_n a_n\; \langle a_n|\Psi\rangle\langle\Psi|a_n\rangle \\
&= \sum_n a_n\; \langle a_n|\hat{\varrho}|a_n\rangle \\
&= \sum_n \langle a_n|\hat{\varrho}\hat{A}|a_n\rangle \\
&= Tr\left(\hat{\varrho}\hat{A}\right) = Tr\left(\hat{A}\hat{\varrho}\right) \qquad (6.23)
\end{aligned}$$

- Transition probabilities

$$\begin{aligned} w_n &= |\langle a_n|\Psi\rangle|^2 = \langle\Psi|a_n\rangle\langle a_n|\Psi\rangle \\ &= \langle\Psi|\hat{P}_n|\Psi\rangle \\ &= Tr\ \left(\hat{P}_n\hat{\varrho}\right) \end{aligned} \tag{6.24}$$

Mixed States

The concept of density operators becomes particularly useful when mixed states are considered. Mixed states are associated with incomplete information about the system, i.e., all we know is that the system is in one of the pure states $|\Psi_k\rangle \in \mathcal{H}$ with the associated probabilities $p_k \geq 0$ [8]. In statistical mechanics one says that all these states characterize the same "macro state", but correspond to different "micro states". The whole set $\{|\Psi_k\rangle\}$ is called an *ensemble*.

Again we can consider expectation values: they are the mean values of the ensemble

$$\begin{aligned} \langle\hat{A}\rangle &= \sum_k p_k\ \langle\hat{A}\rangle_k \\ &= \sum_k p_k\ \langle\Psi_k|\hat{A}|\Psi_k\rangle \\ &= \sum_{kn} p_k\ \langle\Psi_k|a_n\rangle\ a_n\ \langle a_n|\Psi_k\rangle \\ &= \sum_n a_n\ \langle a_n|\underbrace{\sum_k \Psi_k\rangle\ p_k\ \langle\Psi_k}_{=:\hat{\varrho}}|a_n\rangle \\ &= \sum_n a_n\ \langle a_n|\hat{\varrho}|a_n\rangle = \sum_n \langle a_n|\hat{A}\hat{\varrho}|a_n\rangle \\ &= Tr\left(\hat{\varrho}\hat{A}\right) = Tr\left(\hat{A}\hat{\varrho}\right). \end{aligned}$$

Here we have defined the density operator for mixed states according to

$$\hat{\varrho} = \sum_k |\Psi_k\rangle\ p_k\ \langle\Psi_k|. \tag{6.25}$$

<u>Remarks:</u>

(i) Transition probabilities: $w_n = Tr\left(\hat{P}_n\hat{\varrho}\right)$ (same as for pure states)

(ii) v. Neumann equation is unchanged (note that $\dot{p}_k = 0$)

(iii) The density operator for a pure state is recovered if: $p_k = 1$ for $k = k_0$; $p_n = 0$ otherwise

(iv) Entropy

$$\begin{aligned} S &:= -k_B\langle ln\hat{\varrho}\rangle \\ &= -k_B\left(\hat{\varrho}\ ln\hat{\varrho}\right) \end{aligned} \tag{6.26}$$

$$\begin{cases} = 0 & \text{if } \hat{\varrho} = |\Psi\rangle\langle\Psi| \\ > 0 & \text{else} \end{cases}$$

---

[8] with $\sum_k p_k = 1$

$\hookrightarrow$ pure states contain more information than mixed states.

Density Operators for Entangled States

We apply the density operator concept to the entangled state (6.16), which is a pure state:

$$\begin{aligned}\hat{\varrho} &= |\chi\rangle\langle\chi| \\ &= (c_1\ |a_1\rangle\ |\phi_1\rangle + c_2\ |a_2\rangle\ |\phi_2\rangle)\,(c_1^*\ \langle a_1|\ \langle\phi_1| + c_2^*\ \langle a_2|\ \langle\phi_2|) \\ &= |c_1|^2\ |a_1\rangle|\phi_1\rangle\ \langle a_1|\langle\phi_1| + |c_2|^2\ |a_2\rangle|\phi_2\rangle\ \langle a_2|\langle\phi_2| \\ &\quad + c_1\ c_2^*\ |a_1\rangle|\phi_1\rangle\ \langle a_2|\langle\phi_2| + c_1^*\ c_2\ |a_2\rangle|\phi_2\rangle\ \langle a_1|\langle\phi_1| \\ &= \sum_{mn} \varrho_{mn}|a_m\rangle|\phi_m\rangle\ \langle a_n|\langle\phi_n|.\end{aligned}$$

The associated *density matrix* is given by

$$\underline{\underline{\varrho}} \equiv (\varrho_{mn}) = \begin{pmatrix} |c_1|^2 & c_1\ c_2^* \\ c_1^*\ c_2 & |c_2|^2 \end{pmatrix}. \tag{6.27}$$

The latter equation suggests the following interpretation: the diagonal elements of $\underline{\underline{\varrho}}$ are probabilities, while the nondiagonal elements are manifestations of the entanglement (sometimes called quantum correlations). If we had to deal with a density matrix without nondiagonal elements we could interpret it in a classical way:

$$\underline{\underline{\varrho}}_g = \begin{pmatrix} |c_1|^2 & 0 \\ 0 & |c_2|^2 \end{pmatrix}$$

characterizes a system, which is found in the state $|a_1\rangle\,|\phi_1\rangle$ with the probability $|c_1|^2$, and in the state $|a_2\rangle\,|\phi_2\rangle$ with the probability $|c_2|^2$. Here we have classical correlations, i.e., unique relations between the states of the quantum system and the apparatus. This becomes more apparent if we consider the associated density operator

$$\begin{aligned}\hat{\varrho}_g &= |c_1|^2\ |a_1\rangle\langle a_1|\ |\phi_1\rangle\langle\phi_1| + |c_2|^2\ |a_2\rangle\langle a_2|\ |\phi_2\rangle\langle\phi_2| \\ &=: \sum_k\ p_k|\chi_k\rangle\langle\chi_k|.\end{aligned} \tag{6.28}$$

It has the form of a density operator for mixed states. We can conclude that mixed states define classical alternatives as possible outcomes of measurements. It would be nice if we had to deal only with density operators of this type, in which the worrisome quantum correlations between microscopic quantum systems and macroscopic measuring devices are absent. So, let us ask: Can we somehow justify the transition $\hat{\varrho} \longrightarrow \hat{\varrho}_g$ for a measurement process?

6.4 Decoherence

Yes, we can! The desired transition is provided by the physical mechanism of *decoherence*. It is based on an almost trivial insight:

> Physical systems are never isolated, but couple to their environment. For macroscopic systems (measuring devices in particular) these couplings cannot be neglected.

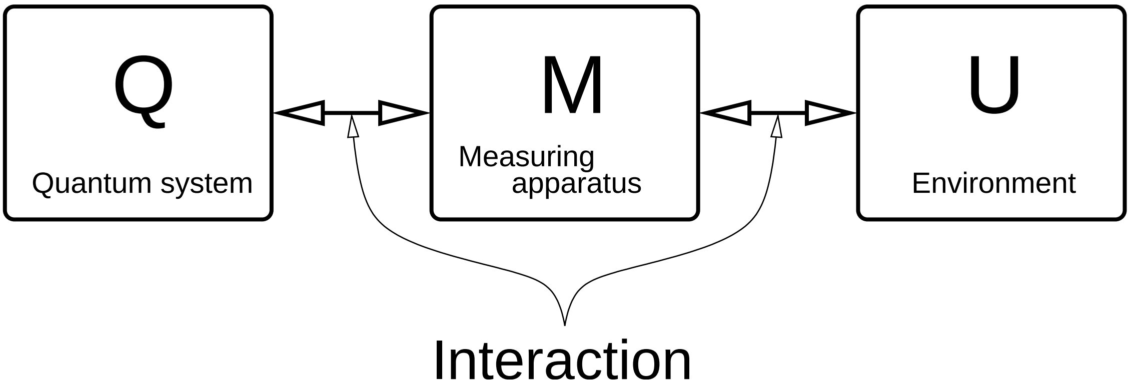

Fig. 6.5: Composite system including the environment

6.4.1 Basic Idea

We assume that the coupling to the environment U is described in the same way as the interaction between the quantum system Q and the measuring apparatus M. Let us start with the entangled state (6.16) for the composite system QM and a state $|U_0\rangle \in \mathcal{H}_\mathcal{U}$ that characterizes U before the coupling

$$\begin{aligned} |\Psi\rangle \quad & = |\chi\rangle\ |U_0\rangle = (c_1\ |a_1\rangle\ |\phi_1\rangle + c_2\ |a_2\rangle\ |\phi_2\rangle)\, |U_0\rangle \\ \in \quad & \\ \mathcal{H}_\mathcal{Q} \otimes \mathcal{H}_\mathcal{M} \otimes \mathcal{H}_\mathcal{U} \quad & \\ & \xrightarrow{\text{coupling}}\ c_1\ |a_1\rangle\ |\phi_1\rangle\ |U_1\rangle + c_2\ |a_2\rangle\ |\phi_2\rangle\ |U_2\rangle. \end{aligned} \tag{6.29}$$

We have just gone one step further in v. Neumann's chain and have obtained a state, in which the quantum system, the apparatus, and the environment are entangled — not really an improvement! But now comes the crucial[9] argument that goes like this: the states $|U_1\rangle$, $|U_2\rangle$ of the environment are neither measured nor controlled. Rather, we want to make a statement about the subsystem QM. Formally, this means that we have to integrate over the unobserved degrees of freedom of U, i.e., we have to consider the trace of the density operator of QMU

$$\begin{aligned} \hat{\varrho}^{loc}_{QM} :&= Tr_u\ \hat{\varrho} \\ &= \sum_i \langle U_i|\Psi\rangle\ \langle\Psi|U_i\rangle \\ &= \sum_i \langle U_i|\ [\ |U_1\rangle\ c_1\ |a_1\rangle\ |\phi_1\rangle\ + |U_2\rangle\ c_2\ |a_2\rangle\ |\phi_2\rangle\ ] \\ &\quad \times [\ c_1^*\ \langle a_1|\ \langle\phi_1|\ \langle U_1|\ + c_2^*\ \langle a_2|\ \langle\phi_2|\ \langle U_2|\ ]\, |U_i\rangle. \end{aligned}$$

If the states of the environment are mutually orthogonal and normalized, i.e., $\langle U_i|U_j\rangle = \delta_{ij}$ the "local density operator" for the subsystem QM reduces to

$$\begin{aligned} \hat{\varrho}^{loc}_{QM} &= (c_1\ |a_1\rangle\ |\phi_1\rangle\ )\,(c_1^*\ \langle a_1|\ \langle\phi_1|\ ) + (c_2\ |a_2\rangle\ |\phi_2\rangle\ )\,(c_2^*\ \langle a_2|\ \langle\phi_2|\ ) \\ &= |c_1|^2\ |\chi_1\rangle\langle\chi_1| + |c_2|^2\ |\chi_2\rangle\langle\chi_2| \\ &= \sum_k\ p_k\ |\chi_k\rangle\langle\chi_k|. \end{aligned} \tag{6.30}$$

Thus, we have obtained a density operator of the desired form without quantum correlations! The prescription "coupling to the environment + tracing out the environmental degrees of freedom" is what is called decoherence.

---

[9] or magic

6.4.2 Discussion

So far we have demonstrated the decoherence mechanism only for a specific example. Let us now make the discussion a bit more general.

More General Discussion of the Measurement Process

- A general "von Neumann operator" can be defined by

$$\hat{V}(t) = g(t) \sum_n |a_n\rangle\langle a_n| \otimes \hat{O}_M^{(n)}. \tag{6.31}$$

  Our previous example fits into this definition:

$$\hat{V}(t) = g(t)\ \hat{A}\ \hat{p}_M = g(t) \sum_n |a_n\rangle\langle a_n|\ \otimes \hat{O}_M^{(n)}$$

  with

$$\hat{O}_M^{(n)} = a_n\ \hat{p}_M.$$

- Time development (in symbolic notation[10])

$$\left(\sum_n c_n\ |a_n\rangle\right) |\phi_0\rangle \ \overset{t}{\rightarrow}\ \sum_n c_n\ |a_n\rangle\ |\phi_n\rangle \tag{6.32a}$$

$$\text{with}\quad |\phi_n\rangle = \exp\left(-\frac{i}{\hbar}\ \lambda\ \hat{O}_M^{(n)}\right)\ |\Phi_0\rangle \tag{6.32b}$$

$$\text{and}\quad \lambda = \int_0^{\varepsilon} g(t)\ dt$$

- Density operator of QM

$$\hat{\varrho}_{QM} = \sum_{nm} |a_n\rangle|\phi_n\rangle\ c_n\ c_m^*\ \langle a_m|\langle\phi_m| \tag{6.32c}$$

- Coupling to the environment

$$\left(\sum_n c_n\ |a_n\rangle|\phi_n\rangle\right)\ |U_0\rangle\ \overset{t}{\rightarrow} \sum_n c_n\ |a_n\rangle|\phi_n\rangle\ |U_n\rangle \tag{6.33}$$

- Density operator of QMU

$$\hat{\varrho}_{QMU} = \sum_{mn} |a_n\rangle|\phi_n\rangle\ |U_n\rangle \qquad \underbrace{c_n\ c_m^*}_{\text{matrix elements }\ \varrho_{nm}} \qquad \langle a_m|\langle\phi_m|\langle U_m| \tag{6.34}$$

- Reduced (local) density operator for QM

$$\begin{aligned}\hat{\varrho}_{QM}^{loc} &= Tr_u\ \hat{\varrho}_{QMU}\\ &= \sum_k \langle U_k|\hat{\varrho}_{QMU}|U_k\rangle\\ &= \sum_{mnk} \langle U_k|U_n\rangle\ \langle U_m|U_k\rangle|a_n\rangle\ |\phi_n\rangle\ c_n\ c_m^*\langle a_m|\langle\phi_m|\\ &= \sum_{mn} |a_n\rangle\ |\phi_n\rangle\ \left(\langle U_m|U_n\rangle\ c_n\ c_m^*\ \langle a_m|\langle\phi_m|\right)\end{aligned} \tag{6.35}$$

---

[10] which can easily be made explicit by approximating the time-evolution operator as in Sec. 6.3.1.

If $\langle U_i|U_j\rangle = \delta_{ij}$[11]

$$\hat{\varrho}^{loc}_{QM} = \sum_n |a_n\rangle\ |\Phi_n\rangle\ |c_n|^2\ \langle a_n|\langle\Phi_n|. \tag{6.36}$$

This operator is of the same form as (6.30).

Preliminary Remarks Concerning Interpretation

The physical mechanism of decoherence, i.e., the scheme indicated above is generally accepted. However, there are different points of views how it has to be interpreted. Here are a few statements (without deeper analysis):

- The interference terms (nondiagonal elements of the density operator) are “locally destroyed", i.e., they are not accessible in local observations of QM.
- The "preferred basis" into which the system decoheres are determined by the nature of the coupling to the environment.
- Let us consider the entropy of the system QM:

  $$S_{QM} = -k_B\ \langle ln\hat{\varrho}_{QM}\rangle\ = 0$$

  $$S^{loc}_{QM} \qquad\qquad > 0.$$

  There is an apparent loss of information through decoherence.
- $\hat{\varrho}^{loc}_{QM}$ does not characterize a real ensemble, but a so-called improper mixture. This is evidenced by the fact that $\hat{\varrho}^{loc}_{QM}$ does not obey a v. Neumann equation. Rather, it corresponds to an “open" quantum system that is governed by a so-called Master equation.
- The problem of macroscopic intereferences is solved (eliminated) by decoherence. But still, the local density operator does not tell us which of the 'classical' alternatives will be observed in an actual measurement, i.e., the indeterminism of QM is still there. Different authors favor different 'solutions'. The two most prominent ones are

  $$\begin{array}{lll} \hat{\varrho}^{loc}_{QM} & \xrightarrow{\text{collapse}} & |a_k\rangle\ |\phi_k\rangle\ \langle a_k|\langle\phi_k| \\ \hat{\varrho}^{loc}_{QM} & \xrightarrow{\text{many worlds}} & |a_1\rangle\ |\phi_1\rangle\ \langle a_1|\langle\phi_1| \quad \text{world 1} \\ & & |a_2\rangle\ |\phi_2\rangle\ \langle a_2|\langle\phi_2| \quad \text{world 2} \\ & \vdots & \end{array}$$

  In both cases a given observer (in a given world) will measure one and only one alternative. This implies that finally there is a gain of information (since the measured alternative corresponds to a pure state).

Schrödinger's Cat Illuminated by Decoherence

The fate of the hapless cat [8] is (partly) determined by decoherence. The total system consisting of the radioactive substance (Q), the apparatus (M), and the cat (C) forms an entangled state. After one hour (when the probability that one of the atoms has decayed and triggered the apparatus is 0.5) the state is given by

$$|\chi_{QMC}\rangle = \frac{1}{\sqrt{2}}(\ |1\rangle\ |\phi_1\rangle\ |\text{alive}\rangle + |0\rangle\ |\phi_0\rangle\ |\text{dead}\rangle)$$

---

[11] This means that the environmental states are able to discriminate the states of QM.

“Eine Katze wird in eine Stahlkammer gesperrt, zusammen mit folgender Höllenmaschine (...): in einem Geigerschen Zählrohr befindet sich eine winzige Menge radioaktiver Substanz, so wenig, dass im Lauf einer Stunde vielleicht eines von diesen Atomen zerfällt, ebenso wahrscheinlich aber auch keines; geschieht es, so spricht das Zählrohr an und betätigt über ein Relais ein Hämmerchen, das ein Kölbchen mit Blausäure zertrümmert. (...) Die Ψ-Funktion des ganzen Systems würde das so zum Ausdruck bringen, dass in ihr die lebende und die tote Katze zu gleichen Teilen gemischt und verschmiert sind.”
Schrödinger 1935

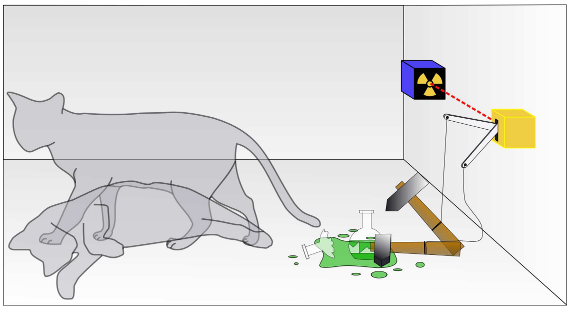

Fig. 6.6: Schrödinger’s 'burleskes Gedankenexperiment' in his own words. Translation of Schrödinger’s text [8] by J.D. Trimmer, published in *The Proceedings of the American Philosophical Society* 124, p.323 (1980): “A cat is penned up in a steel chamber, along with the following device (which must be secured against direct interference by the cat): in a Geiger counter there is a tiny bit of radioactive substance, so small, that perhaps in the course of the hour one of the atoms decays, but also, with equal probability, perhaps none; if it happens, the counter tube discharges and through a relay releases a hammer which shatters a small flask of hydrocyanic acid. If one has left this entire system to itself for an hour, one would say that the cat still lives if meanwhile no atom has decayed. The psi-function of the entire system would express this by having in it the living and dead cat (pardon the expression) mixed or smeared out in equal parts.” (Picture taken from `http://en.wikipedia.org/wiki/File:Schrodingers_cat.svg`)

$$\xrightarrow{\text{decoherence}} \hat{\varrho}^{loc}_{QMC} = \frac{1}{2}\left[\ |1\rangle\ |\phi_1\rangle\ |\text{alive}\rangle\ \langle 1|\ \langle\phi_1|\langle\text{alive}|\ + |0\rangle\ |\phi_0\rangle\ |\text{dead}\rangle\ \langle 0|\ \langle\phi_0|\langle\text{dead}|\ \right]$$

⇒ classical alternatives!
That is to say: there are no cats in superposition states!

Universality of Decoherence

The fact that systems couple to the environment is, of course, not restricted to measuring devices, but of a very general nature. Thus, decoherence also occurs without measurements. It is an ubiquitous process. Accordingly, we can leave out the apparatus and consider a quantum system Q that couples to the environment U

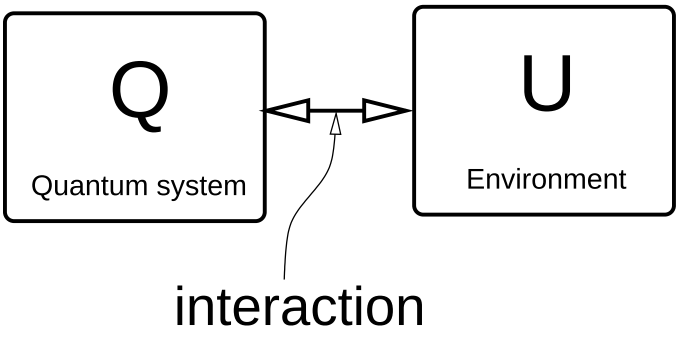

Fig. 6.7: Decoherence without measurements

$$\left(\sum_n c_n\,|a_n\rangle\right)\,|U_0\rangle \overset{\text{t}}{\to} \sum_n c_n\,|a_n\rangle\,|U_n\rangle$$

$$\begin{aligned}\hat{\varrho}_{QU} &= \sum_{mn}\,|a_n\rangle\,|U_n\rangle\,c_n\,c_m^*\,\langle a_m|\,\langle U_m|\\ \hat{\varrho}_Q^{loc} &= Tr_u\,\hat{\varrho}_{QU} = \sum_{mn}\,|a_n\rangle\,\left(\langle U_m|U_n\rangle\,c_n\,c_m^*\,\right)\langle a_m|\end{aligned} \tag{6.37}$$

if $\langle U_m|U_n\rangle = \delta_{mn}$

$$\hookrightarrow\ \hat{\varrho}_Q^{loc} = \sum_n\,|a_n\rangle\,|c_n|^2\,\langle a_n|.$$

This implies that the Schrödinger (or v. Neumann) equation never suffices to describe the dynamics of a quantum system. However, there are well-known cases, where this is obviously the case, otherwise one would never observe quantum interferences like in the double-slit experiment. This poses the question about the nature and the strength of the coupling to the environment. In other words: what can we say about the quantitative aspects of decoherence?

6.4.3 Decoherence Through Scattering Processes

Let us consider an important (may be the most important) decoherence mechanism: decoherence through scattering processes. All physical systems are exposed to them. For instance, we would not see anything if there were no photons which scatter from the objects. Also air molecules scatter from objects in the atmosphere or on the surface of the earth. Even the cosmic background radiation has to be taken into account.

Let us outline a simplified description of these ubiquitous scattering process[12]. The state of a quantum system Q can be written as

$$|\psi_0\rangle = \int\,|\boldsymbol{r}\rangle\,\langle\boldsymbol{r}|\psi\rangle\,d^3r = \int\,\psi(\boldsymbol{r})\,|\boldsymbol{r}\rangle\,d^3r.$$

That is, we choose the real space representation, because scattering processes are local in space. Now we consider one particle (which can also be a photon) as environment U. Its state is denoted by $|\phi\rangle$. According to our general scheme we have

$$\int\,d^3r\,\psi(\boldsymbol{r})\,|\boldsymbol{r}\rangle\,|\phi\rangle\,\overset{\text{t}}{\to}\,\int\,d^3r\,\psi(\boldsymbol{r})\,|\boldsymbol{r}\rangle\,|\phi_{\boldsymbol{r}}\rangle\ .$$

The scattered particle is not observed. Hence, we have to trace out its degrees of freedom and obtain

$$\hat{\varrho}_Q^{loc} = \int d^3r \int d^3r'\,|\boldsymbol{r}\rangle\left(\langle\phi_{\boldsymbol{r}'}|\phi_{\boldsymbol{r}}\rangle\,\psi(\boldsymbol{r})\,\psi^*(\boldsymbol{r}')\right)\langle\boldsymbol{r}'|.$$

Apparently, the density matrix elements are

$$\hat{\varrho}_Q^{loc}(\boldsymbol{r},\boldsymbol{r}') = \langle\phi_{\boldsymbol{r}'}|\phi_{\boldsymbol{r}}\rangle\,\psi(\boldsymbol{r})\psi^*(\boldsymbol{r}').$$

To proceed one has to analyze the scattering process. This can be done by standard methods of quantum scattering theory. The result has the following form

$$\langle\phi_{\boldsymbol{r}'}|\phi_{\boldsymbol{r}}\rangle\ = \begin{cases}0 & \text{if } |\boldsymbol{r}-\boldsymbol{r}'| >> \lambda_B\\ 1-O(|\boldsymbol{r}-\boldsymbol{r}'|^2) & \text{if } |\boldsymbol{r}-\boldsymbol{r}'| << \lambda_B,\end{cases} \tag{6.38}$$

---

[12] All relevant details can be found in chapter 3 of [9].

where $\lambda_B = \frac{h}{p}$ is the de Broglie wavelength of the scattered particle. In the first case a single scattering process can resolve the distance $|\boldsymbol{r} - \boldsymbol{r}'|$, i.e., the two positions $\boldsymbol{r}$ and $\boldsymbol{r}'$ are discriminated and complete decoherence occurs. In the second case the coherence is only damped. Depending on the wavelength the damping might be very small and the decoherence very inefficient. However, in reality an object is not only exposed to one but to many (N) scattering processes. Then the damping factor can be shown to be of the form

$$\langle \phi_{r'} | \phi_r \rangle^{\,N} \xrightarrow[N \to \infty]{} \exp\left(-\Lambda \; t \; |\boldsymbol{r} - \boldsymbol{r}'|^2\right)$$

where

$$\begin{aligned} \Lambda = k^2 \; \sigma_{eff} \; \frac{Nv}{V} \quad & \text{localization rate} \\ k = \frac{2\pi}{\lambda} \quad & \text{wave number of the scattered particle} \\ \frac{Nv}{V} \quad & \text{current density of the scattered particles} \\ \sigma_{eff} \quad & \text{effective total scattering cross section} \end{aligned}$$

Λ determines how quickly the interferences between different positions are destroyed. Equivalently, one can define a coherence length according to

$$l(t) = \frac{1}{\sqrt{\Lambda \; t}} \qquad [cm]$$

such that the density matrix elements take the form

$$\begin{aligned} \hat{\varrho}_Q^{loc}(\boldsymbol{r}, \boldsymbol{r}'; t) &= \psi(\boldsymbol{r})\psi^*(\boldsymbol{r}') \exp\left[-\frac{|\boldsymbol{r} - \boldsymbol{r}'|^2}{l^2(t)}\right] \\ & \| \\ \hat{\varrho}_Q^{loc}(\boldsymbol{r}, \boldsymbol{r}', t) &= \hat{\varrho}_Q(\boldsymbol{r}, \boldsymbol{r}') \; \exp\left[-\frac{|\boldsymbol{r} - \boldsymbol{r}'|^2}{l^2(t)}\right]. \end{aligned} \tag{6.39}$$

Discussion

(i)
$$l(t) \xrightarrow[t \to \infty]{} 0 \; ?$$

A detailed analysis shows that $l(t \to \infty) \approx \frac{h}{\sqrt{mk_BT}} = \lambda_{th}^B$:
“All macroscopic objects are localized to their thermal de Broglie wavelength."
For example, for a dust particle at T = 300 K: $\lambda_{th}^B \approx 10^{-14}$cm.
For an electron in the ground state of the hydrogen atom $\lambda_{th}^B \approx 10^{-8}$cm.

(ii) Some explicit numbers [9]:

	$a = 10^{-3}$ cm dust particle	$a = 10^{-5}$ cm dust particle	$a = 10^{-6}$ cm large molecule
Cosmic background radiation	10^6 (a)	10^{-6}	10^{-12} (d)
300 K photons	10^{19}	10^{12}	10^6
Sunlight (on earth)	10^{21}	10^{17}	10^{13}
Air molecules	10^{36}	10^{32}	10^{30}
Laboratory vacuum (10^3 particles/cm^3)	10^{23} (b)	10^{19}	10^{17} (c)

(a) localized to a with 1 s
(b) localized to a with 10^{-17} s
(c) localized to a with 10^{-5} s
(d) localized to a with 10^{24} s

(iii) As mentioned above the equation of motion for $\hat{\varrho}_Q^{loc}$ has the form of a Master equation:

$$i\hbar \frac{d}{dt}\hat{\varrho}_Q^{loc} = \left[\hat{H}_{\text{internal}}, \hat{\varrho}_Q^{loc}\right] + \frac{\partial}{\partial t}\hat{\varrho}_Q^{loc}\,|_{\text{scattering}}$$

The form of the last term can be deduced from a formal discussion of open quantum systems or is modelled. The internal dynamics, expressed by the commutator, may lead to a spreading of the wave packet, but this spreading is counteracted by the (typically much stronger) decoherence effect.

(iv) One can conclude that the decoherence effect is responsible for the locality of macroscopic objects. Locality is not a property of these objects, but is produced by the interaction with the environment. This is a stunning and beautiful result. Classicality (i.e. locality) is not something that is forced upon objects if they exceed a certain magnitude, but it is a consequence of a fundamental quantum mechanical property — entanglement. Note that this is in striking contrast to Bohr's point of view. However, it is an open (and controversial) question whether all classical concepts can be explained by environment-induced decoherence.

(v) As an aside one can also conclude that objects appear localized in position space (and not in momentum space), because the responsible interactions (scattering processes) are mediated by local potentials.

