Foreword

This script was written for the course *Theoretical Statistical Physics* which is one of the ten core courses for the master studies of physics at Heidelberg University, although in practise it is also attended by many bachelor students from the fifth semester. There exist many very good textbooks on statistical physics and the purpose of this script is soley to document my personal choice of the relevant material.

Several guiding principles determined the design of this course. First I completely agree with Josef Honerkamp who in his book *Statistical Physics* notes that statistical physics is much more than statistical mechanics. A similar notion is expressed by James Sethna in his book *Entropy, Order Parameters, and Complexity*. Indeed statistical physics teaches us how to think about the world in terms of probabilities. This is particularly relevant when one deals with real world data. Therefore applications of statistical physics can also be found in data-intensive research areas such as astrophysics, environmental physics, biophysics, econophysics, machine learning, pattern recognition or image processing. As an instructive example, consider so-called Boltzmann machines that can be trained to recognize the faces of your friends in images posted in social media such as Facebook. If you investigate how these algorithms work, you will realize that they derive from the Ising model, arguably the most important model of statistical physics and an important subject for this course.

Second I am strongly motivated by the axiomatic approach to thermodynamics (actually a misnomer, thermostatics would be more appropriate because it deals with equilibrium, not dynamics) as layed out in the beautiful book *Thermodynamics and an introduction to Thermostatistics* by Herbert Callen. Thermodynamics as a phenomenological theory of heat transfer can be quite cumbersome at times, but when being approached from the axiomatic side, it becomes the convincing and universal theory that it actually is. The book by Callen also draws heavily on the work by Edwin Jaynes on the relationship between statistical physics and information theory as pioneered by Claude Shannon. Although somehow debated, this link shows once again that statistical physics is more than statistical mechanics. Information theory provides very helpful insight into the concept of entropy, which is the cornerstone of statistical mechanics. Recently this area has been revived by the advent of stochastic thermodynamics, which shows that entropy is not only an ensemble property, but can also be defined for single trajectories.

Last but not least, statistical physics is much more than thermodynamic equilibrium and if time permits, a course on statistical physics should also cover the basics of non-equilibrium physics, including the Boltzmann equation, Langevin dynamics and the Fokker-Planck equation. Finally a comprehensive course on statistical physics should also include some numerical component, because modern statistical physics cannot be practised without computational approaches, as nicely demonstrated in the book by
James Sethna.

These considerations might explain the structure of this script. We start with an introduction to the concepts of probability theory, which should be useful also in other contexts than only statistical mechanics. We then introduce the fundamental postulate of equilibrium physics, namely that each microstate is equally probable, leading to the microcanonical ensemble and the principle of maximal entropy. We then discuss the canonical and grandcanonical ensembles, when reservoirs exist for exchange of heat and particle number, respectively. We then apply these concepts to quantum fluids, in particular the Fermi fluid (e.g. electrons in a solid) and the Bose gas (e.g. black body radiation or the Debye model for crystal vibrations). These are interacting systems, but this is accounted for by the right way to count, not by investigating direct interactions. Yet, here we encounter our first phase transition, the Bose-Einstein condensation. Finally phase transitions generated by direct interactions are discussed through the examples of the Ising model and the van der Waals gas. We close with a discussion of thermodynamics, from which we see that statistical physics and thermodynamics essentially use the same formal structure, but that they complement each other in a unique manner: statistical physics focuses on microscopic mechanisms, and thermodynamics on macroscopic phenomena. In principle this then would be the perfect starting point to discuss stochastic thermodynamics, where work and heat are treated as fluctuating quantities, leading to the concept of negative entropy production.

Finally one should notice that subjects which are not covered in the script due to space reasons. We do not cover transport theory, which would also include the