(vi) There are convincing experimental evidences for environment-induced decoherence, e.g. [10, 11].

6.5 Concluding Remarks

We have only touched upon the interpretational problems of quantum mechanics. As mentioned at the beginning of this chapter there are many more issues that can be discussed and have been discussed under this headline. Our main objective has been to analyze the measurement process and discuss the experimentally confirmed mechanism of decoherence to some extent. Decoherence solves at least some of the mysteries of quantum mechanics, in particular the (usual) absence of interference effects in macroscopic systems.

Still, there are open questions that will keep physicists and philosophers (and others) busy for some time to come. For instance, how come that only one of the classical alternatives that the theory predicts is realized as the outcome of a quantum measurement? Is this accomplished by a (still mysterious) collapse, or are all possible outcomes realized — each one in its own world?

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This site is maintained by E. Joos

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Chapter 7

Irreversible Thermodynamics

Irreversible thermodynamics tries to extend equilibrium thermodynamics to non-equilibrium systems. The laws of irreversible thermodynamics are abundant. Examples are the heat equation, which relates the heat flux to a temperature gradient, Fick's law, which relates particle diffusion to a concentration gradient, or Ohm's law, which relates an electric current to a gradient of the electric potential.

The idea behind irreversible thermodynamics is the the growth of entropy drives thermodynamic processes. This allows us to describe the approach to equilibrium. Instead of studying discrete systems as in equilibrium thermodynamics, we now deal with the densities of the extensive variables.

7.1 Basic assumption

In irreversible thermodynamics we assume that the system is close to thermodynamic equilibrium, that is we assume that it is locally in equilibrium. Specifically we assume that the local value of the entropy as function of the extensive properties is the same as in thermal equilibrium. This implies that we can define local values for the intensive variables.

The second assumption is that the dynamics of the system is only determined by the current state and not the past. We say that the dynamics is a Markov process.

7.2 Rate of entropy production

In order to describe the driving force for irreversible processes, the entropy production, we need to investigate the rate of growth of the entropy.

First we define a entropy density

$$s(\rho_E, \{\rho_k\}) = \lim_{V\to 0} \frac{1}{V} S(\rho_E V, \{\rho_k V\})$$

where $S(E, \{X_k\})$ is the entropy depending on internal energy and other extensive parameters. For an ideal gas we would simply use the Sackur-Tetrode equation. The energy density ρ_E and the densities ρ_k of the other extensive variables X_k are defined as

$$\rho_E(\vec{r}) = \lim_{|\Omega|\to 0;\ \vec{r}\in\Omega} \frac{E}{|\Omega|}$$

$$\rho_k(\vec{r}) = \lim_{|\Omega|\to 0;\ \vec{r}\in\Omega} \frac{X_k}{|\Omega|}$$

where E and X_k are the energy and the other extensive variables within the volume Ω. As usual we consider a sequence of regions Ω with increasingly smaller maximum diameter, that all include the point $\vec{r}$.

Let us consider the rate of entropy production in a volume V

$$\frac{dS}{dt}=\frac{d}{dt}\int_V d^3r\; s(\rho_E,\{\rho_k\})=\int_V d^3r\;\left(\frac{\partial s}{\partial\rho_E}\dot\rho_E+\sum_k\frac{\partial s}{\partial\rho_k}\dot\rho_k\right)$$

Now we exploit that the extensive variables are conserved quantities and use their conservation laws

$$\dot\rho_E+\vec\nabla\vec j_E=0$$
$$\dot\rho_k+\vec\nabla\vec j_k=0$$

where $\vec j_E$ is the energy current density and $\vec j_k$ are the current densities of the other extensive variables. We obtain

$$\begin{aligned}\frac{dS}{dt}&=-\int_V d^3r\left(\frac{\partial s}{\partial\rho_E}\vec\nabla\vec j_E+\sum_k\frac{\partial s}{\partial\rho_k}\vec\nabla\vec j_k\right)\\&=-\int_V d^3r\vec\nabla\underbrace{\left(\frac{\partial s}{\partial\rho_E}\vec j_E+\sum_k\frac{\partial s}{\partial\rho_k}\vec j_k\right)}_{=:j_S}+\int_V d^3r\left(\vec j_E\vec\nabla\frac{\partial s}{\partial\rho_E}+\sum_k\vec j_k\vec\nabla\frac{\partial s}{\partial\rho_k}\right)\end{aligned}\tag{7.1}$$

We define the **entropy-current density**

$$\vec j_S\overset{\text{def}}{=}\frac{\partial s}{\partial\rho_E}\vec j_E+\sum_k\frac{\partial s}{\partial\rho_k}\vec j_k=\frac{1}{T}\vec j_E-\sum_k\frac{f_k}{T}\vec j_k\tag{7.2}$$

We have used the fundamental relation $dU=TdS+\sum_k f_k dX_k$, which we have rewritten in the form $dS=\frac{1}{T}dU-\sum_k\frac{f_k}{T}dX_k$, so that $\frac{\partial s}{\partial\rho_E}=\frac{\partial S}{\partial U}=\frac{1}{T}$ and $\frac{\partial s}{\partial\rho_k}=\frac{\partial S}{\partial X_k}=-\frac{f_k}{T}$.

The first term in Eq. 7.1 can be mapped on a surface integral

$$\int_V d^3r\;\vec\nabla\vec j_S=\oint_{\partial V}d\vec A\,\vec j_S$$

and thus describes the flux of entropy through the surface ∂V out of the volume. If the volume extends over all space, the surface integral vanishes[1], and thus does not contribute to the over-all entropy production.

Thus, we obtain for the entropy density $s(\vec r,t)$, defined by $S(t)=\int_\Omega d^3r\;s(\vec r,t)$,

$$\begin{aligned}\frac{\partial s(\vec r,t)}{\partial t}+\vec\nabla\vec j_S(\vec r,t)&=\vec j_E\vec\nabla\frac{\partial s}{\partial\rho_E}+\sum_k\vec j_k\vec\nabla\frac{\partial s}{\partial\rho_k}\\&=\vec j_E\vec\nabla\frac{1}{T}-\sum_k\vec j_k\vec\nabla\frac{f_k}{T}\end{aligned}\tag{7.3}$$

where the term of the right hand describes the source density of the entropy. The entropy is not conserved and thus can be spontaneously created. The driving force towards thermodynamical equilibrium is the source density of the entropy.

We call

$$F_E=\vec\nabla\frac{\partial s}{\partial\rho_E}=\vec\nabla\frac{1}{T}\tag{7.4}$$

$$F_k=-\vec\nabla\frac{\partial s}{\partial\rho_k}=\vec\nabla\frac{f_k}{T}\tag{7.5}$$

---

[1] The surface integral over an infinite volume vanishes only if the integrands vanish at infinity, which is implicitly assumed in this argument. The argument can fail if this is not the case. An example are infinitely extended systems.

the **affinities**. The affinities are the gradients of the Lagrange multipliers. The relation to the intensive variables is done using the fundamental relation Eq. **??**. We can easily see that the entropy production vanishes, when the intensive variables are spatially constant. By the way, we are lead here to a definition of spatially dependent Lagrange multipliers.

With this definition the source density of the entropy is

$$j_E F_E + \sum_k j_k F_k$$

7.3 Transport coefficients

We identified the driving forces towards thermal equilibrium, but we do not have a handle on describing the rates for the individual processes. Hence we make an empirical Ansatz, which leads to parameters that must be specified by experiments.

$$\vec{j}_i = \sum_j L_{i,j} F_j \tag{7.6}$$

where the parameters $L_{i,j}$ are the **kinetic coefficients**. Note, that the energy is treated like any other extensive variable, so that the indices i, j may also refer to the energy. The kinetic coefficients depend on the values of the intensive variables and their gradients. The above equation can be seen as the first term of a Taylor series of $\vec{j}_i$ in the affinities.

Examples for kinetic coefficients are**(Editor: The examples are copied blindly and is probably not correct.)**

- thermal conductivity

$$\vec{j}_E = \kappa \vec{\nabla} T = -\kappa T^2 \vec{\nabla} \frac{1}{T}$$

- Ohm's law relates the current to the voltage $I = \frac{1}{R} U$, where I is the electric current, R is the resistance and U is the voltage. In differential form Ohm's law has the form $j_q = \sigma \nabla \Phi$, where j_q is the electric current density, σ is the electric conductivity and Φ is the electric potential.
- Fick's law relates the current j of some species with the gradient of its density ρ by $j = -D \nabla \rho$, where D is the diffusion constant.

7.4 Onsager's Reciprocity Theorem

The kinetic coefficients are not all independent. Onsager's theorem[2] states that

$$L_{i,j}(\vec{B}) = L_{j,i}(-\vec{B})$$

The kinetic coefficients need not depend on the magnetic field. If they do not the equation is simply that the transport coefficients are symmetric. Onsager's theorem is based on time-translation and time-inversion symmetry of the underlying equations of motion. We included the dependence on the magnetic field, because the latter changes sign upon time inversion.

Consider the correlation of two fluctuations at different times:

$$\langle \delta X_i(t) \delta X_j(t') \rangle \stackrel{\text{def}}{=} \Big\langle (X_i(t) - \langle X_i \rangle)(X_i(t') - \langle X_i \rangle) \Big\rangle$$

---

[2] Lars Onsager. Norwegian Chemist 1903-??. Nobel price in Chemistry 1968. Professor of Theoretical Chemistry at Yale University, USA.

If we consider time translation symmetry, we can set one of the time arguments to zero. Time inversion symmetry then requires

$$\langle \delta X_i(0)\delta X_j(t)\rangle = \langle \delta X_i(0)\delta X_j(-t)\rangle$$

Exploiting time translation symmetry, we obtain

$$\langle \delta X_i(0)\delta X_j(t)\rangle = \langle \delta X_i(0)\delta X_j(-t)\rangle = \langle \delta X_i(t)\delta X_j(0)\rangle = \langle \delta X_j(0)\delta X_i(t)\rangle$$

$$\begin{aligned}
\langle \delta X_i(0)\frac{\delta X_j(t)-\delta X_j(0)}{t}\rangle &= \langle \delta X_j(0)\frac{\delta X_i(t)-\delta X_i(0)}{t}\rangle \\
\overset{t\to 0}{\Rightarrow} \langle \delta X_i(0)\delta \dot{X}_j(0)\rangle &= \langle \delta X_j(0)\delta \dot{X}_i(0)\rangle \\
\Rightarrow \langle \delta X_i \sum_k L_{j,k}\delta F_k\rangle &= \langle \delta X_j \sum_k L_{i,k}\delta F_k\rangle \\
\Rightarrow \sum_k L_{j,k}\langle \delta X_i\delta F_k\rangle &= \sum_k L_{i,k}\langle \delta X_j\delta F_k\rangle
\end{aligned}$$

As we will show later**(Editor: This is not yet shown in the section about Fluctuations!)** , the correlations are

$$\langle \delta X_i \delta F_j\rangle = -k_B\delta_{i,j}$$

so that we obtain

$$L_{j,i} = L_{i,j}$$

7.4.1 A more convenient form

Let us now cast the currents in a more physical form: We use Eq. 7.2 to express the energy current density by the current densities of entropy and the other extensive variables.

$$\vec{j}_S \overset{Eq.~7.2}{=} \frac{1}{T}\vec{j}_E - \sum_k \frac{f_k}{T}\vec{j}_k \qquad \Rightarrow \qquad \vec{j}_E = \underbrace{T\vec{j}_S}_{\vec{j}_Q} + \sum_k f_k\vec{j}_k$$

the relation $dQ = TdS$ suggests to define a **heat current**

$$\vec{j}_Q \overset{\text{def}}{=} T\vec{j}_S = \vec{j}_E - \sum_k f_k\vec{j}_k \tag{7.7}$$

The heat current into a volume is the energy current into the volume minus the energy current that can be accounted for by the current of the extensive variables.

Similarly we can write the entropy source term as

$$\begin{aligned}
\frac{\partial s(\vec{r},t)}{\partial t} + \vec{\nabla}\vec{j}_S(\vec{r},t) &\overset{Eq.~7.3}{=} \vec{j}_E\vec{\nabla}\frac{1}{T} - \sum_k \vec{j}_k\vec{\nabla}\frac{f_k}{T} \\
&= \underbrace{\left(\vec{j}_Q + \sum_k f_k\vec{j}_k\right)}_{\vec{j}_E}\vec{\nabla}\frac{1}{T} - \sum_k \vec{j}_k\vec{\nabla}\frac{f_k}{T} \\
&= \vec{j}_Q\vec{\nabla}\frac{1}{T} + \sum_k \vec{j}_k\left(-\frac{1}{T}\vec{\nabla}f_k\right)
\end{aligned}$$

This suggests that it is suitable to introduce new affinities $\bar{F}$

$$
\begin{aligned}
\bar{F}_Q &\overset{\text{def}}{=} \vec{\nabla}\frac{1}{T} = F_E \\
\bar{F}_k &\overset{\text{def}}{=} -\frac{1}{T}\vec{\nabla} f_k = -\vec{\nabla}\frac{f_k}{T} + f_k\vec{\nabla}\frac{1}{T} = F_k + f_k F_E
\end{aligned}
$$

and to express the kinetic equations by the heat current and the new affinities.

$$
\begin{aligned}
\vec{j}_Q &= \bar{L}_{Q,Q}\underbrace{\vec{\nabla}\frac{1}{T}}_{F_E} + \sum_k \bar{L}_{Q,k}\underbrace{\left(-\frac{1}{T}\vec{\nabla} f_k\right)}_{\bar{F}_k} \\
\vec{j}_k &= \bar{L}_{k,Q}\underbrace{\vec{\nabla}\frac{1}{T}}_{F_E} + \sum_k \bar{L}_{k,k}\underbrace{\left(-\frac{1}{T}\vec{\nabla} f_k\right)}_{\bar{F}_k}
\end{aligned}
$$

with new kinetic coefficients indicated by a bar.

It may be of interest to transform the kinetic coefficients of the two representations into each other, which is done in the following: Note that we use in the following the kinetic coefficients with an index E related for the energy-components, while the indices k, k' do not include the energy component.

$$
\begin{aligned}
\vec{j}_Q \quad &\overset{Eq.~7.7}{=} \quad \vec{j}_E - \sum_k f_k \vec{j}_k \\
&\overset{Eqs.~7.6,7.5}{=} L_{E,E}\vec{\nabla}\frac{1}{T} + \sum_k L_{E,k}\left(-\vec{\nabla}\frac{f_k}{T}\right) - \sum_k f_k L_{k,E}\vec{\nabla}\frac{1}{T} - \sum_{k,k'} f_{k'} L_{k',k}\left(-\vec{\nabla}\frac{f_k}{T}\right) \\
&= \quad \left(L_{E,E} - \sum_k f_k L_{k,E}\right)\vec{\nabla}\frac{1}{T} + \sum_k\left(L_{E,k} - \sum_{k'} f_{k'} L_{k',k}\right)\left(-\vec{\nabla}\frac{f_k}{T}\right) \\
&= \quad \left(L_{E,E} - \sum_k f_k L_{k,E}\right)\vec{\nabla}\frac{1}{T} + \sum_k\left(L_{E,k} - \sum_{k'} f_{k'} L_{k',k}\right)\left(-f_k\vec{\nabla}\frac{1}{T} - \frac{1}{T}\vec{\nabla} f_k\right) \\
&= \quad \underbrace{\left(L_{E,E} - \sum_k f_k L_{k,E} - \sum_k L_{E,k} f_k + \sum_{k,k'} f_{k'} L_{k',k} f_k\right)}_{\bar{L}_{Q,Q}}\vec{\nabla}\frac{1}{T} \\
&\qquad + \sum_k \underbrace{\left(L_{E,k} - \sum_{k'} f_{k'} L_{k',k}\right)}_{\bar{L}_{Q,k}}\left(-\frac{1}{T}\vec{\nabla} f_k\right) \\
&= \quad \bar{L}_{Q,Q}\vec{\nabla}\frac{1}{T} + \sum_k \bar{L}_{Q,k}\frac{1}{T}\vec{\nabla} f_k \\
\vec{j}_k \quad &= \quad L_{k,E}\vec{\nabla}\frac{1}{T} + \sum_{k'} L_{k,k'}\left(-\vec{\nabla}\frac{f_{k'}}{T}\right) \\
&= \quad L_{k,E}\vec{\nabla}\frac{1}{T} + \sum_{k'} L_{k,k'}\left(-f_{k'}\vec{\nabla}\frac{1}{T} - \frac{1}{T}\vec{\nabla} f_{k'}\right) \\
&= \quad \underbrace{\left(L_{k,E} - \sum_{k'} L_{k,k'} f_{k'}\right)}_{\bar{L}_{k,Q}}\vec{\nabla}\frac{1}{T} + \sum_{k'}\underbrace{L_{k,k'}}_{\bar{L}_{k,k'}}\left(-\frac{1}{T}\vec{\nabla} f_{k'}\right) \\
&= \quad \bar{L}_{k,Q}\vec{\nabla}\frac{1}{T} + \sum_{k'} \bar{L}_{k,k'}\frac{1}{T}\vec{\nabla} f_{k'}
\end{aligned}
$$

Concluding we obtain the kinetic equations

$$\vec{j}_Q = \bar{L}_{Q,Q}\underbrace{\vec{\nabla}\frac{1}{T}}_{\bar{F}_Q} + \sum_k \bar{L}_{Q,k}\underbrace{\frac{1}{T}\vec{\nabla}f_k}_{\bar{F}_k}$$

$$\vec{j}_k = \bar{L}_{k,Q}\underbrace{\vec{\nabla}\frac{1}{T}}_{\bar{F}_Q} + \sum_{k'} \bar{L}_{k,k'}\underbrace{\frac{1}{T}\vec{\nabla}f_{k'}}_{\bar{F}_{k'}}$$

One can easily verify that the Onsager relations also hold for the new kinetic coefficients, that is

$$\bar{L}_{i,j}(\vec{B}) = \bar{L}_{j,i}(-\vec{B})$$

In the following we will only use the new representation and we will drop the bars on top of the symbols.

7.5 Principle of minimum entropy production

See nobel lecture of Ilya Prigogine...

See also [16].

7.6 Application: Determine kinetic coefficients and Seebeck effect

The **Seebeck effect** describes the conversion of a temperature gradient into an electric current.

In our analysis of the topic we first write down the kinetic equations for a coupled heat and particle current.

$$j_Q = L_{Q,Q}\nabla\frac{1}{T} + L_{Q,N}\left(-\frac{1}{T}\vec{\nabla}\mu\right)$$

$$j_N = L_{N,Q}\nabla\frac{1}{T} + L_{N,N}\left(-\frac{1}{T}\vec{\nabla}\mu\right)$$

The electric current density j_q is equal to the current density of charged particles j_N multiplied with their charge q, that is $\vec{j} = q\vec{j}_N$. Note that for electrons the electric current and the article current are antiparallel!

The first step will be to identify the kinetic coefficients with experimentally accessible quantities:

Determine $L_{N,N}$

Definition 7.1 *ELECTRIC CONDUCTIVITY*

The **electric conductivity** σ *is defined as the electric current density per unit potential gradient at constant temperature, that is*

$$\vec{j}_q = \textbf{œ}\vec{E}$$

where the electric field $\vec{E}$ *can be related to the gradient of the chemical potential via* $-\vec{\nabla}\mu = q\vec{E}$. q *is the charge of the particles.*

The electric current $\vec{j}_q$ is related to the electron current $\vec{j}_N$ by

$$j_q = -e j_n$$

, where e is the elementary charge. The electric field is related to the gradient of the chemical potential for electrons by

$$\vec{E} = \frac{1}{e}\vec{\nabla}\mu_N$$

Thus we obtain

$$j_N = -\sigma\frac{1}{e^2}\vec{\nabla}\mu_N = \sigma\frac{T}{e^2}\left(-\frac{1}{T}\vec{\nabla}\mu_N\right) \qquad \text{at constant } T$$

Comparison with the kinetic equation Eq. 7.8 with $\vec{\nabla}T = 0$ yields

$$L_{N,N} = \sigma\frac{T}{e^2} \tag{7.8}$$

Determine $L_{Q,Q}$

Definition 7.2 *HEAT CONDUCTIVITY*

The **heat conductivity** *is the heat current density per unit temperature gradient at zero electric current, that is*

$$\vec{j}_Q = -\kappa\vec{\nabla}T \qquad \textit{for zero electric current}$$

Before we can start, we need to determine the gradient of the chemical potential, when the electron flux vanishes. Thus we start with Eq. 7.8 and set the electron current to zero.

$$\begin{aligned} j_N &= L_{N,Q}\nabla\frac{1}{T} + L_{N,N}\left(-\frac{1}{T}\vec{\nabla}\mu\right) \overset{!}{=} 0 \\ \left(-\frac{1}{T}\vec{\nabla}\mu\right) &= -\frac{1}{L_{N,N}}L_{N,Q}\nabla\frac{1}{T} \end{aligned}$$

$L_{N,N}$ has already been linked to the electric conductivity. We insert the result into he first kinetic equation Eq. 7.8 and obtain

$$\begin{aligned} j_Q &= L_{Q,Q}\nabla\frac{1}{T} + L_{Q,N}\left(-\frac{1}{T}\vec{\nabla}\mu\right) \\ &= L_{Q,Q}\nabla\frac{1}{T}T + L_{Q,N}\left(-\frac{1}{L_{N,N}}L_{N,Q}\nabla\frac{1}{T}\right) \\ &= \left[L_{Q,Q} - L_{Q,N}\frac{1}{L_{N,N}}L_{N,Q}\right]\underbrace{\left(-\frac{1}{T^2}\nabla T\right)}_{\nabla\frac{1}{T}} \\ &= \underbrace{-\frac{1}{T^2}\left[L_{Q,Q} - L_{Q,N}\frac{1}{L_{N,N}}L_{N,Q}\right]}_{\kappa}\nabla T \end{aligned}$$

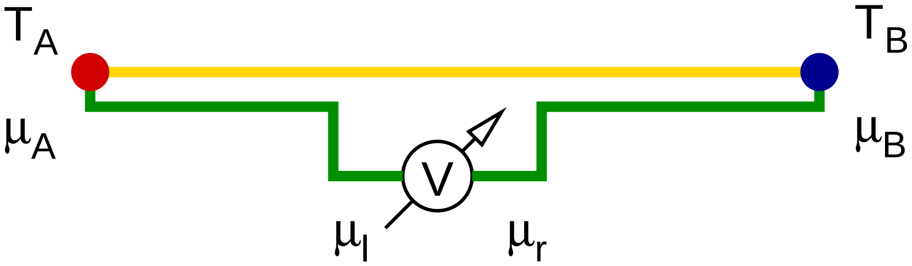
Thus we obtain

$$\kappa = \frac{1}{T^2}\left(L_{Q,Q} - L_{Q,N}\frac{1}{L_{N,N}}L_{N,Q}\right) \tag{7.9}$$

The third equation follows from Onsager's Theorem which says that

$$L_{N,Q} = L_{Q,N}$$

The last kinetic equation is obtained using the Seebeck effect[3] : In this experiment two wires made of different materials are connected once at a higher temperature and a second time at a lower temperature. In one of the wires we a voltmeter is introduced. The voltmeter blocks the electric current but allows the thermal current to pass.



http://www.answers.com/topic/

The potential difference can be obtained by integrating the chemical potential from one contact of the voltmeter to the other.

$$eV = \int_r^B d\vec{r}\,\vec{\nabla}\mu + \int_B^A d\vec{r}\,\vec{\nabla}\mu + \int_A^r d\vec{r}\,\vec{\nabla}\mu$$

Since no current is flowing, that is $\vec{j}_N = 0$, we can use Eq. 7.8 to relate the gradient of the chemical potential to the temperature gradient.

$$\vec{\nabla}\mu = \frac{L_{N,Q}}{L_{N,N}} T\vec{\nabla}\frac{1}{T} = -\frac{L_{N,Q}}{L_{N,N}}\frac{1}{T}\vec{\nabla}T$$

Of course we must distinguish the kinetic coefficients of the two materials. We label them by a superscript "y" for yellow and "g" for green.

$$\begin{aligned}
eV &= -\int_r^B d\vec{r}\,\frac{L^g_{N,Q}}{L^g_{N,N}}\frac{1}{T}\vec{\nabla}T - \int_B^A d\vec{r}\,\frac{L^y_{N,Q}}{L^y_{N,N}}\frac{1}{T}\vec{\nabla}T - \int_A^r d\vec{r}\,\frac{L^g_{N,Q}}{L^g_{N,N}}\frac{1}{T}\vec{\nabla}T \\
&= -\int_{T_r}^{T_B} dT\,\frac{L^g_{N,Q}}{L^g_{N,N}}\frac{1}{T} - \int_{T_B}^{T_A} dT\,\frac{L^y_{N,Q}}{L^y_{N,N}}\frac{1}{T} - \int_{T_A}^{T_l} dT\,\frac{L^g_{N,Q}}{L^g_{N,N}}\frac{1}{T} \\
&= \int_{T_A}^{T_B} dT\,\frac{L^y_{N,Q}}{L^y_{N,N}}\frac{1}{T} - \int_{T_A}^{T_B} dT\,\frac{L^g_{N,Q}}{L^g_{N,N}}\frac{1}{T} \\
&= \left[\frac{L^y_{N,Q}}{L^y_{N,N}} - \frac{L^g_{N,Q}}{L^g_{N,N}}\right]\int_{T_A}^{T_B} dT\,\frac{1}{T}
\end{aligned}$$

Now we determine the voltage change with changing T_A and obtain

$$\frac{dV}{dT_A} = -\frac{1}{eT_A}\left[\frac{L^y_{N,Q}}{L^y_{N,N}} - \frac{L^g_{N,Q}}{L^g_{N,N}}\right]$$

which yields the relative **thermoelectric power** of the two materials.

---

[3] Thomas Johann Seebeck, Estonian Physicist (1770-1831). Seebeck was born in Reval (today Tallinn), Estonia, to a wealthy Baltic German merchant family. He received a medical degree in 1802 from the University of GÃűttingen, but preferred to study physics. In 1821 he discovered the thermoelectric effect, where a junction of dissimilar metals produces an electric current when exposed to a temperature gradient. This is now called the Peltier-Seebeck effect and is the basis of thermocouples and thermopiles.

Definition 7.3 *THERMOELECTRIC POWER*
The relative **thermoelectric power**,**thermopower** *or* **Seebeck coefficient** $E_1 - E_2$ *of two materials is defined as*

$$E_1 - E_2 = \frac{dV}{dT}$$

where V *is the voltage drop in a ring of two wires connecting a warm and a cold reservoir with a temperature difference* T*.*

Knowing the a thermoelectric power, we obtain the remaining equation

$$\begin{aligned} E &= \frac{-L_{N,Q}}{eTL_{N,N}} = -\frac{eL_{N,Q}}{\sigma T^2} \\ \Rightarrow L_{N,Q} &= L_{Q,N} = \frac{\sigma E T^2}{e} \end{aligned} \tag{7.10}$$

can determine all four kinetic coefficients, which was required to determine all four kinetic coefficients.

$$\begin{aligned} L_{N,Q} &\overset{Eq.\ 7.10}{=} L_{Q,N} = \frac{\sigma E T^2}{e} \\ L_{N,N} &\overset{Eq.\ 7.8}{=} \frac{\sigma T}{e^2} \\ L_{Q,Q} &\overset{Eq.\ 7.9}{=} \kappa T^2 + \frac{L_{Q,N}L_{N,Q}}{L_{N,N}} \overset{Eqs.\ 7.10,7.8}{=} \kappa T^2 + \frac{e^2}{\sigma T}\left(\frac{\sigma E T^2}{e}\right)^2 \\ &= \kappa T^2 + \sigma E^2 T^3 \end{aligned}$$

7.6.1 Peltier effect

The Peltier effect described the heat evolution at constant temperature, when a current is driven across a contact of two materials.

Chapter 8

Transport

8.1 Time evolution of the state operator

We start from the time-dependent Schrödinger equation

$$i\hbar\partial_t|\Psi\rangle = \hat{H}|\Psi\rangle$$

and derive from it the time derivative of the state operator.

$$\begin{aligned} i\hbar\partial_t\hat{\rho} &= i\hbar\partial_t\left(\sum_i |\Psi_i\rangle P_i\langle\Psi_i|\right) = i\hbar\sum_i \left(|\partial_t\Psi_i\rangle P_i\langle\Psi_i| + |\Psi_i\rangle P_i\langle\partial_t\Psi_i|\right) \\ &= \sum_i \left(\hat{H}|\Psi_i\rangle P_i\langle\Psi_i| - |\Psi_i\rangle P_i\langle\Psi_i|\hat{H}\right) \\ &= \hat{H}\sum_i |\Psi_i\rangle P_i\langle\Psi_i| - \sum_i |\Psi_i\rangle P_i\langle\Psi_i|\hat{H} = \hat{H}\hat{\rho} - \hat{\rho}\hat{H} = [\hat{H},\hat{\rho}] \end{aligned}$$

Thus we obtain the **von Neumann equation**, which says that the dynamics of the state operator is determined by its commutator with the Hamilton operator.

$$\partial_t\hat{\rho} = \frac{i}{\hbar}[\hat{\rho},\hat{H}] \tag{8.1}$$

This is a differential equation for the state operator.

8.2 Liouville Equation

Let us consider an ensemble of particles with an density

$$\rho(r,p,t) = \sum_i P_i\delta(\vec{r}-\vec{r}_i(t))\delta(\vec{p}-\vec{p}_i(t))$$

in phase space.[1]. For a system with N particles, $\vec{r}$ and $\vec{p}$ are $3N$-dimensional vectors. Each index i refers to one complete copy of the system, which is weighted with a probability P_i. The particles move on a trajectory $(\vec{r}_i(t),\vec{p}_i(t))$ in phase space.

We can express the distribution as

$$\rho(\vec{r},\vec{p},t) = \int d^{3N}r_0 \int d^{3N}p_0\ \rho(\vec{r}_0,\vec{p}_0,0)\delta(\vec{r}-\vec{r}(t))\delta(\vec{p}-\vec{p}(t))$$

---

[1] The phase space is the space spanned by the position and momentum coordinates of all particles in the system. See ΦSX: Classical Mechanics

Here $(\vec{r}(t), \vec{p}(t)$ is the trajectory that starts at $(\vec{r}_0, \vec{p}_0)$.

We can show the relation as follows

$$\begin{aligned}
\rho(\vec{r}, \vec{p}, t) &= \int d^{3N} r_0 \int d^{3N} p_0 \, \left(\sum_i P_i \delta(\vec{r}_0 - \vec{r}_i(0)) \delta(\vec{p}_0 - \vec{p}_i(0)) \right) \delta(\vec{r} - \vec{r}(t)) \delta(\vec{p} - \vec{p}(t)) \\
&= \sum_i P_i \int d^{3N} r_0 \int d^{3N} p_0 \; \delta(\vec{r}_0 - \vec{r}_i(0)) \delta(\vec{p}_0 - \vec{p}_i(0)) \delta(\vec{r} - \vec{r}(t)) \delta(\vec{p} - \vec{p}(t)) \\
&= \sum_i P_i \delta(\vec{r} - \vec{r}_i(t)) \delta(\vec{p} - \vec{p}_i(t))
\end{aligned}$$

Now we want to derive a differential equation for the distribution ρ, that describes its dynamics. We make a Taylor expansion $\vec{r}(\delta) = \vec{r}(0) + \Delta\frac{d\vec{r}}{dt} + O(\Delta) = \vec{r}_0 + \Delta\frac{d\vec{r}}{dt} + O(\Delta)$.

$$
\begin{aligned}
\rho(\vec{r},\vec{p},\Delta) &= \int d^{3N}r_0 \int d^{3N}p_0\ \rho(\vec{r}_0,\vec{p}_0,0)\delta(\vec{r}-\vec{r}_0-\Delta\frac{d\vec{r}}{dt})\delta(\vec{p}-\vec{p}_0-\Delta\frac{d\vec{p}}{dt}) \\
&= \rho(\vec{r}-\Delta\frac{d\vec{r}}{dt})\delta(\vec{p}-\Delta\frac{d\vec{p}}{dt}) \\
&\overset{Taylor}{=} -\Delta\frac{d\vec{r}}{dt}\vec{\nabla}_r\rho(\vec{r},\vec{p},0) - \Delta\frac{d\vec{p}}{dt}\vec{\nabla}_p\rho(\vec{r},\vec{p},0) \\
&\overset{HamiltonEq.}{=} -\Delta\sum_{j=1}^{3N}\left[\frac{\partial H}{\partial p_j}\frac{\partial \rho}{\partial r_j} - \frac{\partial H}{\partial r_j}\frac{\partial \rho}{\partial p_j}\right]
\end{aligned}
$$

If we divide by Δ, form the limes $\Delta \to 0$ and then generalize the result from $t = 0$ to arbitrary t, we obtain the **Liouville equation**.

$$
\frac{\partial \rho}{\partial t} + \sum_{j=1}^{3N}\left[\frac{\partial H}{\partial p_j}\frac{\partial \rho}{\partial r_j} - \frac{\partial H}{\partial r_j}\frac{\partial \rho}{\partial p_j}\right] = 0 \qquad (8.2)
$$

The Liouville equation can be seen as the particle conservation law (see ΦSX:Classical mechanics).

We can express the equation above also in terms of the Poisson brackets, known from classical mechanics.

$$
\{A, B\} = \sum_{j=1}^{3N}\left(\frac{\partial A}{\partial p_j}\frac{\partial B}{\partial r_j} - \frac{\partial B}{\partial p_j}\frac{\partial A}{\partial r_j}\right)
$$

, so that the Liouville equation obtains the form**Editor: check sign of the definition of the Poisson bracket**

$$
\frac{\partial \rho}{\partial t} + \{H, \rho\} = 0
$$

This shows a formal relation between the Liouville equation with the corresponding equation for the density operator. The main difference is that the commutator is replaced by the Poisson bracket. There is actually one formal way to introduce quantum mechanics, which is based on replacing Poisson brackets by commutators.

It can easily been shown that the equilibrium distributions $\rho(\vec{r},\vec{p},t) = \mathcal{N}e^{-\frac{1}{k_BT}H(\vec{r},\vec{p})}$ are stationary. More generally we show that every distribution of the form $\rho(r,p,t) = y(H(\vec{r},\vec{p}))$ is stationary

$$
\frac{\partial \rho}{\partial t} = -\sum_{j=1}^{3N}\left[\frac{\partial H}{\partial p_j}\frac{dy}{dH}\frac{\partial H}{\partial r_j} - \frac{\partial H}{\partial r_j}\frac{dy}{dH}\frac{\partial H}{\partial p_j}\right] = 0
$$

8.3 Boltzmann Equation

The Liouville equation has been expressed in terms of the many-particle probability density. This may be too much information. Let us therefore introduce the one-particle density

$$
\begin{aligned}
f_1(\vec{r},\vec{p},t) = \int d^3r_1 \ldots \int d^3r_N \int d^{3N}p_1 \ldots \int d^3p_N \\
\left[\sum_j \delta(\vec{r}-\vec{r}_j)\delta(\vec{p}-\vec{p}_j)\right] \rho_N(\{\vec{r}_i\},\{\vec{p}_i\})
\end{aligned}
$$

Let us similarly define the two-particle density

$$f_2(\vec{r},\vec{p},\vec{r}',\vec{p}',t)=\int d^3r_1\dots\int d^3r_N\int d^{3N}p_1\dots\int d^3p_N$$
$$\left[\sum_{i<j}\delta(\vec{r}-\vec{r}_i)\delta(\vec{p}-\vec{p}_i)\delta(\vec{r}'-\vec{r}_j)\delta(\vec{p}'-\vec{p}_j)\right]\rho_N(\{\vec{r}_i\},\{\vec{p}_i\})$$

Two relations may be helpful.

$$\int d^3r\int d^3p\ f_1(\vec{r},\vec{p},t)=N$$
$$f_1(\vec{r},\vec{p},t)=\frac{1}{N-1}\int d^3r'\int d^3p'\ f_2(\vec{r},\vec{p},\vec{r}',\vec{p}',t)$$

$$\partial_t f_1(\vec{r},\vec{p},t)=\int d^3r_1\dots\int d^3r_N\int d^{3N}p_1\dots\int d^3p_N\ \left[\sum_j\delta(\vec{r}-\vec{r}_j)\delta(\vec{p}-\vec{p}_j)\right]$$
$$\partial_t\rho_N(\{\vec{r}_i\},\{\vec{p}_i\})$$
$$=\int d^3r_1\dots\int d^3r_N\int d^{3N}p_1\dots\int d^3p_N\ \left[\sum_j\delta(\vec{r}-\vec{r}_j)\delta(\vec{p}-\vec{p}_j)\right]$$
$$\Big\{\sum_{i=1}^{N}\left[\frac{\partial H_0(\vec{r}_i\vec{p}_i)}{\partial p_i}\vec{\nabla}_r\rho_N-\frac{\partial H_0(\vec{r}_i\vec{p}_i)}{\partial r_i}\vec{\nabla}_p\rho_N\right]+\sum_{i<j}\vec{\nabla}_{r_i}W(\vec{r}_i-\vec{r}_j)\vec{\nabla}_{p_i}\rho_N\Big\}$$

In the derivation of the Liouville equation given above the distribution ρ has been the probability density for the complete system, which is normalized to one $\int d^{3N}r\int d^{3N}p\ \rho(\vec{r},\vec{p},t)=1$. For a single particle we can use the same distribution, but in the 6-dimensional phase space. For identical particles non-interacting particles, we may sum the probability densities ρ_i of the individual particles to the particle density $f(\vec{r},\vec{p},t)=\sum_i\rho_i(\vec{r},\vec{p},t)$, which is now the particle density.

The probability density for uncorrelated particles is

$$\rho(\{\vec{r}_j\},\{\vec{p}_j\})=\prod_{j=1}^{N}\frac{1}{N}f(\vec{r}_i,\vec{p}_i,t)$$

Let us use this as Ansatz in the Liouville equation for a many-particle Hamiltonian

$$H(\{\vec{r}_j\},\{\vec{p}_j\})=\sum_{j=1}^{N}H_0(\vec{r}_i,\vec{p}_i,t)+\frac{1}{2}\sum_{i\neq j}W(\vec{r}_i-\vec{r}_j)$$

Inserting the product Ansatz for the probability density into the Liouville equation, we obtain after division by ρ/N^N

$$\sum_i\frac{1}{f(\vec{r}_i,\vec{p}_i)}\frac{\partial f(\vec{r}_i,\vec{p}_i)}{\partial t}=\sum_{j=1}^{N}\left[\frac{\partial H_0}{\partial p_j}\frac{1}{f(\vec{r}_i,\vec{p}_i)}\vec{\nabla}_r f(\vec{r}_i,\vec{p}_i,t)-\frac{\partial H_0}{\partial r_j}\frac{1}{f(\vec{r}_i,\vec{p}_i)}\vec{\nabla}_p f(\vec{r}_i,\vec{p}_i,t)\right]\tag{8.3}$$
$$=\frac{1}{2}\sum_{i\neq j}f(\vec{r}_i,\vec{p}_i,t)W(\vec{r}_i-\vec{r}_i)f(\vec{r}_j,\vec{p}_j,t)\tag{8.4}$$
$$\tag{8.5}$$

$$\frac{\partial f}{\partial t}+\sum_{j=1}^{3}\left[\frac{\partial H_0}{\partial p_j}\frac{\partial f}{\partial r_j}-\frac{\partial H_0}{\partial r_j}\frac{\partial f}{\partial p_j}\right]=0\tag{8.6}$$

If the Hamiltonian has the form $H_0(\vec{p},\vec{r}) = \epsilon(\vec{p}) + V(\vec{r})$ the Liouville equation can be written in the form

$$\frac{\partial f}{\partial t} + \vec{v}_g(\vec{p})\vec{\nabla}_r f + \vec{F}\vec{\nabla}_p f = 0 \tag{8.7}$$

$\epsilon(\vec{p})$ is the dispersion relation for this particle and $\vec{v}(\vec{p}) = \vec{\nabla}_p \epsilon(\vec{p})$ is the velocity, which should be identified with the quantum mechanical group velocity. $\vec{F} = -\vec{\nabla} V(\vec{r})$ is the force acting on the particles.

8.4 Kubo Greenwood Formula

Chapter 9

Interacting Systems and Phase Transitions

Sofar we have investigated noninteracting system. Interactions add substantial complexity, but also result in far richer physical effects. One effect is that a system can change it properties in an abrupt manner as one of the parameters is changed. These effects are phase transitions. An example of a phase transition is the freezing and boiling of water. Another example is presence of a spontaneous magnetization in ferromagnets.

Let us consider a few examples for Phase transitions:

- melting (solid→liquid)-freezing (liquid→ solid)
- boiling(liquid→gas) -condensation (gas→liquid)
- sublimation (solid→gas)
- ferromagnetic → paramagnetic transition
- normal to superconducting transition
- Bose-Einstein condensation
- Superfluidity of He
- transitions between different crystal structures, such as the martensitic phase transition between ferrite (body-centered cubic iron) and austenite (face-centered cubic iron).

Order Parameter

Phase transition usually lead the system from an ordered to a disordered state. The order can be characterized by an **Order Parameter**. The order parameter is approximately zero in the ordered state and finite in the disordered state. The order parameter can be scalar, complex or generally multivalued.

- for the melting transition the order parameter would be the intensity of Bragg-peaks
- for the boiling transition the order parameter is the density, which changes from a small value to a much larger value
- for the ferromagnetic-paramagnetic transition, the order parameter is the magnetization.

Classification of phase transitions

Phase transitions are classified as first-order or second order phase transitions.

A phase transition which releases or absorbs a finite amount of latent heat is called **first order transition**. A phase transition that does not absorb or release a finite amount of latent heat is called **continuos** or **second-order phase transition**.

A first order phase transition usually results in an inhomogeneous mixed state with coexisting ordered and disordered regions. For example the boiling of water is a first order phase transition. When water boils, we observe bubbles. This can be explained as follows. Consider liquid water at the boiling point. A small region will convert to the gas phase. While doing so, it absorbs heat, which leads to a heat flux towards the water bubble. Thus the surrounding is lacking energy, which it would need to itself change its state of aggregation. Thus the gas state needs to nucleate. Bubbles are created and grow as additional heat is added to the system.

Bifurcation diagrams

Let us consider the free energy as function of a one-dimensional order parameter and an external parameter such as the temperature $F(\Phi,T)$. The actual value of Φ as function of temperature is determined as the minimum of the free energy. There are two ways that the order parameter can change abruptly, and both can be described by a polynomial form of the free energy.

- In one case we have one minimum which splits into two minima. This is a model for a second order phase transition.

  $$\begin{aligned} F(\Phi,T) &= \frac{1}{2}(T-T_c)\Phi^2+\frac{1}{4}\Phi^4 \\ \frac{\partial F}{\partial \Phi} &= 0 \Rightarrow \Phi(T)=\pm\sqrt{T_c-T}; \Phi(T)=0 \end{aligned}$$

  We find one minimum for $T > T_c$ and two minima at $\Phi = \pm\sqrt{T_c - T}$ for $T < T_c$. The order parameter changes continuous but not differentiable, and it can assume one of two values below the critical temperature T_c.

  If we draw the order parameter as function of an external parameter such as the temperature, we obtain a **bifurcation diagram**. above the **critical temperature**, the temperature of the phase transition, the free energy has a single minimum. Below, it develops two different minima, with the same free energy. Hence both states are equally probable.

- The free energy develops a second minima for an order parameter different from the free energy minimum. At first, this minimum is metastable but then it lowers relative to the global minimum until it becomes the global minimum itself. As a result the order parameter jumps discontinuously from one value to another. This is an example for a second order phase transition.

  $$\begin{aligned} F(\Phi,T) &= -\frac{1}{2}\Phi^2-\frac{2}{3}(T-T_c)\Phi^3+\frac{1}{4}\Phi^4 \\ \frac{\partial F}{\Phi} &= 0 \Rightarrow \Phi(T)=\frac{T-T_c}{\pm}\sqrt{1-(T-T_c)^2}; \Phi(T)=0 \end{aligned}$$

  For $T = T_c$ we find two equivalent minima at $\Phi\pm1$. For $T < T_c$ the left is the global minimum and for $T > T_c$ it is the right minimum.

Editorial Remark: end itemize probably at the wrong place

While we have assumed here that the order parameter is one dimensional, it is just as well possible that it has higher dimensions. An example is a ferromagnet: below the Curie temperature, the magnetization has a finite value, but can point into any direction.

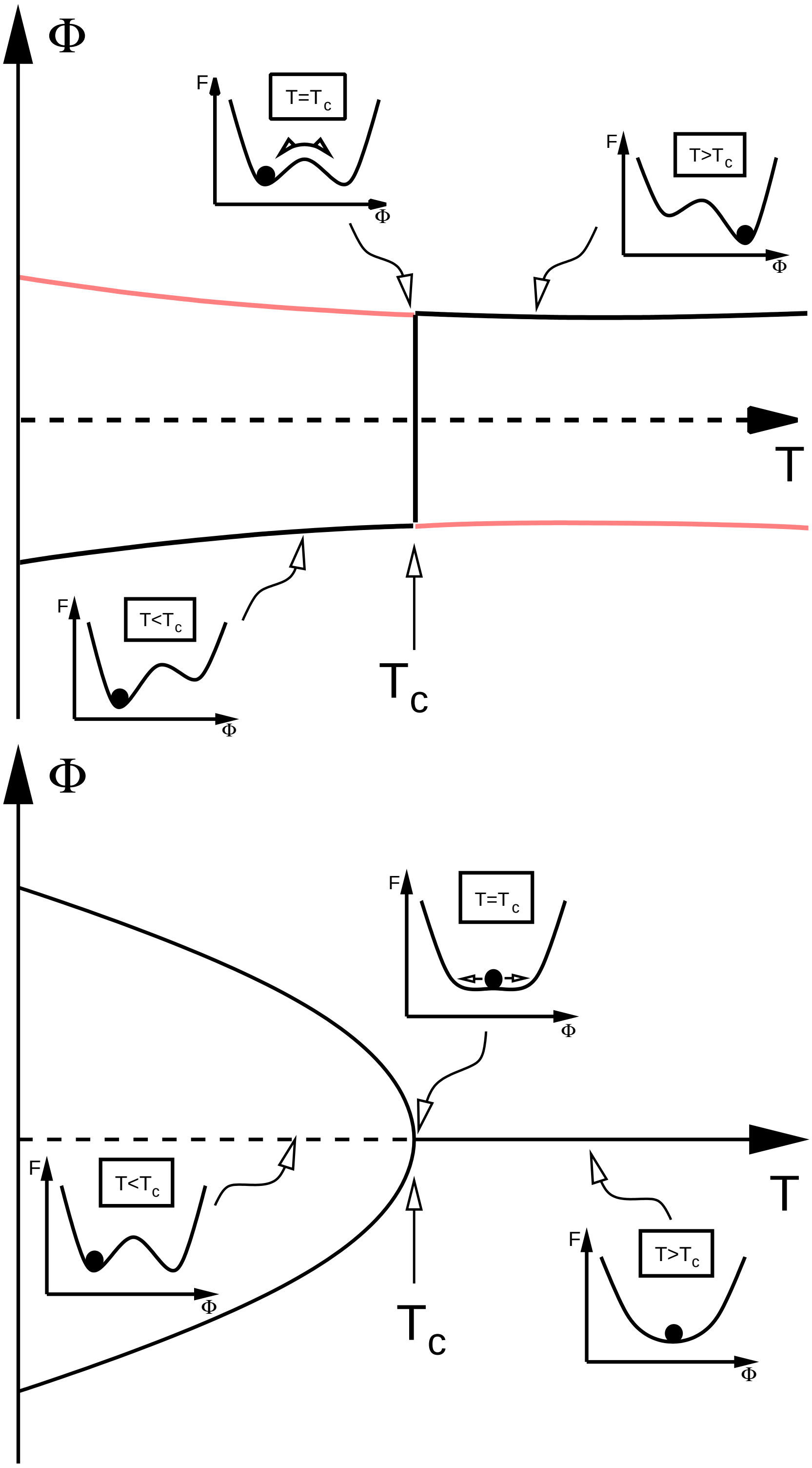


Fig. 9.1: Bifurcation diagram for a first-order transition (above) and a second-order transition (below). The insets indicate the free energy as function of the order parameter Φ for the various temperature regimes, that is below, at and above the transition temperature T_c.

An important question, we need to address is also the spatial dependence of the order parameter: Even below the Curie temperature, a magnet does not produce a magnetic field unless it is magnetized. This is because the crystal has different domains, where each domain has a defined magnetization direction. The magnetization direction of the domains however is randomly distributed. As a result, the macroscopically magnetization of a ferromagnet can vanish.

9.1 Ehrenfest classification of phase transitions

Phase transitions have been divided into different classes[17] by Ehrenfest[1].

In a **first-order phase transition** the chemical potentials change discontinuously with temperature. In a **second-order phase transition** the chemical potentials remain continuous, but the derivatives of the chemical potentials change discontinuously.

9.2 Mean Field Theory

In our study of interacting systems we begin again with the most simple system namely the two state model. The interacting two state system is called the Ising model. It has its origin in the description of magnetism.

The Ising model consists of many two-state systems with a nearest neighbor interaction

$$E=-\sum_i \mu\sigma_i B-\sum_{i,j} J_{i,j}\sigma_i\sigma_j$$

where $J_{i,j}=0$ except for nearest neighbor sites where it is $J_{i,j}=J$. σ_i describes the direction of the spin on site i. It can have values $+1$ and -1. The interaction is such that two neighboring spins that are parallel are energetically favored over a state with antiparallel spins. This feature will lead to a collective alignment at sufficiently low temperatures.

Despite its simplicity the Ising model cannot be solved analytically in three dimensions. Therefore it is important to use approximations. One of the most successful approximation schemes is the mean field theory or Weiss molecular field theory.

The approximation is the assumption that the spins are not correlated that is $\langle\sigma_i\sigma_j\rangle=\langle\sigma_i\rangle\langle\sigma_j\rangle$. Thus we rewrite The expression for the energy in the form

$$\langle E\rangle=\langle\sum_i \mu\sigma_i B_{eff,i}\rangle$$

with

$$\mu B_{eff,i}=\mu B-qJ\langle\sigma\rangle \tag{9.1}$$

where $qJ=\sum_j J_{i,j}$ and q is the number of nearest neighbors. In a three dimensional cubic lattice for example we obtain $q=6$.

The partition function and the free energy are obtained from our study of the non-interacting two-state system

$$Z(\beta,B)=\sum_{\{\sigma_i}\mathrm{e}^{-\beta\sum_i \mu B_{eff}\sigma_i}=\Big[2\cosh(\beta\mu B_{eff})\Big]^N$$

$$F=-k_BT\ln[Z]=-Nk_BT\ln[2\cosh(\frac{\mu B_{eff}}{k_BT})]$$

where N is the total number of spins.

---

[1] **Editor: Bibliogrpahical note on Paul Ehrenfest here**

The magnetization of non-interacting spins is

$$M = \frac{dF}{dB_{eff}} = -N\mu \tanh(\beta\mu B_{eff})$$

On the other hand B_{eff} is related via Eq. 9.1 to the true magnetic field and the magnetization.

Thus we obtain an expression

$$M = N\mu \tanh(\beta\mu B + \beta J \frac{M}{N\mu})$$

which can be solved for the magnetization $M(B,T)$ as function of magnetic field and temperature.

Let us first investigate the implications. For zero field we approximate $\tanh(x) = x - x^3/3 + O(x^5)$, where $x = M/(N\mu)$

$$\begin{aligned} x = \tanh(\beta J x) &\approx \beta J x - \frac{1}{3}(\beta J x)^3 \\ x &= 0 \\ x(J < k_BT) &= \pm\sqrt{3(\beta J - 1)}\beta J \end{aligned}$$

Using the approximate form, which is valid for small magnetizations, we find one solution with vanishing magnetization. This solution is a minimum of the free energy for temperatures above the **critical temperature** $T_c = J/k_B$. For temperatures below the critical temperature this solution becomes unstable, and instead two equivalent solutions occur with finite magnetization

$$M(J < k_BT) \approx \pm N\mu\sqrt{3(\beta J - 1)}\beta J = \pm\sqrt{3}N\mu\sqrt{\frac{T - T_c}{T_c}}$$

Thus we see here our first phase transition. for $k_BT < J$ we observe a spontaneous or **remanent magnetization** proportional to $\sqrt{\frac{T-T_c}{T_c}}$.

9.2.1 Some remarks:

It should be noted that the exchange interaction is not a magnetic interaction but a so-called exchange interaction. Therefore it is much stronger than if it were of magnetic origin.

The mean field theory is quite convincing. However, it is an approximation, because the spins on different sites are statistically correlated. This can easily been seen. Consider a spin pointing in positive z-direction. If the exchange coupling is such that it favors parallel spins over antiparallel spins, the neighboring spins will on average be more frequently parallel than antiparallel than on average.

We may ask why a piece of iron is not always a permanent magnet. The reason is that in a macroscopic sample not all spins are aligned. The magnet forms **domains** of aligned spins with **domain walls** separating them. When we magnetize a piece of iron, it is not the magnetic moments on the atoms that changes, but the size of domains which grow, if the spins in the domains are oriented favorable for the magnetic field, while those with the unfavorable direction shrink.

9.2.2 Phase equilibria

Editor: define "tie line", "lever rule", "tangent rule", "triangular phase diagrams".

Gibbs Phase rule

Editor: see Atkins, Physical Chemistry

Gibbs phase rule says

$$f = c - p + 2 \tag{9.2}$$

p is the number of phases. A gas or a gaseous mixture is a single phase. Ice is a single phase, even though it may occur in distinct pieces. A mixture[2] of two immiscible[3] liquids has two phases. A mixture of two miscible liquids has one phase.

c is the number of components in equilibrium. The number of components is the minimum number of species necessary to define the composition of all phases present in the system.

f is the variance, defined as the number of intensive variables that can changed independently, without changing the number of phases.

Gibbs phase rule is justified as follows. Let us consider a system of c components at a given pressure and temperature. The composition of each phase is defined by $c-1$ mole fractions x_i, because $\sum_{i=1}^{c} x_i = 1$. To describe the composition of each of the p phases, one needs $p(c-1)$ variables. Now we add 2 degrees of freedom for temperature and pressure. The chemical potentials of each component in the p phases must be identical in thermal equilibrium which yields $c(p-1)$ equations. Thus the number of degrees of freedom is $f = p(c-1)+2-c(p-1) = pc-p+2-pc+c = c-p+2$.

Thus for a one component system such as water, the number of degrees of freedom is $f = 1-p+2$. That is three phases, water, ice and gas can only be in equilibrium at one point in the phase diagram, the **triple point**. Hence pressure and temperature remains fixed. The equilibrium of two phases, such as water and ice defines a line in the phase diagram: At a given pressure, water and ice can coexist only at a given temperature. The single phase regions, that is for water or for ice or the gas, we obtain two-dimensional regions in the $p-T$ diagram.

9.2.3 Coexistence,Hysteresis, discontinuity of the specific heat

9.2.4 Critical exponents

9.3 The Van der Waals Gas

[4]

Let us start out with the Helmholtz potential of the ideal gas.

$$A(T,V,N) = Nk_BT\left(\ln\left[\frac{\lambda_T^3 N}{V}\right]-1\right)$$

where $\lambda_T = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}$ is the thermal de-Broglie wavelength.

For a real gas we need to modify it in two respects.

- real molecules are no point particles by have an effective potential into which other atoms cannot penetrate.
- real molecules attract each other.

Thus we modify the potential by effectively reducing the effective volume by a the molecular volume b of the molecules.

$$A(T,V,N) = Nk_BT\left(\ln\left[\frac{\lambda_T^3 N}{V-Nb}\right]-1\right)$$

For water the Van-der Waals parameters are

$$a_{H_2O} = 1.546717\times10^{-48}\mathrm{Pa\ m}^6 \qquad b_{H_2O} = 5.062984\times10^{-29}\mathrm{m}^3$$

---

[2] “mixture” translates as “Mischung” into German

[3] “immiscible” translates as “nicht mischbar” into German

[4] Johannes Diderik Van der Waals, Dutch Physicist 1937-1923, Nobel prize in Physics "fÃijr seine Arbeiten Ãijber die Zustandsgleichung der Gase und FlÃijssigkeiten"

The parameter b corresponds to a molecular volume. If we express b by a sphere, the radius for water would correspond to 2.3 Å.

The interaction energy can approximately be taken into account, by subtracting the effective attraction energy, which is proportional to N times a term that is again proportional to the density.

$$A(T,V,N) = Nk_BT\left(\ln\left[\frac{\lambda_T^3 N}{V-Nb}\right]-1\right)-\frac{1}{2}a\frac{N^2}{V}$$

For the ideal gas the ideal gas law was of fundamental importance. Here we develop a similar law for the van der Waals gas. The ideal gas law has been obtained by evaluating the pressure as function of temperature and particle number. Therefore we proceed here similarly.

$$\begin{aligned}
U(S,V,N) &= \min_T A(T,V,N) + TS \\
p &= -\left.\frac{dU}{dV}\right|_{S,N} = -\frac{d}{dV}\left[A(T_0(S,V,N),V,N)+T_0(S,V,N)S\right] \\
&= -\frac{\partial A}{\partial V} - \underbrace{\left(\frac{\partial A}{\partial T}+S\right)}_{=0}\frac{dT(S,V,N)}{dV} \\
&= -\left.\frac{dA}{dV}\right|_{V,N} \\
&= \frac{Nk_BT}{V-Nb} - a\frac{N^2}{V^2}
\end{aligned}$$

This yields the **van der Waals equation**

$$\left(p + a\frac{N^2}{V^2}\right)(V-Nb) = Nk_BT$$

The Van der Waals equation replaced the ideal gas equation of the Boltzmann gas.

Note that the van der Waals equation provides several (up to three) solutions for the volume at a given temperature and pressure.

For water, $a = 557.29\times 10^{-9}\frac{\mathrm{Pa\,m^6}}{\mathrm{mol^2}}$ and $b = 0.31\times 10^{-6}\,\frac{\mathrm{m^3}}{\mathrm{mol}}$ (Wikipedia: Van der Waals Gleichung)

9.3.1 Isotherms of the p-V diagram

We can no evaluate the pressure as function of volume at a given temperature

$$p(V,T,N) = \frac{Nk_BT}{V-Nb} - a\frac{N^2}{V^2}$$

Let us determine the maxima.

$$\begin{aligned}
\frac{dp}{dV} &= -\frac{Nk_BT}{(V-Nb)^2} + 3a\frac{N^2}{V^3} \\
&= \frac{1}{V^3}\left[-Nk_BTV\left(\frac{1}{1-\frac{Nb}{V}}\right)^2 + 3aN^2\right]
\end{aligned}$$

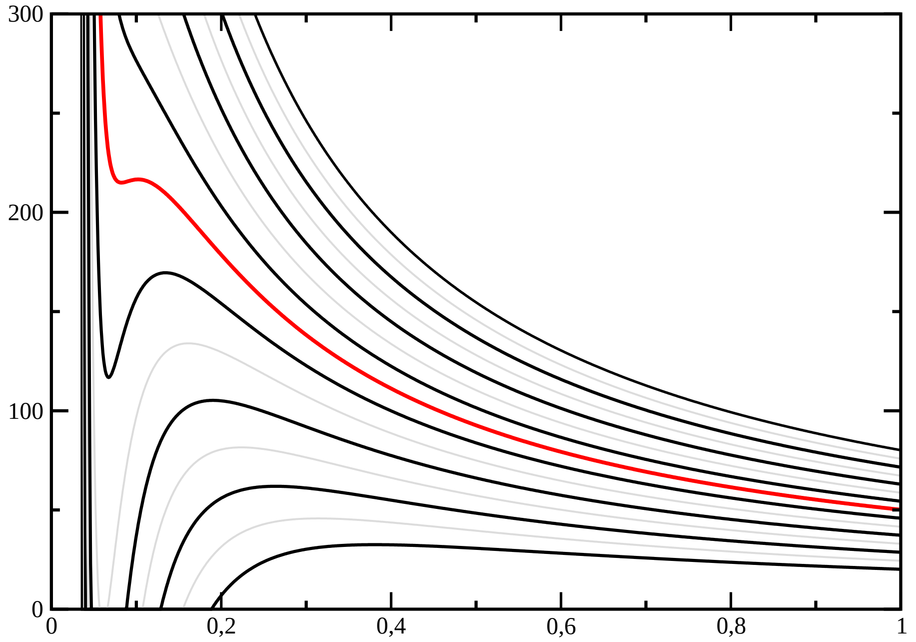


Fig. 9.2: Isotherms of water according to the van-der Waals equation. Vertical axis: pressure in bar, horizontal axis Volume per mol in litre. The isotherms range from 300 K to 1000 K. The black lines are multiple of 100 K. The red line corresponds to 650 K, just below the critical temperature.

For $V >> Nb$, we obtain approximately

$$\begin{aligned}
V_0 &\approx \frac{3aN}{k_BT} \\
p(V_0) &= \frac{Nk_BT}{\frac{3aN}{k_BT} - Nb} - a\frac{N^2(k_BT)^2}{(3aN)^2} \\
&= \frac{k_BT}{\frac{3a}{k_BT} - b} - a\frac{(k_BT)^2}{(3a)^2} \\
&= (k_BT)^2\frac{1}{3a - bk_BT} - a\frac{1}{(3a)^2}
\end{aligned}$$

9.3.2 Gibbs energy of the Van der Waals gas

$$\begin{aligned}
G(T,p,N) &= \min_V A(T,V,N) + pV \\
&= \min_V \left[Nk_BT\left(\ln\left[\frac{\lambda_T^3 N}{V_0(T,p,N) - Nb}\right] - 1\right) - \frac{1}{2}a\frac{N^2}{V_0(T,p,N)} + pV_0(T,p,N)\right]
\end{aligned}$$

9.3.3 Phase diagram of the van der Waals gas

Let us now investigate the density of the van der Waals gas as function of temperature and pressure. We choose the density because it acts as an order parameter for the solid liquid transition.

$$
\begin{aligned}
\left(p+a\rho^2\right)\left(\frac{1}{\rho}-b\right)&=k_BT\\
\left(p+a\rho^2\right)(1-\rho b)-k_BT\rho&=0\\
ab\rho^3+a\rho^2-(pb+k_BT)\rho+p&=0\\
\rho^3+\frac{1}{b}\rho^2-\frac{(pb+k_BT)}{ab}\rho+\frac{p}{ab}&=0
\end{aligned}
$$

Kurvendiskussion:

- Extrema:

$$
\begin{aligned}
3\rho^2+\frac{2}{b}\rho-\frac{(pb+k_BT)}{ab}&=0\\
\rho^2+\frac{2}{3b}\rho-\frac{(pb+k_BT)}{3ab}&=0\\
\rho&=-\frac{1}{3b}\pm\sqrt{\left(\frac{1}{3b}\right)^2+\frac{(pb+k_BT)}{3ab}}
\end{aligned}
$$

9.4 Alloy phase diagrams

Consider an alloy of two components, A and B.

The enthalpy of the alloy depends on the concentration c_A of phase A

$$
H(S,c_A,p,N)=N\left[H_Ac_A+H_B(1-c_A)+\Delta c_A(1-c_A)\right]
$$

The entropy can directly be obtained from the two state system

$$
S(c_A)=-Nk_B\left[c_A\ln(c_A)+(1-c_A)\ln(1-c_A)\right]
$$

Assuming that the interaction between the sites is negligible

Thus one obtains the Gibbs potential

$$
\begin{aligned}
G(T,c_A,p,N)=N\Big\{&H_Ac_A+H_B(1-c_A)+\Delta c_A(1-c_A)\\
&+k_BT\left[c_A\ln(c_A)+(1-c_A)\ln(1-c_A)\right]\Big\}
\end{aligned}
$$

9.5 Phase separation

If the interaction between the two atoms is repulsive we can obtain phase separation into a phase of predominantly A with a small amount of B, and another phase of predominantly B with a small amount of A. The two phases are separated by a miscibility gap.

Let us assume that two phases α and β are in equilibrium.

$$
\begin{aligned}
G=\;&G_\alpha(N_{A,\alpha},N_{B,\alpha})+G_\beta(N_{A,\beta},N_{B,\beta})\\
&-\lambda_1\left(N_{A,\alpha}+N_{A,\beta}-N_{A,tot}\right)-\lambda_2\left(N_{B,\alpha}+N_{B,\beta}-N_{B,tot}\right)
\end{aligned}
$$

where N_{tot} is the total number of atoms.

We introduce the new variables, namely the amount of material α

$$\begin{aligned} N_\alpha &= N_{A,\alpha} + N_{B,\alpha} \,; \qquad & N_\beta &= N_{A,\beta} + N_{B,\beta} \\ c_\alpha &= N_{A,\alpha}/N_\alpha \,; \qquad & c_\beta &= N_{A,\alpha}/N_\beta \end{aligned}$$

so that

$$\begin{aligned} N_{A,\alpha} &= c_\alpha N_\alpha \,; \qquad & N_{B,\alpha} &= (1-c_\alpha)N_\alpha \\ N_{A,\beta} &= c_\beta N_\beta \,; \qquad & N_{B,\beta} &= (1-c_\beta)N_\beta \end{aligned}$$

Now we introduce the chemical potential $\mu_\alpha(c) = \frac{G_\alpha(cN,(1-c)N)}{N}$

$$\begin{aligned} G = {}& N_\alpha \mu_\alpha(c_\alpha)) + N_\beta \mu_\beta(c_\beta) \\ & -\lambda_1 \left(N_\alpha c_\alpha + N_\beta c_\beta - N_{A,tot}\right) - \lambda_2 \left(N_\alpha(1-c_\alpha) + N_\beta(1-c_\beta) - N_{B,tot}\right) \end{aligned}$$

The equilibrium conditions are

$$\begin{aligned} 0 &= \frac{\partial G}{\partial N_\alpha} = \mu_\alpha(c_\alpha)) - \lambda_1 c_\alpha - \lambda_2(1-c_\alpha) \\ 0 &= \frac{\partial G}{\partial N_\beta} = \mu_\beta(c_\beta)) - \lambda_1 c_\beta - \lambda_2(1-c_\beta) \\ 0 &= \frac{\partial G}{\partial c_\alpha} = N_\alpha \frac{d\mu_\alpha(c_\alpha))}{dc_\alpha} - \lambda_1 N_\alpha + \lambda_2 N_\alpha \\ 0 &= \frac{\partial G}{\partial c_\beta} = N_\beta \frac{d\mu_\beta(c_\beta)}{dc_\beta} - \lambda_1 N_\beta + \lambda_2 N_\beta \end{aligned}$$

The last two equations yield

$$\frac{d\mu_\alpha(c_\alpha)}{dc_\alpha} = \lambda_1 - \lambda_2 = \frac{d\mu_\beta(c_\beta)}{dc_\beta}$$

which says that the chemical potentials of the two phases must be identical.

Now we use this result with the first two equilibrium conditions

$$\begin{aligned} 0 &= \mu_\alpha(c_\alpha)) - (\lambda_1 - \lambda_2)c_\alpha - \lambda_2 \\ &= \mu_\alpha(c_\alpha)) - \frac{d\mu_\alpha(c_\alpha)}{dc_\alpha} c_\alpha - \lambda_2 \\ 0 &= \mu_\beta(c_\beta)) - (\lambda_1 - \lambda_2)c_\beta - \lambda_2 \\ &= \mu_\beta(c_\beta)) - \frac{d\mu_\alpha(c_\alpha)}{dc_\alpha} c_\beta - \lambda_2 \end{aligned}$$

and obtain

$$\begin{aligned} \mu_\alpha(c_\alpha) - \frac{d\mu_\alpha(c_\alpha)}{dc_\alpha} c_\alpha &= \mu_\beta(c_\beta) - \frac{d\mu_\beta(c_\alpha)}{dc_\alpha} c_\beta \\ \frac{\mu_\alpha(c_\alpha) - \mu_\beta(c_\beta)}{c_\alpha - c_\beta} &= \frac{d\mu_\alpha(c_\alpha)}{dc_\alpha} = \frac{d\mu_\beta(c_\beta)}{dc_\beta} \end{aligned}$$

This is the so-called **tangent rule**: The equations are fulfilled if the two points in the μ versus c_α diagram have the same tangent.

Note that one uses usually the molar Gibbs potential instead of μ. The two are up to a factor, the Avogadro constant, identical.

Since the entropy starts with infinite negative slope any material with a repulsive interaction will develop a miscibility gap. As we increase the concentration of B we first form a solution of the α

phase with an increasing amount of atoms B dissolved. At a critical concentration, which depends on temperature, the second phase β develops, with the maximum amount of A atoms dissolved in it. As we increase the concentration, the phase β grows at the expense of the α phase, while the compositions of both phases remain identical. The relative amounts of material in phases α and β is directly proportional to the distance of the average concentration from the boundaries of the miscibility gap. Let c_α and c_β be the concentrations at the boundaries of the miscibility gap, let x be the ratio of phase α and let $\langle c_A\rangle$ be the average concentration.

$$\begin{aligned}\langle c_A\rangle &= \frac{N_\alpha c_\alpha + N_\beta c_\beta}{N_\alpha + N_\beta} \overset{x=N_\alpha/(N_\alpha+N_\beta)}{=} x c_\alpha + (1-x)c_\beta \\ \Rightarrow x &= \frac{\langle c_A\rangle - c_\beta}{c_\alpha - c_\beta}\end{aligned}$$

Once the concentration reaches the other boundary of the miscibility gap, the phase α has vanished, and further increase or β will reduce the amount of A atoms dissolved in phase β.

The miscibility gap closes at a certain temperature. This temperature often lies above the melting point, which leads to the typical eutectic phase- diagram.

9.6 Solidification

We assume that there are two different Gibbs potentials, one, G_s for the solid and one $G_l$for the liquid.

The melting point is defined as the point where the chemical potentials of solid and liquid phase are identical. Let us consider the concentrations of the solid and the liquid phases by c_s and c_l.

$$\mu_s(T_m, c_s) = \mu_l(T_m, c_l)$$

Due to the Euler equation the Gibbs potential is linear with the particle number $G = \mu N$

$$\begin{aligned}G &= \mu_s N_s + \mu_l N_l \overset{\mu_s=\mu_l}{=} \mu_s(N_s + N_l) = \underbrace{\mu_s N_{tot}}_{G_s} \overset{\mu_s=\mu_l}{=} \underbrace{\mu_l N_{tot}}_{G_l} \\ \Rightarrow G_s &= G_l\end{aligned}$$

Thus we find that the Gibbs potentials of solid and liquid phases are identical at the melting point. Thus the melting point of phase A is defined by

$$\begin{aligned}G_l(T_{m,A}, c_A = 1) &= G_s(T_{m,A}, c_A = 1) \\ G_l(T_{m,B}, c_A = 0) &= G_s(T_{m,B}, c_A = 0)\end{aligned}$$

9.7 Landau Theory

Appendix A

Random Number generators

A.1 Implementation of the Minimal Standard Linear Congruential Pseudo Random Number generator

This is the Fortran 90 implementation analogous to the one published by Park and Miller[11]. In order to allow testing the implementation, Park and Miller quote the result for the seed after 10000 calls of this subroutine 2147483531.

It is strongly recommended to first copy this implementation exactly and without the slightest change. Then one should perform the abovementioned test.

```
!
!     ...1.........2.........3.........4.........5.........6.........7.........8
      subroutine random_minstandard(ran)
!     **************************************************************************
!     ** Minimal standard linear congruential random number generator        **
!     ** S.K.Park and K.W.Miller, Communications of the ACM, 31, 1192 (1988)  **
!     **                                                                      **
!     ** this version only works if huge(seed).ge.2147483647                 **
!     **************************************************************************
      implicit none
      real(8)   ,intent(out):: ran
      integer(4),parameter  :: m=2147483647  !=2_8**31-1_8
      integer(4),parameter  :: a=16807
      integer(4),parameter  :: q=127773    !=int(m/a)
      integer(4),parameter  :: r=2836      !=mod(m,a)
      integer(4),save       :: seed=1
      integer(4)            :: hi,lo,test
!     **********************************************************
      hi=int(seed/q)
      lo=mod(seed,q)
      test=a*lo-r*hi
      if(test.gt.0) then
        seed=test
      else
        seed=test+m
      end if
      ran=real(seed,8)/real(m,8)
      return
```

```
end
```

A.2 Schrage's method

When implementing the linear congruential random number generators,

$$x_{n+1} = ax_n \mod m$$

one usually runs into overflows, because m is usually chosen as one of the largest numbers that can be represented in the number type.

Under the conditions $0 \leq z < m$ and $r < q$, Schrage's method suggests to use the following replacement

$$ax \mod m = a(x - qk) - rk$$

where

$$\begin{aligned} q &\overset{\text{def}}{=} \text{int}\left(\frac{m}{a}\right) \\ r &= m \mod a \\ k &\overset{\text{def}}{=} \text{int}\left(\frac{x}{q}\right) \end{aligned}$$

Here we used the function int, which is defined analogously to the corresponding fortran function, namely that it cuts the fractional part from the number: it rounds to the next integer with smaller absolute value.

With the function "int" we can define the modulo function as

$$x \mod y = x - y \quad \text{int}\left(\frac{x}{y}\right)$$

Now we start the proof

$$\begin{aligned} r = m \mod a &= m - a \quad \text{int}\left(\frac{m}{a}\right) = m - aq \\ \Rightarrow m &= aq + r \\ ax \mod m &= ax - m \quad \text{int}\left(\frac{ax}{m}\right) \\ &= ax - (aq + r) \quad \text{int}\left(\frac{ax}{aq + r}\right) \\ &= ax - aq \quad \text{int}\left(\frac{ax}{aq + r}\right) - r \quad \text{int}\left(\frac{ax}{aq + r}\right) \\ &= a\left(x - q \quad \text{int}\left(\frac{x}{q + r/a}\right)\right) - r \quad \text{int}\left(\frac{x}{q + r/a}\right) \end{aligned}$$

The next step is only allowed if $r < q$, namely to replace

$$\text{int}\left(\frac{x}{q + r/a}\right) = \text{int}\left(\frac{x}{q}\right)$$

If we use this replacement we obtain

$$ax \mod m = a(x - qk) - rk$$

In the following we need to show that

$$\text{int}\left(\frac{x}{q + r/a}\right) = \text{int}\left(\frac{x}{q}\right)$$

The proof is still commented out and needs to be written in tex

Appendix B

Monte Carlo codes

B.1 Metropolis algorithm for the 2-dimensional Ising model

```
!
!     ...1.........2.........3.........4.........5.........6.........6.........7.........8
      program main
      implicit none
      integer(8),parameter :: n1x=100
      integer(8),parameter :: n2x=100
      real(8)   ,parameter :: jint=1.d0  ! spin-spin interaction
      real(8)   ,parameter :: hext=0.d0  ! external field
      real(8)   ,parameter :: kbt=2.3d0
      integer(8),parameter :: nstep=10**8  ! number of mc steps
      integer(8),parameter :: nsteppersample=nstep/1000
      integer(8)           :: state(n1x,n2x)
      integer(8)           :: i1,i2,istep
      integer(8)           :: isite,i1p,i1m,i2p,i2m,nn
      real(8)              :: mag,magdirect,magav ! magnetization/per site
      real(8)              :: mag2av,magfluct
      real(8)              :: etot,etotdirect,etotav
      real(8)              :: weight
      real(8)              :: deltae
      real(8)              :: ran
      real(8)              :: acceptanceratio
      real(8)              :: svar              !support variable
      logical              :: tflip
      character(n2x)       :: string
!     ************************************************************************************
!     ==  state=0 site is vacant
!     ==  state=1 site is occupied
!     ====================================================================================
!     ==  prepare initial state                                                         ==
!     ====================================================================================
      weight=1.d0/real(n1x*n2x)
      do i1=1,n1x
        do i2=1,n2x
          call random_number(ran)
          state(i1,i2)=nint(ran)
        enddo
```

```
      enddo
!
!     ====================================================================================
!     ==  calculate initial properties                                                  ==
!     ====================================================================================
      call totalenergy(n1x,n2x,hext,jint,state,etot,mag)
      print*,'magnetization',mag
      acceptanceratio=0.d0
      etotav=0.d0
      magav=0.d0
!
!     ====================================================================================
!     ==  monte carlo loop                                                              ==
!     ====================================================================================
      open(10,file='ising2d.dat')
      open(11,file='ising2d.out')
      do istep=1,nstep
!
!       ==================================================================================
!       == select a random site                                                         ==
!       ==================================================================================
        call random_number(ran)
        i1=nint(0.5d0+ran*real(n1x))
        call random_number(ran)
        i2=nint(0.5d0+ran*real(n2x))
!
!       ==================================================================================
!       == determine enery difference for the step                                      ==
!       ==================================================================================
        i1p=1+modulo(i1,n1x)
        i1m=1+modulo(i1-2,n1x)
        i2p=1+modulo(i2,n2x)
        i2m=1+modulo(i2-2,n2x)
        nn=state(i1p,i2)+state(i1m,i2)+state(i1,i2p)+state(i1,i2m)
!       == calculate energy change for a spin flip ======================================
        deltae=-2.d0*real(2*state(i1,i2)-1)*(-hext-jint*real(2*nn-4))
!
!       ==================================================================================
!       == choose acceptance and flip spin                                              ==
!       ==================================================================================
        if(deltae.le.0.d0) then
          tflip=.true.
        else
          call random_number(ran)
          tflip=ran.lt.exp(-deltae/kbt)
        end if
        if(tflip) then
          state(i1,i2)=1-state(i1,i2)
          acceptanceratio=acceptanceratio+1
          etot=etot+deltae
          mag=mag+real(2*(2*state(i1,i2)-1))*weight
        end if
        magav=magav+mag
        mag2av=mag2av+mag**2
```

```
        etotav=etotav+etot
!
!       ==================================================================================
!       == analysis                                                                     ==
!       ==================================================================================
        if(modulo(istep,nsteppersample).eq.0) then
!         == form time average ===========================================================
          svar=1.d0/real(nsteppersample)
          acceptanceratio=acceptanceratio*svar
          magav=magav*svar
          mag2av=mag2av*svar
          etotav=etotav*svar
!         == print result
          magfluct=sqrt(mag2av-mag**2)
!         call totalenergy(n1x,n2x,hext,jint,state,etotdirect,magdirect)
!         write(10,*)istep,etot*weight,etotdirect*weight,acceptanceratio,mag,magdirect
          write(10,*)istep,etotav*weight,magav,magfluct,acceptanceratio
          write(11,*)istep,etot*weight,mag
          call plotstate(11,n1x,n2x,state)
          acceptanceratio=0
          magav=0.d0
          etotav=0.d0
        end if
      enddo
      close(10)
!
!     ====================================================================================
!     ==  analyze result                                                                ==
!     ====================================================================================
      print*,'magnetization',mag
      close(11)
      stop
      end
!
!     ...1.........2.........3.........4.........5.........6.........6.........7.........8
      subroutine totalenergy(n1x,n2x,hext,jint,state,etot,mag)
      implicit none
      integer(8),intent(in) :: n1x
      integer(8),intent(in) :: n2x
      real(8)   ,intent(in) :: hext
      real(8)   ,intent(in) :: jint
      integer(8),intent(in) :: state(n1x,n2x)
      real(8)   ,intent(out):: etot
      real(8)   ,intent(out):: mag
      integer(8)            :: i1,i2
      integer(8)            :: i1p,i1m,i2p,i2m
      integer(8)            :: nn
      real(8)               :: hint
!     ************************************************************************************
      etot=0.d0
      mag=0.d0
      do i1=1,n1x
        do i2=1,n2x
          i1p=1+modulo(i1,n1x)
```

```
          i1m=1+modulo(i1-2,n1x)
          i2p=1+modulo(i2,n2x)
          i2m=1+modulo(i2-2,n2x)
          nn=state(i1p,i2)+state(i1m,i2)+state(i1,i2p)+state(i1,i2m)
          hint=jint*real(2*nn-4)    ! sum_k jint*sigma_k
          etot=etot-(hext+0.5d0*hint)*real(2*state(i1,i2)-1)
          mag=mag+real(2*state(i1,i2)-1)
        enddo
      enddo
      mag=mag/real(n1x*n2x)
      return
      end
!
!     ...1.........2.........3.........4.........5.........6.........6.........7.........8
      subroutine plotstate(nfil,n1x,n2x,state)
!     ************************************************************************************
      implicit none
      integer  ,intent(in) :: nfil
      integer(8),intent(in) :: n1x
      integer(8),intent(in) :: n2x
      integer(8),intent(in) :: state(n1x,n2x)
      integer(8)            :: i1,i2
      character(n2x)        :: string
!     ************************************************************************************
      do i2=1,n2x
        string(i2:i2)='-'
      enddo
      write(nfil,*)'|'//string//'|'
      do i1=1,n1x
        string=''
        do i2=1,n2x
          if(state(i1,i2).eq.1)string(i2:i2)='o'        enddo
        write(nfil,*)'|'//string//'|'
      enddo
      do i2=1,n2x
        string(i2:i2)='-'
      enddo
      write(nfil,*)'|'//string//'|'
      return
      end
```

B.2 N-fold way code for the 2-dimensional Ising model

```
!
!     ...1.........2.........3.........4.........5.........6.........6.........7.........8
      program main
      implicit none
      integer(8),parameter :: n1x=50
      integer(8),parameter :: n2x=50
      integer(8),parameter :: nclasses=10
      real(8)   ,parameter :: jint=1.d0  ! spin-spin interaction
      real(8)   ,parameter :: hext=0.d0 ! external field
```

```
      real(8)   ,parameter :: kbt=2.3d0
      integer(8),parameter :: nstep=10**7 ! number of mc steps
      real(8)   ,parameter :: tslice=1.d+5
      integer(8)           :: nmem(nclasses,n2x)
      integer(8)           :: nmem1
      integer(8)           :: state(n1x,n2x)
      integer(8)           :: class(n1x,n2x)
      integer(8)           :: i,i1,i2,istep,icount
      integer(8)           :: i1p,i1m,i2p,i2m,nn,imem,isvar
      integer(8)           :: iclass,thisclass
      integer(8)           :: nslice
      integer(8)           :: isteplast
      real(8)              :: x(nclasses)
      real(8)              :: p1(nclasses)
      real(8)              :: b
      real(8)              :: deltae(nclasses)
      real(8)              :: svar
      real(8)              :: acceptanceratio
      real(8)              :: etot,etotav
      real(8)              :: mag,magav
      real(8)              :: ran
      real(8)              :: time
      real(8)              :: deltat
      real(8)              :: profile(nclasses)
      real(8)              :: weight
!     ************************************************************************************
      weight=1.d0/real(n1x*n2x)
!
!     ====================================================================================
!     ==  set up process table                                                          ==
!     ==  each process class refers to a spin flip in a given environment               ==
!     ==  each process class is fully defined by the central state and the              ==
!     ==    average orientation of the nearest neigbors                                 ==
!     ====================================================================================
!     ==  class= 1:   central state 0; all neighbors 0                                  ==
!     ==  class= 2:   central state 0; 1 neighbor with state 1                          ==
!     ==  class= 3:   central state 0; 2 neighbors with state 1                         ==
!     ==  class= 4:   central state 0; 3 neighbors with state 1                         ==
!     ==  class= 5:   central state 0; 4 neighbors with state 1                         ==
!     ==  class= 6:   central state 1; all neighbors 0                                  ==
!     ==  class= 7:   central state 1; 1 neighbor with state 1                          ==
!     ==  class= 8:   central state 1; 2 neighbors with state 1                         ==
!     ==  class= 9:   central state 1; 3 neighbors with state 1                         ==
!     ==  class=10:   central state 1; 4 neighbors with state 1                         ==
!     ====================================================================================
      do i=1,nclasses
         isvar=int(real(i-1)/5.d0)    ! state of central atom
         nn=i-1-5*isvar               ! sum of spin up states on nearest neighbors
         deltae(i)=-2.d0*real(2*isvar-1)*(-hext-jint*real(2*nn-4))
         p1(i)=min(1,exp(-deltae(i)/kbt)) ! probability for a spin flip
      enddo
      p1(:)=p1(:)/sum(p1) ! relative jump rates for the different process classes
!
!     ====================================================================================
```

```
!     ==  prepare initial state                                                          ==
!     =====================================================================================
      do i1=1,n1x
        do i2=1,n2x
          call random_number(ran)
          state(i1,i2)=nint(ran)
        enddo
      enddo
!
!     =====================================================================================
!     ==  calculate initial properties                                                   ==
!     =====================================================================================
      call totalenergy(n1x,n2x,hext,jint,state,etot,mag)
      print*,’magnetization’,mag
!
!     =====================================================================================
!     ==  set up process table                                                           ==
!     ==  class assigns each site a process class                                        ==
!     ==  nmem counts the number of sites in each class in a vertical line               ==
!     =====================================================================================
      nmem(:,:)=0
      do i1=1,n1x
        do i2=1,n2x
          i1p=1+modulo(i1,n1x)
          i1m=1+modulo(i1-2,n1x)
          i2p=1+modulo(i2,n2x)
          i2m=1+modulo(i2-2,n2x)
          nn=state(i1p,i2)+state(i1m,i2)+state(i1,i2p)+state(i1,i2m)
          iclass=1+nn+5*state(i1,i2)
          nmem(iclass,i2)=nmem(iclass,i2)+1
          class(i1,i2)=iclass
        enddo
      enddo
!
!     =====================================================================================
!     ==  monte carlo loop                                                               ==
!     =====================================================================================
      open(10,file=’nfold.dat’)
      open(11,file=’nfold.out’)
      time=0.d0
      magav=0.d0
      etotav=0.d0
      nslice=0
      isteplast=0
      do istep=1,nstep
        if(modulo(istep,nstep/100_8).eq.0)print*,’percent finished ’,100*istep/nstep
!
!       ===================================================================================
!       == select a class                                                              ==
!       ===================================================================================
        svar=0.d0
        do i=1,nclasses
          svar=svar+p1(i)*real(sum(nmem(i,:)))
          x(i)=svar
```

```
        enddo
        x=x/svar
!       == the first class corresponds to the interval [0,x(1)],
!       == the second class corresponds to the interval [x(1),x(2)],
!       == the last class corresponds to the interval [x(n-1),x(n)], where x(n)=1.
        call random_number(ran)
        do i=1,nclasses
          if(x(i).gt.ran) then
            thisclass=i  ! process class "thisclass" is selected
            exit
          end if
        enddo
!
!       ==================================================================================
!       == select a random site from this class                                       ==
!       ==================================================================================
        nmem1=sum(nmem(thisclass,:))
        call random_number(ran)
        isvar=nint(0.5d0+ran*real(nmem1-1))  ! process isvar in this class is selected
        isvar=min(isvar,nmem1)   ! atom number in this class
        isvar=max(isvar,1)       ! atom number in this class
!
        icount=0
        do i2=1,n2x
          if(icount+nmem(thisclass,i2).lt.isvar) then
            icount=icount+nmem(thisclass,i2)
          else
            do i1=1,n1x
              if(class(i1,i2).eq.thisclass) then
                icount=icount+1
                if(icount.eq.isvar) then
                  goto 1000
                end if
              end if
            enddo
          end if
        enddo
1000    continue
!
!       ==================================================================================
!       == increment the time                                                         ==
!       ==================================================================================
        call random_number(ran)
        deltat=-log(ran)/p1(i)
        time=time+deltat
!
!       ==================================================================================
!       == update average values                                                      ==
!       ==================================================================================
        magav=magav+mag*deltat
        etotav=etotav+etot*deltat
!
!       ==================================================================================
!       == flip spin                                                                  ==
```

```
!       ==================================================================================
        state(i1,i2)=1-state(i1,i2)
        mag=mag+2*(2*state(i1,i2)-1)*weight
        etot=etot+deltae(thisclass)
!
!       ==================================================================================
!       == update process list                                                          ==
!       ==================================================================================
        i1p=1+modulo(i1,n1x)
        i1m=1+modulo(i1-2,n1x)
        i2p=1+modulo(i2,n2x)
        i2m=1+modulo(i2-2,n2x)
        nmem(class(i1,i2),i2)=nmem(class(i1,i2),i2)-1
        nmem(class(i1m,i2),i2)=nmem(class(i1m,i2),i2)-1
        nmem(class(i1p,i2),i2)=nmem(class(i1p,i2),i2)-1
        nmem(class(i1,i2m),i2m)=nmem(class(i1,i2m),i2m)-1
        nmem(class(i1,i2p),i2p)=nmem(class(i1,i2p),i2p)-1
        if(state(i1,i2).eq.1) then
          class(i1,i2)=class(i1,i2)+5
          class(i1p,i2)=class(i1p,i2)+1
          class(i1m,i2)=class(i1m,i2)+1
          class(i1,i2p)=class(i1,i2p)+1
          class(i1,i2m)=class(i1,i2m)+1
        else
          class(i1,i2)=class(i1,i2)-5
          class(i1p,i2)=class(i1p,i2)-1
          class(i1m,i2)=class(i1m,i2)-1
          class(i1,i2p)=class(i1,i2p)-1
          class(i1,i2m)=class(i1,i2m)-1
        end if
        nmem(class(i1,i2),i2)=nmem(class(i1,i2),i2)+1
        nmem(class(i1m,i2),i2)=nmem(class(i1m,i2),i2)+1
        nmem(class(i1p,i2),i2)=nmem(class(i1p,i2),i2)+1
        nmem(class(i1,i2m),i2m)=nmem(class(i1,i2m),i2m)+1
        nmem(class(i1,i2p),i2p)=nmem(class(i1,i2p),i2p)+1
!
!       ==================================================================================
!       == write result                                                                 ==
!       ==================================================================================
        if(time.gt.tslice) then
           svar=1.d0/tslice
           etotav=etotav*svar
           magav=magav*svar
           acceptanceratio=time/real(istep-isteplast)
           write(10,*)nslice*tslice,etot*weight,etotav*weight,mag,magav,acceptanceratio
           write(11,*)nslice*tslice,etot*weight,mag
           call plotstate(11,n1x,n2x,state)
           isteplast=istep
           nslice=nslice+1
           time=time-tslice
           magav=0.d0
           etotav=0.d0
        end if
      enddo
```

```
      close(10)
!
!     ==================================================================================
!     ==  analyze result                                                              ==
!     ==================================================================================
      close(11)
      print*,'magnetization',2.d0*sum(state)/real(n1x*n2x)-1.d0
      stop
      end
!
!     ...1.........2.........3.........4.........5.........6.........6.........7.........8
      subroutine totalenergy(n1x,n2x,hext,jint,state,etot,mag)
      implicit none
      integer(8),intent(in) :: n1x
      integer(8),intent(in) :: n2x
      real(8)   ,intent(in) :: hext
      real(8)   ,intent(in) :: jint
      integer(8),intent(in) :: state(n1x,n2x)
      real(8)   ,intent(out):: etot
      real(8)   ,intent(out):: mag
      integer(8)            :: i1,i2
      integer(8)            :: i1p,i1m,i2p,i2m
      integer(8)            :: nn
      real(8)               :: hint
!     **********************************************************************************
      etot=0.d0
      mag=0.d0
      do i1=1,n1x
        do i2=1,n2x
          i1p=1+modulo(i1,n1x)
          i1m=1+modulo(i1-2,n1x)
          i2p=1+modulo(i2,n2x)
          i2m=1+modulo(i2-2,n2x)
          nn=state(i1p,i2)+state(i1m,i2)+state(i1,i2p)+state(i1,i2m)
          hint=jint*real(2*nn-4)    ! sum_k jint*sigma_k
          etot=etot-(hext+0.5d0*hint)*real(2*state(i1,i2)-1)
          mag=mag+real(2*state(i1,i2)-1)
        enddo
      enddo
      mag=mag/real(n1x*n2x)
      return
      end
!
!     ...1.........2.........3.........4.........5.........6.........6.........7.........8
      subroutine plotstate(nfil,n1x,n2x,state)
!     **********************************************************************************
      implicit none
      integer   ,intent(in) :: nfil
      integer(8),intent(in) :: n1x
      integer(8),intent(in) :: n2x
      integer(8),intent(in) :: state(n1x,n2x)
      integer(8)            :: i1,i2
      character(n2x)        :: string
!     **********************************************************************************
```

```
      do i2=1,n2x
        string(i2:i2)='-'
      enddo
      write(nfil,*)'|'//string//'|'
      do i1=1,n1x
        string=''
        do i2=1,n2x
          if(state(i1,i2).eq.1)string(i2:i2)='o'
        enddo
        write(nfil,*)'|'//string//'|'
      enddo
      do i2=1,n2x
        string(i2:i2)='-'
      enddo
      write(nfil,*)'|'//string//'|'
      return
      end
```

B.3 Monte Carlo code for 2-dimensional diffusion on a square lattice

```
!
!     ...1.........2.........3.........4.........5.........6.........6.........7.........8
      program main
      implicit none
      integer(8),parameter :: nclasses=64
      integer(8),parameter :: n1x=50
      integer(8),parameter :: n2x=50
      real(8)   ,parameter :: hint=-1.d0  ! spin-spin interaction
      real(8)   ,parameter :: kbt=1.d0
      integer(8),parameter :: nstep=10**6 ! number of mc steps
      integer(8)           :: nmem(nclasses,n2x)
      integer(8)           :: nmem1
      integer(8)           :: state(n1x,n2x)  !occupation
      integer(8)           :: nnarr(n1x,n2x)  !#(nearest neighbors)
      integer(8)           :: class(4,n1x,n2x)
      integer(8)           :: i,istep,icount
      integer(8)           :: nn,nn1,nn2,isvar,idir
      integer(8)           :: i1mm,i1m,i1,i1p,i1pp
      integer(8)           :: i2mm,i2m,i2,i2p,i2pp
      integer(8)           :: j1mm,j1m,j1,j1p,j1pp
      integer(8)           :: j2mm,j2m,j2,j2p,j2pp
      integer(8)           :: iclass,thisclass
      integer(8)           :: thisdir
      real(8)              :: x(nclasses)
      real(8)              :: w(nclasses)
      real(8)              :: p1(nclasses)
      real(8)              :: b
      real(8)              :: deltae,e1,e2
      real(8)              :: svar
      real(8)              :: ran
```

```
!     *************************************************************************************
!     =====================================================================================
!     ==  prepare initial state                                                          ==
!     =====================================================================================
      do i1=1,n1x
        do i2=1,n2x
          call random_number(ran)
          state(i1,i2)=nint(ran)
        enddo
      enddo
!
!     =====================================================================================
!     ==  set up neighorlist                                                             ==
!     =====================================================================================
      call neighborlist(n1x,n2x,state,nnarr)
!
!     =====================================================================================
!     ==  set up process table                                                           ==
!     == a process is characterized by the number of neighbors at the initial and the    ==
!     == final state                                                                     ==
!     =====================================================================================
!     ==  class= 1:   nn1=0, nn2=1                                                       ==
!     ==  class= 2:   nn1=1, nn2=1                                                       ==
!     ==  class= 3:   nn1=2, nn2=1                                                       ==
!     ==  class= 4:   nn1=3, nn2=1                                                       ==
!     ==  class= 5:   nn1=0, nn2=2                                                       ==
!     ==  class= 6:   nn1=1, nn2=2                                                       ==
!     ==    ...                                                                          ==
!     ==  class=15:   nn1=2, nn2=4                                                       ==
!     ==  class=16:   nn1=3, nn2=4                                                       ==
!     =====================================================================================
      i=0
      do nn2=1,4
        do nn1=0,3
          i=i+1
          e1=hint*real(nn1)
          e2=hint*real(nn2-1)
          deltae=e2-e1
          p1(i)=exp(-deltae/kbt)       ! probability for a spin flip
        enddo
      enddo
      svar=1.d0/sum(p1)
      p1(:)=p1(:)*svar
!
!     == report probabilities ============================================================
      print*,'====== probability per class ======='
      do i1=1,4
        write(*,fmt='(4f20.10)')p1(1+4*(i1-1):4*i1)
      enddo
!
!     =====================================================================================
!     ==  determine process classes                                                      ==
!     ==  class(1,i1,i2) process type for jump from (i1,i2) to the right (i2->i2+1)      ==
!     ==  class(2,i1,i2) process type for jump from (i1,i2) to the left  (i2->i2-1)      ==
```

```
!     ==  class(3,i1,i2) process type for jump from (i1,i2) up           (i1->i1+1)     ==
!     ==  class(4,i1,i2) process type for jump from (i1,i2) down         (i1->i1-1)     ==
!     ==  count the number of processes in each class                                   ==
!     ====================================================================================
      call processlist(n1x,n2x,state,class,nmem)
!
!     ====================================================================================
!     ==  monte carlo loop                                                              ==
!     ====================================================================================
      do istep=1,nstep
        if(modulo(istep,nstep/100_8).eq.0)print*,'percent finished ',100*istep/nstep
!
!       ==================================================================================
!       == select a class                                                              ==
!       ==================================================================================
        do i=1,nclasses
          w(i)=real(sum(nmem(i,:)))
        enddo
        w(:)=w(:)/sum(w(:))
        x(:)=p1(:)*w(:)
        x(:)=x(:)/sum(x(:))
        call random_number(ran)
        svar=0.d0
        do i=1,nclasses
          svar=svar+x(i)
          if(svar.gt.ran) then
            thisclass=i
            exit
          end if
        enddo
!
!       ==================================================================================
!       == select a random site from this class                                         ==
!       ==================================================================================
        nmem1=sum(nmem(thisclass,:))
        call random_number(ran)
        isvar=1+int(ran*nmem1)
        isvar=min(isvar,nmem1)   ! atom number in this class
!
        icount=0
        do i2=1,n2x
          if(icount+nmem(thisclass,i2).lt.isvar) then
            icount=icount+nmem(thisclass,i2)
          else
            do i1=1,n1x
              do idir=1,4
                if(class(idir,i1,i2).eq.thisclass) then
                  icount=icount+1
                  if(icount.eq.isvar) then
                    thisdir=idir
                    goto 1000
                  end if
                end if
              enddo
```

```
            enddo
          end if
        enddo
1000    continue
!
!       ==========================================================================
!       == move atom
!       ==========================================================================
!       == neighborhood of initial state
        i1pp=1+modulo(i1+1,n1x)
        i1p =1+modulo(i1,n1x)
        i1m =1+modulo(i1-2,n1x)
        i1mm=1+modulo(i1-3,n1x)
        i2pp=1+modulo(i2+1,n2x)
        i2p =1+modulo(i2,n2x)
        i2m =1+modulo(i2-2,n2x)
        i2mm=1+modulo(i2-3,n2x)
!
!       == final state
        j1=i1
        j2=i2
        if(thisdir.eq.1) then
          j2=i2p
        else if(thisdir.eq.2) then
          j2=i2m
        else if(thisdir.eq.3) then
          j1=i1p
        else if(thisdir.eq.4) then
          j1=i1m
        end if
!
!       == neighborhood of final state=================================================
        j1pp=1+modulo(j1+1,n1x)
        j1p =1+modulo(j1,n1x)
        j1m =1+modulo(j1-2,n1x)
        j1mm=1+modulo(j1-3,n1x)
        j2pp=1+modulo(j2+1,n2x)
        j2p =1+modulo(j2,n2x)
        j2m =1+modulo(j2-2,n2x)
        j2mm=1+modulo(j2-3,n2x)
!
!       ==  consistency check ===================================================
        if(state(i1,i2).eq.0) then
          print*,'class ',class(thisdir,i1,i2)
          stop 'error initial state unoccupied'
        end if
        if(state(j1,j2).eq.1) then
          print*,'class ',class(thisdir,i1,i2)
          print*,'x1 ',i1,i2
          print*,'x2 ',j1,j2
         stop 'error final state occupied'
        end if

!       == perform jump ==========================================================
```

```
        state(i1,i2)=0
        state(j1,j2)=1
!
!       == update neighborlist =========================================================
        nnarr(i1m,i2)=nnarr(i1m,i2)-1
        nnarr(i1p,i2)=nnarr(i1p,i2)-1
        nnarr(i1,i2p)=nnarr(i1,i2p)-1
        nnarr(i1,i2m)=nnarr(i1,i2m)-1
        nnarr(j1m,j2)=nnarr(j1m,j2)+1
        nnarr(j1p,j2)=nnarr(j1p,j2)+1
        nnarr(j1,j2p)=nnarr(j1,j2p)+1
        nnarr(j1,j2m)=nnarr(j1,j2m)+1
!
!       ================================================================================
!       == update process list                                                        ==
!       ================================================================================
        do idir=1,4
          call updateprocesslist(idir,i1,i2,n1x,n2x,state,nnarr,class,nmem)
          call updateprocesslist(idir,j1,j2,n1x,n2x,state,nnarr,class,nmem)
        enddo
!
!=========================================================================
!       == two steps straight right,left,up,down
        call updateprocesslist(1_8,i1,i2mm,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(2_8,i1,i2pp,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(3_8,i1mm,i2,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(4_8,i1pp,i2,n1x,n2x,state,nnarr,class,nmem)

        call updateprocesslist(2_8,i1,i2m,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(1_8,i1,i2p,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(4_8,i1m,i2,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(3_8,i1p,i2,n1x,n2x,state,nnarr,class,nmem)

!       ==  left lower diagonal
        call updateprocesslist(1_8,i1m,i2m,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(3_8,i1m,i2m,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(2_8,i1m,i2,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(4_8,i1,i2m,n1x,n2x,state,nnarr,class,nmem)

!       == right lower diagonal
        call updateprocesslist(2_8,i1m,i2p,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(3_8,i1m,i2p,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(1_8,i1m,i2,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(4_8,i1,i2p,n1x,n2x,state,nnarr,class,nmem)

!       == left upper diagonal
        call updateprocesslist(1_8,i1p,i2m,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(4_8,i1p,i2m,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(2_8,i1p,i2,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(3_8,i1,i2m,n1x,n2x,state,nnarr,class,nmem)
!
!       == right upper diagonal
        call updateprocesslist(2_8,i1p,i2p,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(4_8,i1p,i2p,n1x,n2x,state,nnarr,class,nmem)
```

```
        call updateprocesslist(1_8,i1p,i2,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(3_8,i1,i2p,n1x,n2x,state,nnarr,class,nmem)
!
!=========================================================================
!       == two steps straight right,left,up,down
        call updateprocesslist(1_8,j1,j2mm,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(2_8,j1,j2pp,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(3_8,j1mm,j2,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(4_8,j1pp,j2,n1x,n2x,state,nnarr,class,nmem)

        call updateprocesslist(2_8,j1,j2m,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(1_8,j1,j2p,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(4_8,j1m,j2,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(3_8,j1p,j2,n1x,n2x,state,nnarr,class,nmem)

!       ==  left lower diagonal
        call updateprocesslist(1_8,j1m,j2m,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(3_8,j1m,j2m,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(2_8,j1m,j2,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(4_8,j1,j2m,n1x,n2x,state,nnarr,class,nmem)

!       == right lower diagonal
        call updateprocesslist(2_8,j1m,j2p,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(3_8,j1m,j2p,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(1_8,j1m,j2,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(4_8,j1,j2p,n1x,n2x,state,nnarr,class,nmem)

!       == left upper diagonal
        call updateprocesslist(1_8,j1p,j2m,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(4_8,j1p,j2m,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(2_8,j1p,j2,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(3_8,j1,j2m,n1x,n2x,state,nnarr,class,nmem)
!
!       == right upper diagonal
        call updateprocesslist(2_8,j1p,j2p,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(4_8,j1p,j2p,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(1_8,j1p,j2,n1x,n2x,state,nnarr,class,nmem)
        call updateprocesslist(3_8,j1,j2p,n1x,n2x,state,nnarr,class,nmem)

      enddo
!
!     ==========================================================================
!     ==  analyze result                                                      ==
!     ==========================================================================
      open(11,file='diffusion.out')
      call plotstate(11,n1x,n2x,state)
      close(11)
      stop
      end
!
!     ...1........2........3........4........5........6........6........7........8
      subroutine neighborlist(n1x,n2x,state,nnarr)
      implicit none
      integer(8),intent(in) :: n1x
```

```
      integer(8),intent(in) :: n2x
      integer(8),intent(in) :: state(n1x,n2x)
      integer(8),intent(out):: nnarr(n1x,n2x)
      integer(8)            :: i1,i2
      integer(8)            :: i1p,i1m,i2p,i2m
!     ************************************************************************************
      do i1=1,n1x
        do i2=1,n2x
          i1p=1+modulo(i1,n1x)
          i1m=1+modulo(i1-2,n1x)
          i2p=1+modulo(i2,n2x)
          i2m=1+modulo(i2-2,n2x)
          nnarr(i1,i2)=state(i1p,i2)+state(i1m,i2)+state(i1,i2p)+state(i1,i2m)
        enddo
      enddo
      return
      end
!
!     ...1.........2.........3.........4.........5.........6.........6.........7.........8
      subroutine updateprocesslist(idir,i1,i2,n1x,n2x,state,nnarr,class,nmem)
!     ====================================================================================
!     ==  update process classes                                                        ==
!     **  assumes that occupations "state" and neighborlist "nnarr" are updated         **
!     ==  class(1,i1,i2) process type for jump from (i1,i2) to the right (i2->i2+1)     ==
!     ==  class(2,i1,i2) process type for jump from (i1,i2) to the left  (i2->i2-1)     ==
!     ==  class(3,i1,i2) process type for jump from (i1,i2) up          (i1->i1+1)     ==
!     ==  class(4,i1,i2) process type for jump from (i1,i2) down        (i1->i1-1)     ==
!     ==  count the number of processes in each class                                   ==
!     ====================================================================================
      implicit none
      integer(8),intent(in) :: idir
      integer(8),intent(in) :: i1
      integer(8),intent(in) :: i2
      integer(8),intent(in) :: n1x
      integer(8),intent(in) :: n2x
      integer(8),intent(in) :: state(n1x,n2x)
      integer(8),intent(in):: nnarr(n1x,n2x)
      integer(8),intent(inout):: class(4,n1x,n2x)
      integer(8),intent(inout):: nmem(64,n2x)
      integer(8)            :: j1,j2
      integer(8)            :: nn1,nn2
!     ************************************************************************************
!
!     == disconnect all processes ========================================================
      if(class(idir,i1,i2).ne.0) then
        nmem(class(idir,i1,i2),i2)=nmem(class(idir,i1,i2),i2)-1
        class(idir,i1,i2)=0
      end if
!
!     == no hops from this site if not occupied
      if(state(i1,i2).eq.0) return
!
!     == select final position
      j1=i1
```

```
      j2=i2
      if(idir.eq.1) then
        j2=1+modulo(i2,n2x)
      else if(idir.eq.2) then
        j2=1+modulo(i2-2,n2x)
      else if(idir.eq.3) then
        j1=1+modulo(i1,n1x)
      else
        j1=1+modulo(i1-2,n1x)
      end if

!     == include hop
      if(state(j1,j2).eq.0) then
        nn1=nnarr(i1,i2)
        nn2=nnarr(j1,j2)
        class(idir,i1,i2)=1+nn1+4*(nn2-1)
        nmem(class(idir,i1,i2),i2)=nmem(class(idir,i1,i2),i2)+1
      end if
      return
      end
!
!     ...1.........2.........3.........4.........5.........6.........6.........7.........8
      subroutine processlist(n1x,n2x,state,class,nmem)
!     ==========================================================================
!     ==  determine process classes                                           ==
!     ==  class(1,i1,i2) process type for jump from (i1,i2) to the right (i2->i2+1)     ==
!     ==  class(2,i1,i2) process type for jump from (i1,i2) to the left  (i2->i2-1)     ==
!     ==  class(3,i1,i2) process type for jump from (i1,i2) up           (i1->i1+1)     ==
!     ==  class(4,i1,i2) process type for jump from (i1,i2) down         (i1->i1-1)     ==
!     ==  count the number of processes in each class                         ==
!     ==========================================================================
      implicit none
      integer(8),intent(in) :: n1x
      integer(8),intent(in) :: n2x
      integer(8),intent(in) :: state(n1x,n2x)
      integer(8),intent(out):: class(4,n1x,n2x)
      integer(8),intent(out):: nmem(64,n2x)
      integer(8)            :: i1,i2,idir
      integer(8)            :: i1p,i1m,i2p,i2m
      integer(8)            :: nn1,nn2
      integer(8)            :: nnarr(n1x,n2x)
!     **************************************************************************
      call neighborlist(n1x,n2x,state,nnarr)
      nmem(:,:)=0
      class(:,:,:)=0
      do i1=1,n1x
        do i2=1,n2x
          if(state(i1,i2).eq.0) then
            class(:,i1,i2)=0
            cycle
          end if
          i1p=1+modulo(i1,n1x)
          i1m=1+modulo(i1-2,n1x)
          i2p=1+modulo(i2,n2x)
```

```
          i2m=1+modulo(i2-2,n2x)
          nn1=nnarr(i1,i2)
!         == hop to the right side
          idir=1
          if(state(i1,i2p).eq.1) then
            class(idir,i1,i2)=0  ! no jumps from this site possible
          else
            nn2=nnarr(i1,i2p)
            class(idir,i1,i2)=1+nn1+4*(nn2-1)
            nmem(class(idir,i1,i2),i2)=nmem(class(idir,i1,i2),i2)+1
          end if
!         == hop to the left
          idir=2
          if(state(i1,i2m).eq.1) then
            class(idir,i1,i2)=0
          else
            nn2=nnarr(i1,i2m)
            class(idir,i1,i2)=1+nn1+4*(nn2-1)
            nmem(class(idir,i1,i2),i2)=nmem(class(idir,i1,i2),i2)+1
          end if
!         == hop up
          idir=3
          if(state(i1p,i2).eq.1) then
            class(idir,i1,i2)=0
          else
            nn2=nnarr(i1p,i2)
            class(idir,i1,i2)=1+nn1+4*(nn2-1)
            nmem(class(idir,i1,i2),i2)=nmem(class(idir,i1,i2),i2)+1
          end if
!         == hop down
          idir=4
          if(state(i1m,i2).eq.1) then
            class(idir,i1,i2)=0
          else
            nn2=nnarr(i1m,i2)
            class(idir,i1,i2)=1+nn1+4*(nn2-1)
            nmem(class(idir,i1,i2),i2)=nmem(class(idir,i1,i2),i2)+1
          end if
        enddo
      enddo
      return
      end
!
!     ...1.........2.........3.........4.........5.........6.........6.........7.........8
      subroutine plotstate(nfil,n1x,n2x,state)
!     ************************************************************************************
      implicit none
      integer  ,intent(in) :: nfil
      integer(8),intent(in) :: n1x
      integer(8),intent(in) :: n2x
      integer(8),intent(in) :: state(n1x,n2x)
      integer(8)            :: i1,i2
      character(n2x)        :: string
!     ************************************************************************************
```

```
do i2=1,n2x
  string(i2:i2)='-'
enddo
write(nfil,*)'|'//string//'|'
do i1=1,n1x
  string=''
  do i2=1,n2x
    if(state(i1,i2).eq.1)string(i2:i2)='o'
  enddo
  write(nfil,*)'|'//string//'|'
enddo
do i2=1,n2x
  string(i2:i2)='-'
enddo
write(nfil,*)'|'//string//'|'
return
end
```

Appendix C

A small Dictionary

acceptor	Akzeptor
attempt	Versuch
compartment	Abteil
constraint	Zwangsbedingung
denominator	Nenner
die; pl. dice	Würfel
donor	Donator
dopant atom	Dotieratom
ensemble	Gesamtheit
exert	ausüben
extrinsic	extrinsisch
extensive	extensiv
factorial	Fakultät ($n!$)
forecast	Vorhersage
frequency	Häufigkeit; Frequenz
intensive	intensiv
intrinsic	intrinsisch, eigenleitend
law of mass action	Massenwirkungsgesetz
heat	Wärme
intrinsic	intrinsisch
moment of inertia	Trägheitstensor
multiplier	Multiplikator
numerator	Zähler
number representation	Besetzungszahldarstellung
partition function	Zustandssumme
Planck's law	Planck's Strahlungsgesetz
shallow	oberflächlich, seicht
toy	Spielzeug
transition state	Übergangszustand
trace	Spur
Wiensches verschiebungsgesetz	Wien's displacement law
work	Arbeit

Appendix D

Basic quantum mechanics

D.1 Position operator and position eigenstates

Let us assume that only know bra's and kets but no wave functions. In the following we will define wave functions from the abstract bracket notation. Let us denote the position eigenstates as $|x\rangle$. The position eigenstates is the link between kets and the corresponding wave functions. We require that the unity operator is expressed by the position eigenstates as

$$\hat{1} = \int_x |x\rangle\langle x| \tag{D.1}$$

Given a ket $|\psi\rangle$, the corresponding wave function $\psi(x)$ is defined by the scalar product

$$\psi(x) \overset{\text{def}}{=} \langle x|\psi\rangle$$

Given a wave function $\psi(x)$,we obtain the corresponding ket by

$$|\psi\rangle = \underbrace{\int dx\; |x\rangle\langle x|}_{=\hat{1}}\psi\rangle = \int dx\; |x\rangle\psi(x)$$

What is the wave function $\psi_{x_0}(x)$ corresponding to a position eigenstate $|x_0\rangle$? We obtain the solution by multiplication with the unit operator

$$|x_0\rangle = \int dx\; |x\rangle \underbrace{\langle x|x_0\rangle}_{=\psi_{x_0}(x)}$$

This equation can only be valid if

$$\psi_{x_0}(x) = \langle x|x_0\rangle = \delta(x - x_0)$$

Now we can define the position operator $\hat{x}$ by its eigenvalue equation

$$\hat{x}|x\rangle = |x\rangle x$$

Its explicit form in terms of position eigenstates is obtained as

$$\int dx\, \underbrace{|x\rangle x}_{=\hat{x}|x\rangle}\langle x| = \int dx \hat{x}|x\rangle\langle x| = \hat{x}\underbrace{\int dx|x\rangle\langle x|}_{=\hat{1}} = \hat{x}$$

$$\Rightarrow \hat{x} = \int dx\; |x\rangle x\langle x|$$

Momentum operator and momentum eigenstates

Next we define momentum eigenstates

$$\langle x|p\rangle = \mathrm{e}^{ipx/\hbar}$$

as eigenstates of the translation operator in real space.

Again, we start from the eigenfunctions to define the position operator

$$\frac{\hbar}{i}\partial_x\langle x|p\rangle = \frac{\hbar}{i}\partial_x \mathrm{e}^{ipx/\hbar} = p\langle x|p\rangle$$

$$\overset{\int dx\,|x\rangle\cdot}{\Rightarrow} \underbrace{\int dx\;|x\rangle\frac{\hbar}{i}\partial_x\langle x|}_{\hat{p}}\,p\rangle = \underbrace{\int dx\;|x\rangle\langle x|}_{=\hat{1}}\,|p\rangle p = |p\rangle p$$

Thus we find that the momentum operator defined as

$$\hat{p} = \int dx\;|x\rangle\frac{\hbar}{i}\partial_x\langle x|$$

produces the correct eigenstates and eigenvalues.

Evaluating the matrix elements $\langle p|p'\rangle$ is non-trivial, because the wave functions are not square integrable. We obtain the result through a limit. We introduce periodic boundary conditions to discretize the momentum spectrum. With periodic boundary conditions we allow only states that are periodic with a period L.

$$\underbrace{\langle x+L|p\rangle = \langle x|p\rangle}_{\text{periodicity}} \qquad \Rightarrow \qquad p_n = \frac{2\pi\hbar}{L}n$$

Now we perform the integral over one periodic unit

$$\int_0^L dx\;\langle p_i|x\rangle\langle x|p_j\rangle = \int_0^L dx\;\mathrm{e}^{i(p_j-p_i)x/\hbar} = \left\{\begin{matrix} L & \text{for} & i=j \\ 0 & \text{for} & i\neq j\end{matrix}\right\}$$

$$= L\delta_{i,j} = \frac{2\pi\hbar}{\Delta p}\delta_{i,j}$$

<where $\delta p = p_{i+1} - p_i = \frac{2\pi\hbar}{L}$.

Now we can perform the limit $L \to \infty$ and obtain[1]

$$\langle p|p'\rangle = \int_{-\infty}^{\infty} dx\;\langle p|x\rangle\langle x|p'\rangle = 2\pi\hbar\delta(p-p')$$

Finally, we need to represent the unit operator in terms of momentum eigenstates. Also here it is advantageous to start from a discrete spectrum. For any complete, but not necessarily orthonormal, basis $\{|u_i\rangle\}$, the unit operator has the form

$$\hat{1} = \sum_{i,j}|u_i\rangle S_{i,j}\langle u_j|$$

where **S** is the inverse of the overlap matrix. The overlap matrix has elements $\langle u_i|u_j\rangle$.

$$\delta_{i,j} = \sum_k S_{i,k}\langle p_k|p_j\rangle = \sum_k S_{i,k}\frac{2\pi\hbar}{\delta p}\delta_{k,j} = S_{i,j}\frac{2\pi\hbar}{\Delta p}$$

$$\Rightarrow S_{i,j} = \frac{\Delta p}{2\pi\hbar}\delta_{i,j}$$

---

[1] we need to show that the integral over the delta function is equal to one:

$$1 = \sum_i \delta_{i,j} = \sum_i \Delta p\frac{1}{\Delta p}\delta_{i,j} \to \int dp'\frac{\delta_{p',j}}{\Delta p} = \int dp\;\delta(p'-p_j)$$

Thus we can use our momentum eigenstates and obtain

$$\hat{1} = \sum_{i,j} |p_i\rangle \frac{\Delta p}{2\pi\hbar}\delta_{i,j}\langle p_j| = \sum_i \frac{\Delta p}{2\pi\hbar}|p_i\rangle\langle p_i| = \int \frac{dp}{2\pi\hbar}\;|p\rangle\langle p| \tag{D.2}$$

Thus the sum over states normalized states is transformed into an integral over states with a probability density equal to one.

Note that an operator may have a spectrum that contains discrete eigenvalues and continuous intervals of eigenvalues.

Hamilton operator

The Hamilton operator is obtained from the classical Hamilton function by replacing the position argument with the position operator and the momentum argument with the momentum operator.

$$\hat{H} \stackrel{\text{def}}{=} H(\hat{p}, \hat{x})$$

The function of an operator is defined by its power-series expansion. If the Hamilton function has the power series expansion of the Hamilton function is

$$H(p, x) = \sum_{i,j} a_{i,j} p^i x^j$$

the Hamilton operator[2] has the form

$$\hat{H} = \sum_{i,j} a_{i,j}\hat{p}^i\hat{x}^j = \sum_{i,j} a_{i,j}\left(\int dx\;|x\rangle\frac{\hbar}{i}\partial_x\langle x|\right)^i\left(\int dx\;|x\rangle x\langle x|\right)^j \tag{D.3}$$

$$= \int dx\;|x\rangle \sum_{i,j} a_{i,j}\left(\frac{\hbar}{i}\partial_x\right)^i (x)^j\;\langle x| \tag{D.4}$$

$$= \int dx\;|x\rangle H(\frac{\hbar}{i}\partial_x, x)\langle x| \tag{D.5}$$

---

[2] The momenta and positions must be ordered such that the resulting operator is hermitian

Appendix E

Background material

E.1 Rotational energy levels

Editor:This is not read see Atkins Physical chemistry, p554 and Atkins Molecular quantum mechanics

For a general molecule we calculate the moment of inertia as

$$I_{i,j} = \sum_{k=1}^{N} m_k r_{k,i} r_{k,j}$$

The rotational energy is

$$E = \frac{1}{2} \vec{L} \mathbf{I}^{-1} \vec{L}$$

This can be simplified by transforming on the principal axes of the moment of inertia, which has eigenvalues I_1, I_2, I_3. Now the energy can be written as

$$E = \sum_{i=1}^{3} \frac{L_i^2}{2I_i}$$

From the angular momentum we obtain

$$
\begin{aligned}
L_z|\ell,m\rangle &= |\ell,m\rangle\hbar m \\
L^2|\ell,m\rangle &= |\ell,m\rangle\hbar^2\ell(\ell+1) \\
L_+|\ell,m\rangle &= |\ell,m+1\rangle\hbar\sqrt{(\ell-m)(\ell+m+1)} \\
L_-|\ell,m\rangle &= |\ell,m-1\rangle\hbar\sqrt{(\ell+m)(\ell-m+1)} \\
L_- &= L_x - iL_y \\
L_+ &= L_x + iL_y \\
L_z^2|\ell,m\rangle &= |\ell,m\rangle\hbar^2 m^2 \\
L_x^2+L_y^2|\ell,m\rangle &= \hbar^2|\ell,m\rangle\left[\ell(\ell+1)-m^2\right] \\
L_x^2 &= \frac{1}{4}(L_++L_-)^2 = \frac{1}{4}(L_+^2+L_+L_-+L_-L_++L_-^2) \\
&= \frac{1}{4}(L_+^2+L^2-L_z^2-\hbar L_z+L_-^2) \\
&= \frac{1}{4}\left(L^2-L_z^2-\hbar L_z+(L_+^2+L_-^2)\right) \\
L_y^2 &= \frac{1}{4}(L_+-L_-)^2 = \frac{1}{4}(L_+^2-L_+L_--L_-L_++L_-^2) \\
&= \frac{1}{4}(L_+^2-L^2+L_z^2+\hbar L_z+L_-^2) \\
&= -\frac{1}{4}\left(L^2-L_z^2-\hbar L_z-(L_+^2+L_-^2)\right)
\end{aligned}
$$

E.2 Equations of state from the equilibrium probabilities

Here we derive the equations of state from the form of the equilibrium probabilities.

Here we derive Eqs. **??**, **??** and Eq. **??** from the microscopic states.
Proof:

- First we show how the expectation values can be obtained from the free energy.

$$
\begin{aligned}
\frac{\partial F(T,f_j)}{\partial f_i} &= \frac{\partial}{\partial f_i}\left(-k_BT\ln[Z(T,f_i)]\right) = -k_BT\frac{1}{Z(T,f_i)}\frac{\partial}{\partial f_i}Z(T,f_i) \\
&= -k_BT\underbrace{\mathrm{e}^{+\frac{1}{k_BT}F}}_{\frac{1}{Z(T,f_i)}}\sum_{\vec{n}}\left(\frac{1}{k_BT}X_{i,\vec{n}}\right)\mathrm{e}^{-\frac{1}{k_BT}(E_{\vec{n}}-\sum_i f_iX_{i,\vec{n}})} \\
&= -\sum_{\vec{n}}X_{\vec{n},i}\underbrace{\mathrm{e}^{-\frac{1}{k_BT}(E_{\vec{n}}-\sum_i f_iX_{i,\vec{n}}-F(T,f_j))}}_{=P_{\vec{n}}(T,f_i)} \\
&= -\sum_{\vec{n}}P_{\vec{n}}X_{i,\vec{n}} = -X_i(T,f_j)
\end{aligned}
$$

cont'd...

- Now we calculate the temperature derivative of the free energy

$$
\begin{aligned}
\frac{\partial F(T,f_j)}{\partial T} &= \frac{\partial}{\partial T}\left(-k_B T \ln[Z(T,f_i)]\right) \\
&= \underbrace{-k_B \ln[Z(T,f_j)]}_{F/T} - k_B T \frac{1}{Z(T,f_i)} \frac{\partial}{\partial T} Z(T,f_i) \\
&= \frac{1}{T}F - k_B T \underbrace{\mathrm{e}^{+\frac{1}{k_B T}F}}_{\frac{1}{Z(T,f_i)}} \\
&\quad \cdot \sum_{\vec{n}} \left(\frac{1}{k_B T^2} \left(E_{\vec{n}} - \sum_i f_i X_{\vec{n},i} \right) \right) \mathrm{e}^{-\frac{1}{k_B T}\left(E_{\vec{n}} - \sum_i f_i X_{\vec{n},i}\right)} \\
&= \frac{1}{T}F - \frac{1}{T} \sum_{\vec{n}} \left(E_{\vec{n}} - \sum_i f_i X_{\vec{n},i} \right) \underbrace{\mathrm{e}^{-\frac{1}{k_B T}\left(E_{\vec{n}} - \sum_i f_i X_{\vec{n},i} - F(T,f_j)\right)}}_{=P_{\vec{n}}(T,f_i)} \\
&= \frac{1}{T}\left(F(T,f_i) - U(T,f_i) + \sum_i f_i X_i(T,f_i) \right)
\end{aligned}
$$

cont'd...

- The entropy as function of the intensive variables is

$$
\begin{aligned}
S(T,f_i) &= -k_B \sum_{\vec{n}} P_{\vec{n}}(T,f_i) \ln[P_{\vec{n}}(T,f_i)] \\
&= \frac{1}{T} \sum_{\vec{n}} P_{\vec{n}}(T,f_i) \left(E_{\vec{n}} - \sum_{i=1}^{n} f_i X_{i,\vec{n}} - F(T,f_i) \right) \\
&= \frac{1}{T} \Big(\sum_{\vec{n}} P_{\vec{n}}(T,f_i) E_{\vec{n}} - \sum_{i=1}^{n} f_i \sum_{\vec{n}} P_{\vec{n}}(T,f_i) X_{i,\vec{n}} \\
&\qquad - F(T,f_i) \underbrace{\sum_{\vec{n}} P_{\vec{n}}(T,f_i)}_{=1} \Big) \\
&= \frac{1}{T}\left(U(T,f_i) - \sum_{i=1}^{n} f_i X_i(T,f_i) - F(T,f_i) \right)
\end{aligned}
$$

The expression for the entropy is identical with the temperature derivative of the free energy. Using one of these expressions we can then evaluate the internal energy

E.3 Configurational entropy

E.3.1 Number of arrangements of N distinguishable particles on N positions

Here we determine the number $r(N)$ of ways N distinguishable particles can be arranged on N lattice sites.

- We can choose from N atoms and place them on the first position.
- For each such choice we can choose from $N-1$ atoms for the second position. Hence there are $N(N-1)$ ways to place the first two atoms.
- For the third position we can choose from $N-2$ atoms, so that we can arrange the first three atoms in $N(N-1)(N-2)$ ways on the first three positions.
- We continue this and obtain $N(N-1)(N-2)\dots(N-i+1)$ for the i-th position.
- Once we arrive at $i=N$, we obtain $N\cdot(N-1)\dots2\cdot1=N!$.

Thus we obtain the result

$$r(N)=N! \tag{E.1}$$

E.3.2 Number of arrangements of indistinguishable particles

Consider M_s lattice sites on which N atoms can be placed. Every position can be occupied by at most one atom. The atoms shall be indistinguishable, so that one configuration is determined only by the positions that are occupied: A permutation of two atoms does not produce a new configuration.

1. The first atom can be placed on any of the M_s lattice sites. Therefore, we obtain $q(1)=M_s$
2. The second atom can be placed on any of the M_s-1 lattice sites. Thus we obtain $M_s(M_s-1)$ configurations. However, each configuration has been counted twice: For every configuration with the first atom on site i and the second atom on site j, there is also one with the first atom on site j and the second on site i. Wen we account for double counting we obtain $q(2,M_s)=\frac{M_s(M_s-1)}{2}$
3. The third atom can be placed M_s-2 sites. Again we need to account for double counting. For any three occupied sites we obtained the following six occupations (123); (132); (213); (231); (312); (321), where the numbers refer to the first, second and third atom and the position in the triple refers to the three occupied lattice sites. There are six possibilities and therefore $q(3,M_s)=\frac{M_s(M_s-1)(M_s-2)}{6}$. Note that the divisor is simply $r(3)$ as defined in Eq. E.1.
4. For the N-th atom we obtain $M_s(M_s-1)\dots(M_s-N+1)=\frac{M_s!}{(M_s-N)!}$ possibilities for distinguishable atoms. The number of ways the M atoms have been arranged for a given set of position is $M!$, as obtained in eq. E.1.

Thus we obtain the configurational degeneracy as

$$q(N,M_s)=\frac{M_s!}{N!(M_s-N)!} \tag{E.2}$$

E.3.3 Configurational entropy

If all configuration can occur with the same a-priori probability, the entropy is given as $S_{conf}=k_B\ln[q(N,M_s)]$ by the configurational degeneracy given in Eq. E.2. Thus we obtain

$$S_{conf}(N,M_s)=k_B\ln[\frac{M_s!}{N!(M_s-N)!}] \tag{E.3}$$

For large numbers, $M_s >> 1; N >> 1; M_s - N >> 1$ we can use Stirling's formula, Eq. F.1. Furthermore we introduce the average occupation $\theta = N/M_s$. We obtain

$$
\begin{aligned}
S_{conf} &= k_B \ln[\frac{M_s!}{N!(M_s-N)!}] \\
&\approx k_B\Big(\underbrace{M_s\ln[M_s]-M_s}_{\approx \ln[M!]}\underbrace{-N\ln[N]+N}_{\approx -\ln[N!]}\underbrace{-(M_s-N)\ln[M_s-N]+(M_s-N)}_{\approx -\ln[(M_s-N)!]}\Big) \\
&= k_B\Big(M_s\ln[M_s]-N\ln[N]-(M_s-N)\ln[M_s-N]\Big) \\
&= M_s k_B\Big(\ln[M_s]-\theta\underbrace{\ln[M_s\theta]}_{=\ln[M_s]+\ln[\theta]}-(1-\theta)\underbrace{\ln[M_s(1-\theta)]}_{=\ln[M_s]+\ln[1-\theta]}\Big) \\
&= M_s k_B\Big(-\theta\ln[\theta]-(1-\theta)\ln[(1-\theta)]\Big)
\end{aligned}
$$

Thus we obtain the following expression for the configurational entropy in the limit of large numbers

$$
S_{conf}(\theta) = -M_s k_B\Big(\theta\ln[\theta]+(1-\theta)\ln[(1-\theta)]\Big) \tag{E.4}
$$

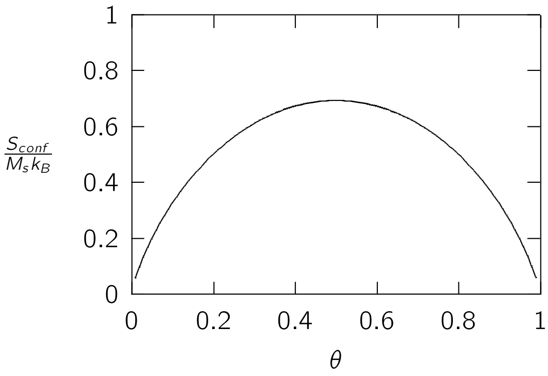


Fig. E.1: Configurational entropy as function of occupation θ

E.4 Free energy of formation and defect concentration

Consider a defect in a host lattice. The energy required to create a defect is the formation energy $E_F = E[N=1] - E[N=0]$, where $E[M_s=1]$ is the total energy of the system with one defect and $E[N=0]$ is the total energy of the defect, free host.

I the defects are sufficiently dilute, so that there is no interaction between defects, we can compose the Free energy for a given number of defects from the total energy $M_s\theta E_F$ and the entropies. We divide the entropy into the configurational entropy and a vibrational entropy Ns_{vib}. s_{vib} is the vibrational entropy per atom.

$$
\begin{aligned}
F(T,N) &= -k_BT\ln[Z] = -k_BT\ln[\frac{M_s!}{N!(M_s-N)!}e^{-\frac{N(E_F-Ts_{vib})}{k_BT}}] \\
&= \underbrace{-k_BT\ln[\frac{M_s!}{N!(M_s-N)!}]}_{=TS_{conf}}+N(E_F-Ts_{vib}) \\
&= M_s\Big(\theta E_F-\theta Ts_{vib}+k_BT\Big(\theta\ln[\theta]+(1-\theta)\ln[1-\theta]\Big)
\end{aligned}
$$

From the free energy we can derive the chemical potential, which can be equated with that of the particle bath to obtain the concentration of defects.

$$\begin{aligned}\mu &= \frac{dF}{dN} = \frac{dF}{d\theta}\frac{d\theta}{dN}\\ &= E_F + k_BT\left(\ln[\theta] + 1 - \ln[1-\theta] - 1\right) - Ts_{vib}\\ &= E_F + k_BT\ln[\frac{\theta}{1-\theta}] - Ts_{vib}\end{aligned}$$

We set this chemical potential equal to that of the particle reservoir, and obtain

$$\begin{aligned}\mu_{bath} = \mu &= E_F + k_BT\ln[\frac{\theta}{1-\theta}] - Ts_{vib}\\ \frac{\theta}{1-\theta} &= e^{-\frac{E_F-\mu_{bath}-Ts_{vib}}{k_BT}}\\ \theta &= \left[1 + \exp(\frac{E_F - \mu_{bath} - Ts_{vib}}{k_BT})\right]^{-1}\end{aligned} \tag{E.5}$$

The result is shown in Fig. E.2

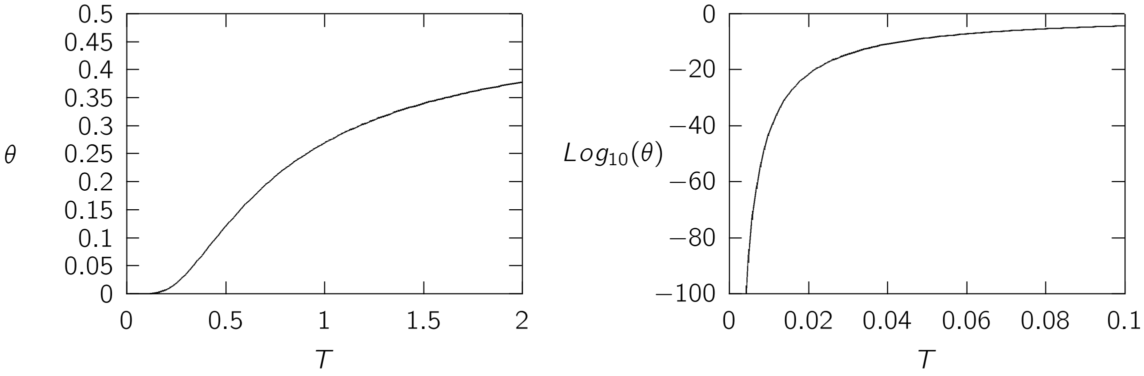


Fig. E.2: Top: Occupation as function of temperature. Bottom: Decadic logarithm of the above. $(E_F - \mu_{bath} - Ts_{vib})/k_B$ has been set to one.

E.4.1 Concentration if the heat bath is a gas

The chemical potential of a gas is

$$\mu = k_BT\ln\left[\frac{p\lambda_T^3}{k_BT}\right] \qquad \text{with} \qquad \lambda_T = \sqrt{\frac{2\pi\hbar}{mk_BT}}$$

We insert this into Eq.E.5 and obtain

$$\begin{aligned}\theta &= \left[1 + \exp(\frac{E_F - \mu_{bath} - Ts_{vib}}{k_BT})\right]^{-1}\\ &= \left[1 + \frac{k_BT}{p\lambda_T^3}\exp(\frac{E_F}{k_BT})\exp(-\frac{s_{vib}}{k_B})\right]^{-1}\end{aligned}$$

In the limit of small partial pressures, that is small coverage, we obtain

$$\theta(p << 1) = \frac{p\lambda_T^3}{k_BT}\exp(-\frac{E_F}{k_BT})\exp(\frac{s_{vib}}{k_B})$$

The concentration depends strongly on s_{vib}. The vibrational entropy is for each vibrational mode is

$$s_{vib} = k_B \ln[1 - \mathrm{e}^{-\hbar\omega/(k_BT)}]$$

If one atom is adsorbed, there are three additional vibrational modes so that the entropy above must be multiplied by three. In general we denote the number additional vibrational modes by d.

$$\theta = \left[1 + \frac{k_BT}{p\lambda_T^3} \cdot \frac{1}{(1-\mathrm{e}^{-\hbar\omega/(k_BT)})^d} \exp(\frac{E_F}{k_BT})\right]^{-1}$$

At low temperatures, that is $k_BT << \hbar\omega$ the exponential containing the vibrational frequencies becomes small compared to unity and drops out. At high temperatures we obtain

$$\theta(k_BT >> \hbar\omega) = \left[1 + \frac{k_BT}{p\lambda_T^3} \cdot \left(\frac{k_BT}{\hbar\omega}\right)^d \exp(\frac{E_F}{k_BT})\right]^{-1}$$

E.5 Concentration of oxygen vacancies in an oxide

E.5.1 Vacancies

First we need to determine the entropy for vacancies in a lattice with M sites. We need to count the number of possibilities to distribute N vacancies onto M lattice sites.

For one vacancy there are clearly M possibilities, hence $S(N=1) = k_B \ln[M]$. For 2 vacancies we can place the first onto one of M lattice sites, and the second onto $M-1$ lattice sites. However, we created each vacancy distribution twice. (The first on place A and the second on place B or the first on site B and the second on place A.) Therefore the entropy is $S(N=2) = k_B \ln[M(M-1)/2]$. Continuing this result we obtain for a general number of vacancies:

$$S(N) = k_B \ln[\frac{M!}{(M-N)!N!}]$$

We use Stirling's Formula $\ln[n!] = n\ln[n] - n + O(1/N)$ and obtain

$$\begin{aligned}
S(N) &= k_B \left(M\ln[M] - M - (M-N)\ln[M-N] + M - N - N\ln[N] + N\right) \\
&= k_B \left(M\ln[M] - (M-N)\ln[M-N] - N\ln[N]\right) \\
&= k_B \left(M\ln[\frac{M}{M-N}] + N\ln[\frac{M-N}{N}]\right)
\end{aligned}$$

Now we introduce the concentration $c = N/M$

$$\begin{aligned}
S(N) &= Mk_B \left(\ln[\frac{1}{1-c}] + c\ln[\frac{1-c}{c}]\right) \\
&= Mk_B \left(-\ln[1-c] + c\ln[1-c] - c\ln[c]\right) \\
&= -Mk_B \left((1-c)\ln[1-c] + c\ln[c]\right)
\end{aligned}$$

Note that the entropy is similar to the Entropy for electrons.

The energy of a system is equal to N times the formation energy of a vacancy, namely $E_F = E(N+1) - E(N)$.

$$E(N) = NE_F = McE_F$$

Combining energy and entropy we obtain the free energy

$$F(N) = E(N) - TS(N) = M\left[cE_F + k_BT\left((1-c)\ln[1-c] + c\ln[c]\right)\right]$$

The chemical potential of oxygen atoms, which is the negative of the chemical potential for a vacancy. It can be calculated from the derivative of the free energy.

$$\begin{aligned}
-\mu_O &= \frac{\partial F(T,N)}{\partial N} \\
&= M\frac{dc}{dN}\frac{\partial}{\partial c}\left[cE_F + k_BT\left((1-c)\ln[1-c] + c\ln[c]\right)\right] \\
&= E_F + k_BT\left(-\ln[1-c] - \frac{1-c}{1-c} + \ln[c] + \frac{c}{c}\right) \\
&= E_F + k_BT\ln[\frac{c}{1-c}]
\end{aligned}$$

Thus we obtain the chemical potential required to produce a given vacancy concentration.

$$\begin{aligned}
\mu_O &= -E_F - k_BT\ln[\frac{c}{1-c}] \\
c &= \frac{1}{1+\mathrm{e}^{\frac{\mu_O+E_F}{k_BT}}}
\end{aligned}$$

E.5.2 Ideal Gas

$$\begin{aligned}
F(T,V,N) &= -Nk_BT + \ln[\frac{V}{N\lambda_T^3}] \\
\lambda_T &= \sqrt{\frac{2\pi\hbar^2}{mk_BT}}
\end{aligned}$$

where m is the mass of the molecule, not the mass of the atom.

The Gibbs Free energy

$$G(T,p,N) = F(T,V,N) + pV \quad \text{, where} \qquad p = \frac{\partial F(T,V,N)}{\partial V}.$$

The chemical potential is the derivative of the Gibbs free energy with respect to particle number

$$\begin{aligned}
\mu|_{p,T} = \frac{\partial G}{\partial N} &= \left[\frac{\partial F}{\partial V} + p\right]\frac{\partial V}{\partial N} + \frac{\partial F}{\partial N} \\
&= -k_BT\left[1 + \ln\left[\frac{V}{N\lambda_T^3}\right]\right] - Nk_BT\left[-\frac{1}{N}\right] \\
&= -k_BT\left[1 + \ln\left[\frac{V}{N\lambda_T^3}\right] - 1\right] \\
&= -k_BT\ln\left[\frac{V}{N\lambda_T^3}\right] \\
&= +k_BT\ln\left[\frac{p\lambda_T^3}{k_BT}\right]
\end{aligned}$$

In the last step, we used the ideal gas law $pV = Nk_BT$ to express the particle density by the partial pressure. (The ideal Gas law follows from $p = \partial F/\partial V$).

E.5.3 Rotator

$$\begin{aligned}
E_{\ell,m} &= \frac{\hbar^2\ell(\ell+1)}{2m^* r^2}\\
Z_1 &= \sum_{\ell,m} \mathrm{e}^{-\beta E_{\ell,m}}\\
&= \sum_{\ell}(2\ell+1)\mathrm{e}^{-\frac{\hbar^2\beta}{2m^* r^2}\ell(\ell+1)}\\
&\approx \int_{-\frac{1}{2}}^{\infty} dx(2x+1)\mathrm{e}^{-\sigma x(x+1)}\\
&= \int_{-\frac{1}{2}}^{\infty} dx\frac{-1}{\sigma}\frac{d}{dx}\mathrm{e}^{-\sigma x(x+1)}\\
&= \frac{1}{\sigma}\mathrm{e}^{\sigma/4}\\
\sigma &= \frac{\hbar^2\beta}{2m^* r^2}
\end{aligned}$$

The integrand has a zero at $x = -\frac{1}{2}$. Starting the integral at this point is introduces a smaller error than starting from zero. The approximation is accurate for high temperatures.

$$\begin{aligned}
F(T,N) &= -k_B T \ln[Z_N] = -Nk_B T \ln[Z_1] = -Nk_B T \ln\left[\frac{1}{\sigma}\mathrm{e}^{\sigma/4}\right]\\
&= Nk_B T \ln\left[\sigma \mathrm{e}^{-\sigma/4}\right]
\end{aligned}$$

The contribution to the chemical potential from the rotation is therefore

$$\begin{aligned}
\mu_{rot} = \frac{\partial F}{\partial N} &= k_B T\\
ln\left[\sigma \mathrm{e}^{-\sigma/4}\right]
\end{aligned}$$

Note, that the mass is the effective mass of the molecule $\frac{1}{m^*} = \frac{1}{m_1} + \frac{1}{m_2}$.

E.5.4 Oxidation

$$\begin{aligned}
O_2 &\leftrightarrow 2O\\
\Rightarrow E[O_2] &= 2E[O] + 2\mu_O\\
\Rightarrow \mu_O &= \frac{1}{2}E[O_2] - E[O]\\
SrTiO_3 &\leftrightarrow SrTiO_{3-x} + xO\\
\Rightarrow E[SrTiO_3] &= E[SrTiO_{3-x}] + xE[O] + x\mu_O\\
\Rightarrow \mu_O &= \frac{E[SrTiO_3] - E[SrTiO_{3-x}]}{x} - E[O] = -E_F - E_O
\end{aligned}$$

The energy is to be taken the free energy.

The energy to remove an oxygen atom from the gas is

$$\mu_O = \frac{1}{2}E[O_2] - E[O] + \frac{k_B T}{2}\ln\left[\frac{p\lambda_T^3}{k_B T}\right]$$

where λ_T need to be evaluated with the molecular mass (and not the atomic mass).

The energy to remove an oxygen from the oxide is

$$\mu_O = -E_F - E_O - k_B T \ln\left[\frac{c}{1-c}\right]$$

In thermal equilibrium the two chemical potentials must be identical

$$\begin{aligned}
-E_F - E_O - k_B T \ln\left[\frac{c}{1-c}\right] &= \frac{1}{2}E[O_2] - E[O] + \frac{k_B T}{2}\ln\left[\frac{p\lambda_T^3}{k_B T}\right] \\
\mathrm{e}^{-\frac{2E_F + E[O_2]}{k_B T}} &= \left(\frac{c}{1-c}\right)^2 \frac{p\lambda_T^3}{k_B T} \\
p &= \left(\frac{1-c}{c}\right)^2 \left(\frac{k_B T}{\lambda_T^3}\right) \mathrm{e}^{-\frac{2E_F + E[O_2]}{k_B T}} \\
c &= \left[1 + \sqrt{\frac{p\lambda_T^3}{k_B T}}\,\mathrm{e}^{\frac{E_F + E[O_2]/2}{k_B T}}\right]^{-1}
\end{aligned}$$

E.6 Origin of the exchange interaction

Editorial Remark: This should go into an appendix The interaction between spins in the Ising model is not of magnetic nature as one might naively expect. The magnetic interaction is long ranged and much smaller than the exchange interactions that play a role in the Ising model.

Let us investigate the exchange interaction. Consider two sites with one electron on each site. The basis set is built up of a single spatial orbital on each site, ϕ and ψ. Each orbital is a two component spinor, where the upper component corresponds to the spin-up contribution and the lower component is the spin-down contribution so that we can build four one-particle orbitals from two spatial wave functions.

$$\begin{aligned}
|\uparrow, 0\rangle &= \begin{pmatrix} \phi(r) \\ 0 \end{pmatrix} = \phi(r)\alpha \\
|\downarrow, 0\rangle &= \begin{pmatrix} 0 \\ \phi(r)\rangle \end{pmatrix} = \phi(r)\beta \\
|0, \uparrow\rangle &= \begin{pmatrix} \psi(r) \\ 0\rangle \end{pmatrix} = \psi(r)\alpha \\
|0, \downarrow\rangle &= \begin{pmatrix} 0 \\ \psi(r)\rangle \end{pmatrix} = \psi(r)\beta
\end{aligned}$$

where $\alpha = (1, 0)$ and $\beta = (0, 1)$.

Out of the one-particle wave functions we build two-particle Slater determinants of the type $|\uparrow, \downarrow\rangle = \frac{1}{\sqrt{2}}\Big(|\uparrow, 0\rangle \times |0, \downarrow\rangle - |0, \downarrow\rangle \times |\uparrow, 0\rangle\Big)$. Out of the 16 product states that can be build from the four one-particle states, 6 are excluded because they differ only by a sign change, 4 are excluded because they involve two identical one-particle states, which is prohibited due to Pauli principle. We are left with 6 states:

$$
\begin{aligned}
|\uparrow\downarrow,0\rangle &= \phi(r_1)\phi(r_2)\frac{\alpha_1\beta_2-\beta_1\alpha_2}{\sqrt{2}} \\
|\uparrow,\uparrow\rangle, &= \frac{1}{\sqrt{2}}\Big(\phi(r_1)\psi(r_2)-\psi(r_1)\phi(r_2)\Big)\alpha_1\alpha_2 \\
|\uparrow,\downarrow\rangle, &= \frac{1}{\sqrt{2}}\Big(\phi(r_1)\psi(r_2)\alpha_1\beta_2-\psi(r_1)\phi(r_2)\beta_1\alpha_2\Big) \\
|\downarrow,\uparrow\rangle, &= \frac{1}{\sqrt{2}}\Big(\phi(r_1)\psi(r_2)\beta_1\alpha_2-\psi(r_1)\phi(r_2)\alpha_1\beta_2\Big) \\
|\downarrow,\downarrow\rangle, &= \frac{1}{\sqrt{2}}\Big(\phi(r_1)\psi(r_2)-\psi(r_1)\phi(r_2)\Big)\beta_1\beta_2 \\
|0,\uparrow\downarrow\rangle &= \psi(r_1)\psi(r_2)\frac{\alpha_1\beta_2-\beta_1\alpha_2}{\sqrt{2}}
\end{aligned}
$$

Two states, namely $|\uparrow\downarrow,0\rangle$ and $|0,\uparrow\downarrow\rangle$, correspond to charge transfer states, where one electron has been transferred from one site to another. We exclude them with the argument that the Coulomb repulsion makes these states very unfavorable.

When we evaluate the expectation value of the Hamiltonian. Note here that the operator yielding the charge density is proportional to the unity operator in spin space.

$$
\begin{aligned}
H = &\sum_i \frac{-\hbar^2}{2m}\nabla_i^2 + V(r_i)\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \\
&+ \frac{e^2}{4\pi\epsilon}\frac{1}{|r_1-r_2|}\begin{pmatrix}|r_1\rangle\langle r_1| & 0\\ 0 & |r_1\rangle\langle r_1|\end{pmatrix}\begin{pmatrix}|r_2\rangle\langle r_2| & 0\\ 0 & |r_2\rangle\langle r_2|\end{pmatrix}
\end{aligned}
$$

we need four variables

$$
\begin{aligned}
\epsilon &= \int d^3r\phi_i^*(r)\Big[\frac{-\hbar^2}{2m}\nabla^2+V(r)\Big]\phi_i(r) \\
U &= \int dr\int dr'\frac{\phi_1^*(r)\phi(r)\phi_1^*(r)\phi(r)}{|r-r'|} \\
K &= \int dr\int dr'\frac{\phi_1^*(r)\phi(r)\phi_2^*(r)\psi(r)}{|r-r'|} \\
J &= \int dr\int dr'\frac{\phi_1^*(r)\psi(r)\phi_2^*(r)\phi(r)}{|r-r'|}
\end{aligned}
$$

In order to diagonalize the Hamiltonian, we form angular momentum eigenstates

$$
\begin{aligned}
|\ell=0,m=0\rangle &= \frac{1}{\sqrt{2}}\Big(|\uparrow,\downarrow\rangle-|\downarrow\uparrow\rangle\Big) \\
|\ell=1,m=1\rangle &= |\uparrow,\uparrow\rangle \\
|\ell=1,m=0\rangle &= \frac{1}{\sqrt{2}}\Big(|\uparrow,\downarrow\rangle+|\downarrow\uparrow\rangle\Big) \\
|\ell=1,m=-1\rangle &= |\downarrow,\downarrow\rangle
\end{aligned}
$$

The energies of the eigenstates can then be evaluated as the diagonal elements of the Hamiltonian

$$
\begin{pmatrix}\langle\uparrow\uparrow|\\ \langle\uparrow\downarrow|\\ \langle\downarrow\uparrow|\\ \langle\downarrow\downarrow|\end{pmatrix} H \begin{pmatrix}|\uparrow\uparrow\rangle\\ |\uparrow\downarrow\rangle\\ |\downarrow\uparrow\rangle\\ |\downarrow\downarrow\rangle\end{pmatrix} = \begin{pmatrix}K-J & 0 & 0 & 0\\ 0 & K & -J & 0\\ 0 & -J & K & 0\\ 0 & 0 & 0 & K-J\end{pmatrix}
$$

We obtain the eigenstates as

$$\begin{aligned}
H|\uparrow,\uparrow\rangle &= K-J|\uparrow,\uparrow\rangle\\
H\frac{1}{\sqrt{2}}\Big(|\uparrow,\downarrow\rangle+|\downarrow,\uparrow\rangle\Big) &= (K-J)\frac{1}{\sqrt{2}}\Big(|\uparrow,\downarrow\rangle+|\downarrow,\uparrow\rangle\Big)\\
H\frac{1}{\sqrt{2}}\Big(|\uparrow,\downarrow\rangle-|\downarrow,\uparrow\rangle\Big) &= (K+J)\frac{1}{\sqrt{2}}\Big(|\uparrow,\downarrow\rangle-|\downarrow,\uparrow\rangle\Big)\\
H|\downarrow,\downarrow\rangle &= K-J|\downarrow,\downarrow\rangle
\end{aligned}$$

The Coulomb integral appears on all diagonal elements, because all states have equal charge density, and only spins are interchanged.

The two states

$$\begin{aligned}
\frac{1}{\sqrt{2}}\Big(|\uparrow,\downarrow\rangle-|\downarrow,\uparrow\rangle\Big) &= \frac{1}{2}\Big(\phi(r_1)\psi(r_2)+\psi(r_1)\phi(r_2)\Big)\Big(\alpha_1\beta_2-\beta_1\alpha_2\Big)\\
\frac{1}{\sqrt{2}}\Big(|\uparrow,\downarrow\rangle+|\downarrow,\uparrow\rangle\Big) &= \frac{1}{2}\Big(\phi(r_1)\psi(r_2)-\psi(r_1)\phi(r_2)\Big)\Big(\alpha_1\beta_2+\beta_1\alpha_2\Big)
\end{aligned}$$

are the singlet state with $S_{z,1}+S_{z,2}=0$ and the triplet state $S_{z,1}+S_{z,2}=\hbar$.

Thus I can write the Hamiltonian as

$$bH = K-J\sigma_1\sigma_2$$

The coupling among the spins is the exchange coupling J.

Appendix F

Mathematical formulas

F.1 Stirling's formula

Stirling's formula

$$\ln[n!] \approx n\ln[n] - n \tag{F.1}$$

and its more accurate version

$$\ln[n!] \approx \left(n + \frac{1}{2}\right)\ln[n] - n + \ln[2\pi] \tag{F.2}$$

is very useful in statistical mechanics because the factorial $n! \overset{\text{def}}{=} 1 \cdot 2 \cdots n$ occurs in many combinatorial problems and the logarithm is required to evaluate entropies.

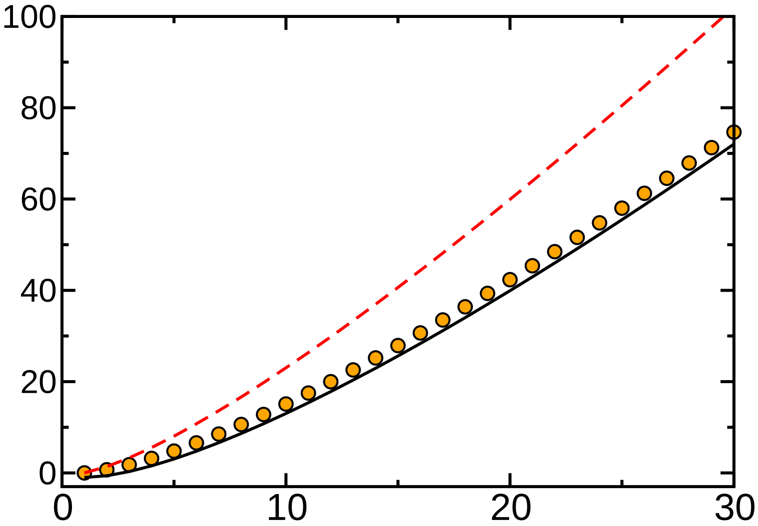


Fig. F.1: Comparison of stirling's formula with exact result. The circles represent $\ln[n!]$. The full line is stirling's formula $n\ln[n] - n$. The dashed line is $n\ln[n]$.

As seen by comparison with Eq. F.2, the error of the approximation Eq. F.1 in Stirling's formula increases like $\ln[n]$ with n. Why could a formula be useful, that does not converge to the correct result at all? It is useful, if the quantity of interest contains $\frac{1}{n}\ln[n!]$ so that we can use

$$\frac{1}{n}\ln[n!] \rightarrow \frac{1}{n}\left[n\ln[n] - n\right] \qquad \text{for} \qquad n \rightarrow \infty$$

Most problems in thermodynamics “effectively” are of this form.

F.1.1 Proof of Stirling’s formula

Here another proof using the saddle point approximation:

The proof is based on a representation of the factorial by an integral: Consider the integral, which we solve by repeated partial integration

$$\begin{aligned}
\int_0^\infty dt\ t^n \mathrm{e}^{-t} &= \int_0^\infty dt\ \left[nt^{n-1}\mathrm{e}^{-t} - \partial_t\left(t^n\mathrm{e}^{-t}\right)\right] \\
&\overset{n\geq 0}{=} n\left(\int_0^\infty dt\ t^{n-1}\mathrm{e}^{-t}\right) \\
&\overset{n-1\geq 0}{=} n(n-1)\left(\int_0^\infty dt\ t^{n-2}\mathrm{e}^{-t}\right) \\
&\overset{n-i\geq 0}{=} n(n-1)\ldots(n-i)\left(\int_0^\infty dt\ t^{n-i-1}\mathrm{e}^{-t}\right) \\
&\overset{1\geq 0}{=} n(n-1)\ldots 1\underbrace{\left(\int_0^\infty dt\ t^{0}\mathrm{e}^{-t}\right)}_{=1} \\
&= n(n-1)\ldots 1 = n!
\end{aligned}$$

Now we bring the integral into a more convenient form

$$n! = \int_0^\infty dt\ t^n\mathrm{e}^{-t} = \int_0^\infty dt\ \mathrm{e}^{n\ln(t)-t}$$

The maximum of the function in the exponent has its maximum at $t = n$. We introduce now a variable transform $s = nt$ so that the position of the maximum is independent of n.

$$\begin{aligned}
n! &\overset{t=ns}{=} n\int_0^\infty ds\ \mathrm{e}^{n\ln[ns]-ns} \\
&\overset{\ln[ab]=\ln[a]+\ln[b]}{=} n\int_0^\infty ds\ \mathrm{e}^{n(\ln[s]-s+\ln[n])}
\end{aligned}$$

Furthermore we separate the value of the maximum out of the integral

$$n! = n\mathrm{e}^{n\ln[n]-n}\int_0^\infty ds\ \mathrm{e}^{n(\ln[s]-s+1)} \tag{F.3}$$

Now we use the so-called **saddle-point approximation**: For an integral of the form $\int_a^b dx\ \mathrm{e}^{nf(x)}$ with a sufficiently large n, only a narrow region near the maximum of $f(x)$ contributes appreciably to the integral. In this region, we can replace $f(x)$ by its Taylor expansion up to second order about the maximum x_0. Within this approximation the integrand is converted into a Gaussian. Since the Gaussian contributes appreciably only in a narrow region around the maximum we may also change the bounds of the integral to infinity. Thus we obtain

$$\int_a^b dx\ \mathrm{e}^{nf(x)} \approx \int_{-\infty}^\infty dx\ \mathrm{e}^{n\left(f(x_0)+\frac{1}{2}\left.\frac{d^2f}{dx^2}\right|_{x_0}(x-x_0)^2\right)}$$

This integral can be solved analytically using $\int_{-\infty}^{\infty} dx\, \mathrm{e}^{-x^2} = \sqrt{\pi}$, i.e. Eq. F.6.

$$
\begin{aligned}
\int_a^b dx\, \mathrm{e}^{nf(x)} &\approx \int_{-\infty}^{\infty} dx\, \mathrm{e}^{nf(x_0)+\frac{1}{2}n\frac{d^2f}{dx^2}\big|_{x_0}(x-x_0)^2} \\
&= \mathrm{e}^{nf(x_0)} \int_{-\infty}^{\infty} dx\, \mathrm{e}^{\frac{1}{2}n\frac{d^2f}{dx^2}\big|_{x_0}x^2} \\
&= \mathrm{e}^{nf(x_0)} \sqrt{\frac{1}{-\frac{n}{2}\frac{d^2f}{dx^2}\Big|_{x_0}}}\, \underbrace{\int_{-\infty}^{\infty} dx\mathrm{e}^{-x^2}}_{\sqrt{\pi}} \\
&= \sqrt{\frac{2\pi}{-n\frac{d^2f}{dx^2}\Big|_{x_0}}}\, \mathrm{e}^{nf(x_0)}
\end{aligned}
\tag{F.4}
$$

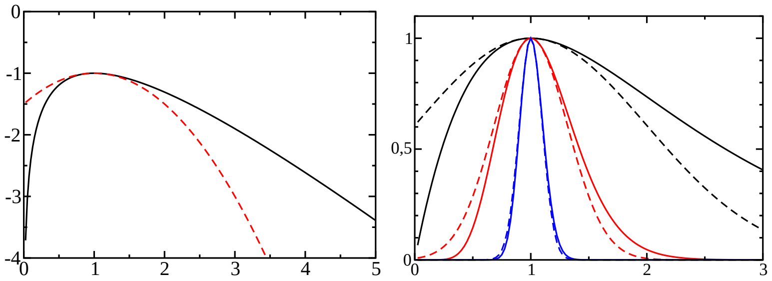


Fig. F.2: Left: The function $\ln[x]-x$ and its Taylor expansion to second order about $x=1$. Right: the function $exp(n(x\ln[x]-x+1))$ and its Gaussian approximation (dashed) for n=1,10,100. Note that the accuracy of the Gaussian approximation becomes better with increasing n.

Using $f(x)=\ln(s)-s+1$ we obtain the position of the maximum at $x_0=1$, and $f(1)=0$, $\partial_x f(x)|_1 = 0$, and $\partial_x^2 f(x)\big|_1 = -1$.

$$\ln(s)-s+1 \overset{Taylor}{=} -\frac{1}{2}(s-1)^2 + O(s-1)^3$$

Thus within the saddle point approximation we obtain Eq. F.3

$$n! = n\mathrm{e}^{n\ln[n]-n}\int_0^{\infty} ds\, \mathrm{e}^{n(\ln[s]-s+1)} \overset{Eq.\,F.4}{\approx} \mathrm{e}^{n\ln[n]-n}\sqrt{2\pi n} \tag{F.5}$$

Now we can take the logarithm of the factorial and obtain:

$$
\begin{aligned}
\ln[n!] &= n\ln[n]-n+\frac{1}{2}\ln[n]+\frac{1}{2}\ln[2\pi] \\
&= \left(n+\frac{1}{2}\right)\ln[n]-n+\frac{1}{2}\ln[2\pi]
\end{aligned}
$$

which is the desired result Eq. F.2, from which Eq. F.1 can be readily obtained by ignoring all terms that grow slower with n than n.

F.1.2 Another derivation of Stirling's formula

In the following another derivation of Stirling's formula is shown. We do not follow the original derivation, but use a few, increasingly accurate, approximations. The reason for this is that it demonstrates a few, rather versatile, concepts for numerical integration.

The simple formula

$$\ln[n!] = \ln[1] + \ln[2] + \ldots + \ln[n] = \sum_{i=1}^{n} \ln[i]$$

Now we convert the sum into an integral.

$$\ln[n!] \approx \int_1^n dx\ \ln[x] = \Big[x\ln[x] - x\Big]_1^n = n\ln[n] - n + 1 \approx n\ln[n] - n$$

and obtain the simple result Eq. F.1. This derivation is very simple to memorize.

Correction 1

The critical step Eq. F.6 has been the conversion of a sum into an integral. It is not clear yet if that is legitimate.

Therefore, we show below how the integral can be made more accurate by approximating the integral by piecewise line segments and later on by piece-wise parabolic segments, etc. These calculations will provide us with increasingly better representations of $\ln[n!]$.

We start with the integral, which we approximate by piecewise straight line segments. For each line segment the integral is the average of the function values at the boundaries of the segment multiplied with the size of the interval.

$$\begin{aligned}
\int_1^n dx\,\ln[x] &\approx \sum_{i=1}^{n-1} \frac{1}{2}\left(\ln(i) + \ln(i+1)\right) \\
&= \frac{1}{2}\ln[1] + \ln[2] + \ln[3] + \ldots + \ln[n-1] + \frac{1}{2}\ln[n] \\
&= \underbrace{\left(\sum_{i=1}^{n}\ln[i]\right)}_{=\ln[n!]} - \frac{1}{2}\underbrace{\ln[1]}_{=0} - \frac{1}{2}\ln[n] \\
\Rightarrow \ln[n!] = \sum_{i=1}^{n}\ln[i] &\approx \left(\int_1^n dx\,\ln[x]\right) + \frac{1}{2}\ln[n] \\
&= [x\ln[x] - x]_1^n + \frac{1}{2}\ln[n] \\
&= \left(n\ln[n] - n - 1\underbrace{\ln[1]}_{=0} + 1\right) + \frac{1}{2}\ln[n] \\
&= n\ln[n] - n + \frac{1}{2}\ln[n] + 1
\end{aligned}$$

Thus we obtain already a better approximation for $\ln[n!]$, namely

$$\ln[n!] \approx n\ln[n] - n + \frac{1}{2}\ln[n] + 1$$

This result is already closer to Eq. F.2.

Correction 2

Let us estimate the error by calculating a correction for the integral.

$$\int_1^n dx\ \ln[x] \approx \underbrace{\sum_{i=1}^{n-1}\frac{\ln(i)+\ln(i+1)}{2}}_{\ln(n!)-\frac{1}{2}\ln(n)}+\Delta$$

Note that Δ enters with a negative sign in our formula for $\ln[n!]$

$$\ln(n!)=\int_1^n dx\ \ln[x]+\frac{1}{2}\ln(n)-\Delta$$

Instead of approximating the integrand by line-segments, we approximate it now by piece-wise parabolas. The parabola shall be determined by the values at the boundaries of the interval and the curvature in the middle of the interval.

Let us describe the parabola for a interval extending from x_1 to x_1+1 by

$$g(x)=a+b(x-x_1)+c(x-x_1)^2$$

Then the line segment $f(x)$ has the form

$$f(x)=a+(b+c)(x-x_1)$$

Thus the correction for the interval is

$$\begin{aligned}\int_{x_1}^{x_1+1} dx\ (g(x)-f(x)) &= \int_{x_1}^{x_1+1} dx\ \left(a+b(x-x_1)+c(x-x_1)^2-a-(b+c)(x-x_1)\right)\\ &= \int_{x_1}^{x_1+1} dx\ \left(c(x-x_1)^2-c(x-x_1)\right)\\ &= c\int_0^1 dx\ \left(x^2-x\right)=c\left[\frac{1}{3}x^3-\frac{1}{2}x^2\right]_0^1=-\frac{c}{6}\end{aligned}$$

The value of c is obtained by equating the second derivative of g with that of the logarithm.

$$\begin{aligned}\left.\frac{d^2g(x)}{dx^2}\right|_{x_1+\frac{1}{2}} &= \left.\frac{d^2\ln(x)}{dx^2}\right|_{x_1+\frac{1}{2}}\\ \Rightarrow 2c &= -\frac{1}{(x_1+\frac{1}{2})^2} \qquad \Rightarrow \qquad c=\frac{-1}{2(x_1+\frac{1}{2})^2}\end{aligned}$$

Thus we obtain the correction for the interval as

$$\int_{x_1}^{x_1+1} dx\ (g(x)-f(x))=\frac{1}{4(x_1+\frac{1}{2})^2}$$

The total error is then obtained by summing the correction for all intervals

$$\Delta=\sum_{i=1}^{n-1}\frac{1}{12(i+\frac{1}{2})^2}$$

We can approximate the sum again by an integral, by approximating the integrand by a set of line segments.

$$\frac{1}{12}\int_1^{n-1} dx \frac{1}{(x+\frac{1}{2})^2} \approx \left(\sum_{i=1}^{n-1}\frac{1}{12(i+\frac{1}{2})^2}\right) - \frac{1}{2}\left(\frac{1}{12(1+\frac{1}{2})^2} + \frac{1}{12(n-1+\frac{1}{2})^2}\right)$$

$$\begin{aligned}
\left(\sum_{i=1}^{n-1}\frac{1}{12(i+\frac{1}{2})^2}\right) &\approx \frac{1}{12}\int_1^{n-1} dx\, \frac{1}{(x+\frac{1}{2})^2} + \frac{1}{2}\left(\frac{1}{12(1+\frac{1}{2})^2} + \frac{1}{12(n-1+\frac{1}{2})^2}\right)\\
&= \frac{1}{12}\left[-\frac{1}{x+\frac{1}{2}}\right]_1^{n-1} + \frac{1}{6}\left(\frac{1}{9} + \frac{1}{(2n-1)^2}\right)\\
&= -\frac{1}{6(2n-1)} + \frac{1}{18} + \frac{1}{54} + \frac{1}{6(2n-1)^2}\\
&= \frac{2}{27} - \frac{1}{6(2n-1)} + \frac{1}{6(2n-1)^2}
\end{aligned}$$

Thus we obtain an error estimate Δ

$$\Delta \approx \frac{2}{27} - \frac{1}{6(2n-1)} + \frac{1}{6(2n-1)^2}$$

We can see that the error contains a constant. Similarly if we would try to correct the piecewise parabolic interpolation with higher polynomials and convert the sum into an integral, we would always obtain a constant term from the correction of the lower boundary of the integral. Thus the constant is no more reliable. The terms depending on n on the other hand disappear for large n.

Our best estimate for $\ln[n!]$ is so far

$$\begin{aligned}
\ln[n!] &\approx n\ln[n] - n + \frac{1}{2}\ln[n] + 1 - \Delta\\
&= (n+\frac{1}{2})\ln[n] - n + \frac{25}{27} + \frac{1}{2(2n-1)} - \frac{1}{2(2n-1)^2}
\end{aligned}$$

Editor: The proof shown seems to be identical with the Euler-McLaurin Formula. See Arfken und Weber p360.

F.2 The geometric series

$$\sum_{i=0}^{N-1} q^i = 1 + q + q^2 + \ldots + q^{N-1} = \frac{1-q^N}{1-q}$$

The equation is proven by multiplication with $1-q$ and comparing each power in q.

$$\begin{aligned}
(1-q)\sum_{i=0}^{N-1} q^i = 1 \quad &+q + q^2 \ldots + q^{N-1}\\
&-q - q^2 - \ldots - q^{N-1} - q^N = 1 - q^N
\end{aligned}$$

The infinite series converges for $|q| < 1$ and has the value

$$\sum_{i=0}^{N-1} q^i = \frac{1}{1-q}$$

F.3 Integral of a Gauss function

Here the identity

$$\int_{-\infty}^{\infty} dx\ \mathrm{e}^{-x^2} = \sqrt{\pi} \tag{F.6}$$

We start out forming the product of two such integrations

$$C^2 = \int_{-\infty}^{\infty} dx\ \mathrm{e}^{-x^2} \times \int_{-\infty}^{\infty} dy\ \mathrm{e}^{-y^2} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dx\ dy\ \mathrm{e}^{-(x^2+y^2)}$$

Now we transform to planar polar coordinates (r, ϕ) and use that the angular integral is 2π and that $dxdy = r\ drd\phi$.

$$C^2 = 2\pi \int_0^{\infty} dr\ r\mathrm{e}^{-r^2} = 2\pi \frac{1}{-2} \int_0^{\infty} dr\ \frac{d\mathrm{e}^{-r^2}}{dr} = \pi$$

which proves the above relation

F.4 The integral

Here the equation

$$\int_0^{\infty} dx \sqrt{x} \mathrm{e}^{-x} = \frac{\sqrt{\pi}}{2}$$

is derived.

We first perform a variable transform to $y = \sqrt{x}$.

$$\begin{aligned}
I &= \int dx \sqrt{x}\mathrm{e}^{-x} = 2\int dy y^2 \mathrm{e}^{-y^2} \\
&= \int dy y(2y\mathrm{e}^{-y^2}) \\
&= -\int dy y \frac{d}{dy}\mathrm{e}^{-y^2} \\
&= -\int dy \Big[\frac{d}{dy}(y\mathrm{e}^{-y^2}) - (\frac{d}{dy}y)\mathrm{e}^{-y^2})\Big] \\
&= \int dy \mathrm{e}^{-y^2} = \frac{\sqrt{\pi}}{2}
\end{aligned}$$

In the last step we used the integral of a Gauss function as derived in a previous appendix.

F.5 Legendre transform

F.6 Euler equation

The Euler equation says that

$$U(S, V, N) = TS - PV + \mu N \tag{F.7}$$

The Euler equation implies that the total Legendre transform of the internal energy vanishes.

Let us consider a homogeneous system divide it in pieces. In this case the extensive variables scale with the size of the system,

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$$

while the intensive variables remain constant.

Let us differentiate with respect toλ

$$\frac{\partial U}{\partial S}S+\frac{\partial U}{\partial V}V+\frac{\partial U}{\partial N}N=U(S,V,N)$$

By inserting the definitions of the intensive variables $T=\frac{\partial U}{\partial S}$, $p=-\frac{\partial U}{\partial V}$, $\mu=-\frac{\partial U}{\partial N}$. the Euler equation

$$TS-PV+\mu N=U(S,V,N)$$

is obtained.

F.7 Free energy of the ideal Boltzmann gas

Here we derive the Helmholtz free energy from the partition function $Z(T,V,N)$ derived in the section on the Boltzmann gas. It will then lead to the Sackur tetrode equation. However we need to employ here the Stirling's formula, which shows that the entropy of the (TVN ensemble is identical to that of the $TV\mu$ ensemble only in the limit of large N.

The free energy for the ideal Boltzmann gas at a given volume and number of particles is called the Helmholtz free energy[1] , denoted by a symbol A. In physics the common symbol for the Helmholtz free energy is F, whereas chemists have adopted the symbol A. To be more explicit we reserve the symbol F for a generic free energy, whereas for chemical systems such as gases etc., we use the symbols adopted by chemists.

$$\begin{aligned}
A^{BG}(T,V,N) &\overset{Eq.\ ??}{=} -k_BT\ln[Z^{BG}(T,V,N)]\\
&\overset{Eq.\ ??}{=} -k_BT\ln\left[\frac{1}{N!}\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{\frac{3N}{2}}V^N\right]\\
&\overset{Stirling}{\approx} -k_BT\left(-N\ln[N]+N+N\ln\left[\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{\frac{3}{2}}V\right]\right)\\
&= -Nk_BT\left(-\ln[N]+1+\ln\left[\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{\frac{3}{2}}V\right]\right)\\
&= -Nk_BT\left(1+\ln\left[\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{\frac{3}{2}}\frac{V}{N}\right]\right)
\end{aligned}\tag{F.8}$$

Note that we had to make an additional approximation by applying Stirling's formula[2]. Thus this result is only accurate in the sense that the free energy per particle is is correct for large numbers of particles.

Interestingly the volume enters only in the form of the average density N/V. The box dimensions do not show up any longer in the free energy. This indicates[3] that our results are independent of the shape of the box.

---

[1] Hermann Ludwig Ferdinand von Helmholtz. German Physicist 1821-1894. Proposed the conservation of energy.

[2] James Stirling. Scottish Scientist 1692-1770.

[3] It does not necessarily prove it!

F.7.1 Energy and Entropy of the ideal Boltzmann gas

First we determine the entropy

$$\begin{aligned}
S^{BG}(T,V,N) &= -\frac{\partial A^{BG}}{\partial T} \\
&= Nk_B\left(1+\ln\left[\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{\frac{3}{2}}\frac{V}{N}\right]\right)+Nk_BT\frac{3}{2T} \\
&= Nk_B\left(\frac{5}{2}+\ln\left[\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{\frac{3}{2}}\frac{V}{N}\right]\right) \qquad \text{(F.9)}
\end{aligned}$$

Then we use Eq. **??** to obtain the internal energy

$$\begin{aligned}
U^{BG} &\overset{Eq.\ ??}{=} A^{BG}+TS^{BG} \\
&= -Nk_BT\left(1+\ln\left[\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{\frac{3}{2}}\frac{V}{N}\right]\right) \\
&\quad +Nk_BT\left(\frac{5}{2}+\ln\left[\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{\frac{3}{2}}\frac{V}{N}\right]\right) \\
&= \frac{3}{2}Nk_BT \qquad \text{(F.10)}
\end{aligned}$$

This is the so-called **caloric equation of state**.

Later we will need the entropy as function of the extensive variables, which we obtain by using the caloric equation of state Eq. **??** to replace the temperature by the internal energy in the expression for the entropy Eq. F.9. This yields the so-called **Sackur-Tetrode Equation**.

$$\begin{aligned}
S^{BG}(U,V,N) &\overset{Eq.\ F.9}{=} Nk_B\left(\frac{5}{2}+\ln\left[\left(\frac{mk_BT(U)}{2\pi\hbar^2}\right)^{\frac{3}{2}}\frac{V}{N}\right]\right) \\
&\overset{Eq.\ ??}{=} Nk_B\left(\frac{5}{2}+\ln\left[\left(\frac{mU}{3\pi\hbar^2N}\right)^{\frac{3}{2}}\frac{V}{N}\right]\right) \\
&= Nk_B\left(\frac{5}{2}+\ln\left[\left(\frac{m}{3\pi\hbar^2}\right)^{\frac{3}{2}}\frac{VU^{\frac{3}{2}}}{N^{\frac{5}{2}}}\right]\right) \qquad \text{(F.11)}
\end{aligned}$$

which is the well known Sackur-Tetrode equation Eq. **??**

F.8 Thermodynamic potentials for a general N-state system with equidistant energy levels

Let us consider an N-state system with equidistant energy eigenvalues $E(x)=E_0+cx$ for states $x=0,1,2,..,N-1$ with some constant c. For $N=2$ this model describes a two state system such as an electron spin in a magnetic field. For $N=\infty$ this example corresponds to a quantum mechanical harmonic oscillator, or to a one-dimensional particle in a box.

Let us evaluate first the Free energy

$$\begin{aligned}
F(T) &= -k_BT\ln[\sum_{x=0}^{N-1}\mathrm{e}^{-\beta(E_0+cx)}] = E_0-k_BT\ln[\sum_{x=0}^{N-1}(\mathrm{e}^{-\beta c})^x] \\
&= E_0-k_BT\ln[\frac{1-\mathrm{e}^{-\beta cN}}{1-\mathrm{e}^{-\beta c}}] \\
&= E_0-k_BT\ln[1-\mathrm{e}^{-\beta cN}]+k_BT\ln[1-\mathrm{e}^{-\beta c}]
\end{aligned}$$

We have used that the partition sum contains a geometric series, that can be summed analytically, as shown in the appendix.

The entropy is given by

$$\begin{aligned}
S &= -\frac{\partial F}{\partial T} \\
&= k_B\Big[\ln[1-\mathrm{e}^{-\beta Nc}] - \frac{\beta Nc}{1-\mathrm{e}^{\beta Nc}}\Big] - k_B\Big[\ln[1-\mathrm{e}^{-\beta c}] - \frac{\beta c}{1-\mathrm{e}^{\beta c}}\Big]
\end{aligned}$$

The internal energy

$$\begin{aligned}
U = F + TS &= E_0 - \frac{Nc}{1-\mathrm{e}^{\beta Nc}} + \frac{c}{1-\mathrm{e}^{\beta c}} \\
&= E_0 - c\frac{\mathrm{e}^{-\beta c} - \mathrm{e}^{-\beta c(N+1)} - N\mathrm{e}^{-\beta cN} + N\mathrm{e}^{-\beta c(N+1)}}{1-\mathrm{e}^{-\beta c} - \mathrm{e}^{-\beta cN} + \mathrm{e}^{-\beta c(N+1)}}
\end{aligned}$$

Now we would like to investigate the internal energy at high temperatures, that is $\beta \to 0$. Thus we expand the denominator and the ... in terms of βc, and keep the two lowest order terms.

$$= E_0 - c\frac{\sum_i \frac{1}{i!}(-\beta c)^i[1-(N+1)^i - N^{i+1} + N(N+1)^i]}{\sum_i \frac{1}{i!}(-\beta c)^i[\delta_{0,i} - 1 - N^i + (N+1)^i]}$$

i	$[1-(N+1)^i - N^{i+1} + N(N+1)^i]$	$[\delta_{0,i} - 1 - N^i + (N+1)^i]$
0	0	0
1	0	0
2	$N(N-1)$	$2N$
3	$2N(N^2-1)$	$3N(N+1)$

$$\begin{aligned}
U(T\to\infty) &= E_0 + c\frac{\frac{1}{2}N(N-1) - \beta c\frac{1}{3}N(N-1)(N+1)}{N - \beta c\frac{1}{2}N(N+1)} \\
&= E_0 + c\frac{N-1}{2}\frac{1-\beta c\frac{2}{3}(N+1)}{1-\beta c\frac{1}{2}(N+1)} \\
&= E_0 + c\frac{N-1}{2} - \beta c^2\frac{1}{12}(N^2-1) + O(\beta^2)]
\end{aligned}$$

As anticipated the internal energy converges to the average value of all energy levels. This reflects that all states are occupied at high temperature with equal probability.

The result given here cannot generalized to $N=\infty$. Here we need to start out from the free energy of the harmonic oscillator

$$F_{N=\infty}(T) = E_0 + k_BT\ln[1-\mathrm{e}^{-\beta c}]$$

F.9 Entropy of electrons and Mermin functional

The entropy of a system is

$$S = k_B \ln X \tag{F.12}$$

where X is the number of accessible states.

Let us now consider a system of n Fermion-s, where each of the N one-particle states can either be occupied with one electron or remain unoccupied. Furthermore, Fermions are indistinguishable.

The ultimate goal would be to answer questions such as the occupation numbers as function of temperature, or to obtain the Free Energy of such a electronic system. The Free Energy of electron states in the band gap related to defects is for example important to predict the free energy of formation of the defect and hence the defect concentration.

We can now count the number of possible states

$$
\begin{aligned}
X(n=1) &= N \\
X(n=2) &= \frac{N(N-1)}{2} \\
X(n=3) &= \frac{N(N-1)(N-2)}{3!} \\
X(n) &= \frac{N!}{n!(N-n)!}
\end{aligned}
\tag{F.13}
$$

$N!/(N-n)!$ is the number of ways distinguishable particles can be arranged into N one-particle states and therefore the number of many-particle states for distinguishable particles. $n!$ is the number of ways the particles can be rearranged among the occupied states. We have to divide by this number because all those many-particle states are equivalent.

We can now use Stirling's Formula

$$
\begin{aligned}
N! &= N^N e^{-N}\sqrt{2\pi N} \approx N^N \mathrm{e}^{-N} \\
\ln N! &= N\ln(N) - N
\end{aligned}
\tag{F.14}
$$

An approximate derivation is as follows:

$$
\begin{aligned}
\ln(N!) &= \ln(1) + \ln(2) + \ldots + \ln(N) \\
&\approx \int_1^N dx\,\ln(x) + \frac{1}{2}\ln(N) \\
&\approx [N\ln(N) - N] - [1\ln(1) - 1] + \frac{1}{2}\ln(N) \\
&\approx [N\ln(N) - N] + 1 + \frac{1}{2}\ln(N)
\end{aligned}
\tag{F.15}
$$

We come back to counting the number of states in order to evaluate the entropy.

$$
\begin{aligned}
S = k_B \ln X &= k_B\Big([N\ln(N) - N] - [n\ln(n) - n] - [(N-n)\ln(N-n) - (N-n)]\Big) \\
&= k_B\Big(N\ln(N) - n\ln(n) - (N-n)\ln(N-n) \\
&= k_B\Big(N\ln(N) - fN\ln(fN) - (1-f)N\ln((1-f)N)\Big) \\
&= k_B N\Big(\ln(N) - f\ln(f) - f\ln(N) - (1-f)\ln((1-f)) - (1-f)\ln(N)\Big) \\
&= k_B N\Big(-f\ln(f) - (1-f)\ln((1-f))\Big) \\
&= -k_B N\Big(f\ln(f) + (1-f)\ln((1-f))\Big)
\end{aligned}
\tag{F.16}
$$

where $f = n/N$.

The Free energy is

$$
\begin{aligned}
F &= E - TS \\
&= \sum_n f_n\epsilon_n - [\sum_n f_n - N]\mu + k_B T\sum_n\Big(f_n\ln(f_n) + (1-f_n)\ln(1-f_n)\Big)
\end{aligned}
\tag{F.17}
$$

The occupation number f_n are obtained by minimizing the free energy with respect to the occupations.

$$
\begin{aligned}
\frac{dF}{df_n} &= \epsilon_n - \mu + k_B T \Big[\ln(f_n) + 1 - \ln(1-f_n) - 1 \Big] \\
&= \epsilon_n - \mu + k_B T \ln(\frac{f_n}{1-f_n}) = 0 \\
\exp(-\frac{\epsilon_n - \mu}{k_B T}) &= \frac{f_n}{1-f_n} \\
\exp(-\frac{\epsilon_n - \mu}{k_B T}) &= \Big[1 + \exp(-\frac{\epsilon_n - \mu}{k_B T}) \Big] f_n \\
f_n &= \Big[1 + \exp(\frac{\epsilon_n - \mu}{k_B T}) \Big]^{-1}
\end{aligned}
\tag{F.18}
$$

Thus we derived the Fermi distribution function

We can now evaluate the entropy contribution of a state near the Fermi level

$$
\begin{aligned}
S &= \sum_n f_(\epsilon_n) s(\epsilon_n) \\
s(\epsilon) &= -k_B \Big(f \ln(f) + (1-f) \ln((1-f)) \Big) \\
&= -k_B \Big(\ln(1-f) + f \ln(\frac{f}{1-f}) \Big) \\
&= -k_B \Big(\ln(\frac{\exp(\beta(\epsilon-\mu))}{1+\exp(\beta(\epsilon-\mu))} - f \frac{\epsilon-\mu}{k_B T} \Big) \\
&= -k_B \Big(\beta(\epsilon-\mu)) - \ln(1+\exp(\beta(\epsilon-\mu))) - f\beta(\epsilon-\mu) \Big) \\
&= -k_B \Big((1-f)\beta(\epsilon-\mu)) - \ln(1+\exp(\beta(\epsilon-\mu))) \Big)
\end{aligned}
\tag{F.19}
$$

Appendix G

Ideal gas

Let us consider indistinguishable particles. We use periodic boundary conditions.

We can obtain the partition function from the density of states.

$$Z(T,V)=\sum_{states}\mathrm{e}^{-\frac{E(i,j,k)}{k_BT}}$$

$$\int d\epsilon D(\epsilon)\mathrm{e}^{-\frac{\epsilon}{k_BT}}$$

The partition function is

$$\begin{aligned}Z(T,V)&=\sum_{i,j,k=-\infty}^{\infty}\exp\Big[-\frac{1}{2mk_BT}(\frac{2\pi\hbar}{L})^2(i^2+j^2+k^2)\Big]\\&=\Big[\sum_{i=-\infty}^{\infty}\exp\Big[-\frac{1}{2mk_BT}(\frac{2\pi\hbar}{L})^2i^2\Big]^3\\&\approx\Big[\sum_{i=-\infty}^{\infty}\exp\Big(-\pi(\frac{\lambda_Ti}{L})^2\Big)\Big]^3\end{aligned}$$

Here we introduced the **thermal de-Broglie wavelength**[1]

$$\lambda_T=\sqrt{\frac{2\pi\hbar^2}{mk_BT}}\tag{G.1}$$

The de-Broglie wavelength is a measure of the length scale over which we can detect quantum mechanical discretization of the states...???

If the de-Broglie wavelength is much smaller than the dimensions of the box, namely L, the sum can be approximated by an integral

$$\begin{aligned}Z(T,V)&=\Big[\int_{-\infty}^{\infty}dx\exp\Big(-\pi(\frac{\lambda_Tx}{L})^2\Big)\Big]^3\\&=\Big[\frac{L}{\lambda_T}\int dye^{-\pi y^2}\Big]^3\\&=\frac{V}{\lambda_T^3}\end{aligned}$$

---

[1] Louis Victor Pierre Raymond duc de Broglie. French Physicist 1892-1987. Professor for theoretical Physics at Sorbonne in Paris. Founded the particle-wave duality of matter in his doctoral thesis 1924. Nobel price 1929.

Here we have used that $\int_{-\infty}^{\infty} dx e^{\pi x^2} = 1$, and that the volume is $V = L^3$.

Now we generalize this result from one particle to N indistinguishable particles. To obtain the sum over all N-particle states we have to multiply the partition function N times. However in that case we included every set of of a number of times. For example if we have two one-particle states A and B each occupied with one electron, we included the states A(1)B(2) and the state A(2)B(1), where 1 and 2 denote the two particles. To avoid the "double counting" we have to divide the result by the number of permutations of particles $N!$. We use the relation $N! \approx (N/e)^N$

$$\begin{aligned} Z(T, V, N) &= \frac{1}{N!} Z(T, V, 1)^N \\ &\approx \left[\frac{\mathrm{e}V}{N\lambda_T^3}\right]^N \end{aligned}$$

Next we evaluate the Free energy

$$\begin{aligned} F(T, V, N) &= -k_B T \ln Z(T, V, N) \\ &= -N k_B T \ln\left[\frac{\mathrm{e}V}{N\lambda_T^3}\right] \\ &= N k_B T \left[1 - \ln \frac{V}{N\lambda_T^3}\right] \end{aligned}$$

Given that the de-Broglie wavelength is small compared to the length dimensions, we can ignore the term unity and obtain

$$F(T, V, N) = -N k_B T \ln \frac{V}{N\lambda_T^3} \tag{G.2}$$

From the free energy we can derive the pressure at a given temperature and density

$$p = -\frac{\partial F}{\partial V} = k_B T \frac{N}{V} \tag{G.3}$$

This is nothing but the ideal gas equation

$$pV = N k_B T = NRT \tag{G.4}$$

The gas constant is k_B=R=8.314510 J/(mol K). (Pascal:Pa=Jm^{-3};) The gas constant is simply the Boltzmann constant in different units. Typically one represents $k_B = R/N_A$ where N_A is the Avogadro constant. However if we use the unit $mol = N_A$, this relation is absorbed in the units.

The pressure rises linearly with temperature and with the gas density. However the pressure is independent of the type of particles. This implies that any ideal gas with a fixed number of molecules fills the same volume at a given temperature and pressure. Hence the relative masses of the molecules can be measured, by weighing gases in a container of a given volume. It is the reason why balloons filled with helium to make them fly. Helium atoms is lighter than nitrogen molecules and so is the helium gas lighter than nitrogen gas. Therefore the balloon filled with helium will be lighter than the surrounding air and will fly.

Most gases will actually sink to the bottom.

Air consists in fraction of volume of 78.9 % N_2, 20.95 % O_2, 0.93 % Ar and 0.002 % other Nobel gases. (Furthermore it contains water, Dust, CO_2 and carbohydrides such as CH_4, C_2H_4.)[**?**] It has therefore a weight density at atmospheric pressure of ..... Only a small number of gases are lighter than air, namely H_2, He, Ne, CH_4, C_2H_2. This is important to know to prevent explosions, because one has to allow the gases to leave a closed space at the bottom. Often it does not help to open the window, unless there is sufficient circulation. Another important example is the accumulation of carbon dioxide CO_2 in wells or corn silos. As there is no exit for the gas at the bottom, CO_2 will accumulate at the bottom of these wells. People entering will suffocate. Also Radon, a radioactive noble gas tends to accumulate in cellars of houses, where it can pose health problems.

(below 16% oxygen is the strength strongly reduced, below 10% unconsciousness can suddenly occur; CO_2 ist narkotisierend und fuehrt bei ueber 7 % zu bewustlosigkeit. 1L Trockeneis entspricht 500 l CO_2 gas (Erstickungsgefahr) ;N2O ist lachgas)

We can also derive the chemical potential.

$$\begin{aligned}\mu &= -\frac{\partial F}{\partial N} = k_B T \ln \frac{V}{N\lambda_T^3} - k_B T \\ &= -k_B T(\ln[\frac{N}{V}\lambda_T^3] + 1)\end{aligned}$$

The requirement is that the volume per particle must be large compared to the de-Broglie wavelength, allows us to drop the constant term relative to the logarithm.

$$\mu = -k_B T \ln[\frac{N}{V}] + 3k_B T \ln[\lambda_T] \qquad \text{(G.5)}$$

Interestingly a small term depending on the mass of the gas molecules occurs. The thermal de-Broglie wavelength of air at room temperature is 0.2 Å, which is much smaller than the average distance of gas molecules at atmospheric pressure is about 35 AA. At atmospheric pressure the de-Broglie wavelength becomes comparable to the de-Broglie wavelength at about 1K. All materials are liquid or solid at this temperature. He^4, a viscous liquid at low temperatures, becomes superfluid at 2 K, that is it forms a Bose condensate.

Let us perform a Lagrange transform to $U(S, V, N)$

$$\begin{aligned}S &= -\frac{\partial F}{\partial T} \\ &= Nk_B \ln \frac{V}{N\lambda_T^3} + Nk_B T \frac{3}{\lambda_T}\frac{\partial \lambda_T}{\partial T} \\ &= +Nk_B \ln \frac{V}{N\lambda_T^3} + Nk_B T \frac{3}{\lambda_T}(-\frac{1}{2T}) \\ &= +Nk_B \ln \frac{V}{N\lambda_T^3} - \frac{3}{2}Nk_B \frac{1}{\lambda_T} \\ &= -Nk_B\Big[\frac{3}{2\lambda_T} - \ln \frac{V}{N\lambda_T^3}\Big] \\ -TS &= F(T) + \frac{3}{2}Nk_B T \frac{1}{\lambda_T} \\ U &= F + TS = -\frac{3Nk_B T}{2\lambda_T} \\ &= -\frac{3N\sqrt{\pi}}{\hbar\sqrt{m}}(\frac{k_B T}{2})^{\frac{3}{2}}\end{aligned}$$

G.1 Quantities

1 atm	1.01325×10^6 J/m^3 =6.10193×10^{-4} kJ/mol/Å^3
thermal de-Broglie wavelength of air at 300K	0.2 Å
Mean distance between gas molecules at 300 K and 1atm	35 Å
Mean distance between gas molecules at 300 K and 10^{-8} Torr	15 μm
k$_B T$ at 300 K	2.49435 kJ/mol =25.85212 meV
chem. pot. of air at 300K and 1 atm	-0.36 eV

G.2 Aufgaben

G.2.1 Configurational Entropy

Vacant lattice positions, so-called vacancies, in a semiconductor can have an impact on the electronic properties and dopant diffusion. Therefore it is important to estimate the number of lattice vacancies in a semiconductor. The number of lattice positions in Si is estimated from the crystal structure. The cubic unit cell of silicon has a lattice constant of 5.43 Åand contains 8 atoms. Let us assume that the energy to form a vacancy in a crystal is $E_F = 3\ eV$.

What is the fraction of empty lattice sites at 200^{o}C? Determine the free energy as function of the number of vacancies in a given volume and temperature. Determine the number of lattice sites from this free energy.

Help: Consider a lattice with M lattice sites, of which N sites are vacant. Determine the entropy as function of N from the number of configurations with N vacancies. Use Stirling's formula $\ln(n!) \approx n\ln[n] + n$, which is valid for large n.

Answer:

First we determine the partition function as function of number of vacancies

$$Z(T, N) = \sum_i \mathrm{e}^{-\beta E_i}) = \sum_N \mathrm{e}^{-\beta(E(N)-TS(N))}$$

Let us consider a crystal with M sites. A state with N vacancies has the energy NE_f. There are $\frac{M!}{N!(M-N)!}$ different configurations.[2] The number of configurations is related to the entropy by $\mathrm{e}^{S/k_B} = \frac{M!}{N!(M-N)!}$.

$$\begin{aligned}
S &= k_B \ln[\frac{M!}{N!(M-N)!}] = k_B\Big(\ln[M!] - \ln[N!] - \ln[(M-N)!]\Big) \\
&\approx k_B\Big(M\ln[M] - M - N\ln[N] + N - (M-N)\ln[(M-N)] + (M-N)\Big) \\
&= k_B\Big(M\ln[M] - N\ln[N] - (M-N)\ln[M-N]\Big) \\
&= k_B\Big(M\ln[M] - N\ln[N] - (M-N)\ln[M-N]\Big) \\
&= k_B\Big(M\ln[\frac{M}{M-N}] - N\ln[\frac{N}{M-N}]\Big) \\
&= k_B\Big(M\ln[\frac{M}{M-N}] - N\ln[\frac{N}{M-N}]\Big)
\end{aligned}$$

Let us now introduce a new symbol $c \overset{\text{def}}{=} N/M$ for the vacancy concentration.

$$\begin{aligned}
S &= Mk_B\Big(\ln[\frac{1}{1-c}] - c\ln[\frac{c}{1-c}]\Big) \\
&= Mk_B\Big(-\ln[1-c] - c\ln[c] + c\ln[1-c]\Big) \\
&= -Mk_B\Big((1-c)\ln[1-c] + c\ln[c]\Big)
\end{aligned}$$

---

[2] The degeneracy is obtained as follows. I place the first vacancy on one of M positions, the second on one of $M-1$ positions and so on until I have created $M(M-1)\ldots(M-N+1) = M!/(M-N)!$ configurations. Each configuration however has been counted $N!$ times. Therefore I divide by $N!$, the number of permutations of the vacancies among each other.

Thus we obtain the entropy per vacancy[3]

$$s(c)\overset{\text{def}}{=}\frac{S}{M}=-k_B\Big((1-c)\ln[1-c]+c\ln[c]\Big)$$

Now we can obtain the free energy

$$\begin{aligned}F_M(T,c)&=-k_BT\ln\Big[\sum_{N=1}^{M}\mathrm{e}^{S(N)/k_B}\mathrm{e}^{-\beta NE_0}\Big]\\&=-k_BT\ln\Big[\sum_{N=1}^{M}\mathrm{e}^{-\beta(NE_0-TS(N))}\Big]\\&=-k_BT\ln\Big[M\int_0^1 dc\mathrm{e}^{-\beta M(cE_0-Ts(c))}\Big]\\&=-k_BT\ln\Big[M\int_0^1 dc\Big(\mathrm{e}^{-\beta(cE_0-Ts(c))}\Big)^M\Big]\end{aligned}$$

For large M only the maximum value of the integrand will contribute. Therefore we will perform the harmonic approximation of the integrand by expanding $Y=cE_0-Ts(c)$ to second order in c about the maximum of Y. First we determine the maximum of Y [4] :

$$\begin{aligned}Y&=cE_0+k_BT\Big((1-c)\ln[1-c]+c\ln[c]\Big)\\\frac{dY}{dc}&=0=E_0+k_BT\Big(-\ln[1-c]-1+\ln[c]+1\Big)=E_0+k_BT\ln[\frac{c}{1-c}]\\\Rightarrow\frac{c}{1-c}&=\mathrm{e}^{-\beta E_0}\qquad\Rightarrow\qquad c=\mathrm{e}^{-\beta E_0}-c\mathrm{e}^{-\beta E_0}\\\Rightarrow c&=\frac{1}{\mathrm{e}^{\beta E_0}+1}\end{aligned}$$

Let us evaluate the value of Y at its maximum

$$\begin{aligned}Y&=cE_0-Ts(c)=cE_0+k_BT\Big((1-c)\ln[1-c]-c\ln[c]\Big)\\&=\frac{E_0}{1+\mathrm{e}^{\beta E_0}}+k_BT\Big(-\frac{\ln[1+\mathrm{e}^{-\beta E_0}]}{1+\mathrm{e}^{-\beta E_0}}\frac{\ln[1+\mathrm{e}^{\beta E_0}]}{1+\mathrm{e}^{\beta E_0}}\Big)\end{aligned}$$

Now we need the second derivative of Y at its maximum.

Thus we obtain

$$\begin{aligned}F_M&=-k_BT\ln\Big[M\int_0^\infty dc\Big(\mathrm{e}^{-\beta(Y(c_0)+\frac{1}{2}Y''(c-c_0)^2)}\Big)^M\Big]\\&=-k_BT\ln\Big[M\int_0^\infty dc\Big(\mathrm{e}^{-\beta(Y(c_0)+\frac{1}{2}Y''(c-c_0)^2)}\Big)^M\Big]\end{aligned}$$

---

[3] Note here that this expression is identical to the entropy of a one-particle state due to filling with electrons. In this entropy contribution the concentration c is replaced by the fractional occupation.

[4] The resulting expression for the concentration is formally identical with the Fermi distribution function. This finding is not unexpected since only one vacancy can occupy a site, just as for Fermions. **Editorial remark: this is the exact Pendent to the photon gas: chemical potential vanishes**

Appendix H

Greek Alphabet

A	α	alpha	N	ν	nu
B	β	beta	Ξ	ξ	ksi
Γ	γ	gamma	O	$o,$	omicron
Δ	δ	delta	Π	π, ϖ	pi
E	ϵ, ε	epsilon	P	ρ, ϱ	rho
Z	ζ	zeta	Σ	σ, ς	sigma
H	η	eta	T	τ	tau
Θ	θ, ϑ	theta	Υ	υ	upsilon
I	ι	iota	Φ	ϕ, φ	phi
K	κ	kappa	X	χ	chi
Λ	λ	lambda	Ψ	ϕ	phi
M	μ	mu	Ω	ω	omega

Appendix I

Philosophy of the ΦSX Series

In the ΦSX series, I tried to implement what I learned from the feedback given by the students which attended the courses and that relied on these books as background material.

The course should be self-contained. There should not be any statements "as shown easily..." if, this is not true. The reader should not need to rely on the author, but he should be able to convince himself, if what is said is true. I am trying to be as complete as possible in covering all material that is required. The basis is the mathematical knowledge. With few exceptions, the material is also developed in a sequence so that the material covered can be understood entirely from the knowledge covered earlier.

The derivations shall be explicit. The novice should be able to step through every single step of the derivation with reasonable effort. An advanced reader should be able to follow every step of the derivations even without paper and pencil.

All units are explicit. That is, formulas contain all fundamental variables, which can be inserted in any desirable unit system. Expressions are consistent with the SI system, even though I am quoting some final results in units, that are common in the field.

The equations that enter a specific step of a derivation are noted ontop of the equation sign. The experience is that the novice does not immediately memorize all the material covered and that he is struggling with the math, so that he spends a lot of time finding the rationale behind a certain step. This time is saved by being explicit about it. The danger that the student gets dependent on these indications, is probably minor, as it requires some effort for the advanced reader to look up the assumptions, an effort he can save by memorizing the relevant material.

Important results and equations are highlighted by including them in boxes. This should facilitate the preparations for examinations.

Portraits of the key researchers and short biographical notes provide independent associations to the material. A student may not memorize a certain formula directly, but a portrait. From the portrait, he may associate the correct formula. The historical context provides furthermore an independent structure to organize the material.

The two first books are in german (That is the intended native language) in order to not add complications to the novice. After these first books, all material is in English. It is mandatory that the student masters this language. Most of the scientific literature is available only in English. English is currently the language of science, and science is absolutely dependent on international contacts.

I tried to include many graphs and figures. The student shall become used to use all his senses in particular the visual sense.

I have slightly modified the selection of the material commonly tought in most courses. Some topics, which I consider of mostly historical relevance I have removed. Others such as the Noether theorem, I have added. Some, like Chaos, Stochastic processes, etc. I have not added yet.

Appendix J

About the Author

Prof. Dr. rer. nat Peter E. Blöchl studied physics at Karlsruhe University of Technology in Germany. Subsequently he joined the Max Planck Institutes for Materials Research and for Solid state Research in Stuttgart, where he developed of electronic-structure methods related to the LMTO method and performed first-principles investigations of interfaces. He received his doctoral degree in 1989 from the University of Stuttgart.

Following his graduation, he joined the renowned T.J. Watson Research Center in Yorktown Heights, NY in the US on a World-Trade Fellowship. In 1990 he accepted an offer from the IBM Zurich Research Laboratory in Ruschlikon, Switzerland, which had just received two Nobel prices in Physics (For the Scanning Tunneling Microscope in 1986 and for the High-Temperature Superconductivity in 1987). He spent the summer term 1995 as visiting professor at the Vienna University of Technology in Austria, from where was later awarded the habilitation in 1997. In 2000, he left the IBM Research Laboratory after a 10-year period and accepted an offer to be professor for theoretical physics at Clausthal University of Technology in Germany. Since 2003, Prof. Blöchl is member of the Braunschweigische Wissenschaftliche Gesellschaft (Academy of Sciences).

The main thrust of Prof. Blöchl's research is related to ab-initio simulations, that is, parameter-free simulation of materials processes and molecular reactions based on quantum mechanics. He developed the Projector Augmented Wave (PAW) method, one of the most widely used electronic structure methods to date. This work has been cited over 20,000 times. It is among the 100 most cited scientific papers of all times and disciplines[1] , and it is among the 10 most-cited papers out of more than 500,000 published in the 120-year history of Physical Review. [2] Next to the research related to simulation methodology, his research covers a wide area from biochemistry, solid state chemistry to solid state physics and materials science. Prof. Blöchl contributed to 8 Patents and published about 100 research publications, among others in well-known Journals such as "Nature". The work of Prof. Blöchl has been cited over 29,000 times, and he has an H-index of 42.[3]

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[2] Oct. 15, 2014, search in the Physical Review Online Archive with criteria "a-z".

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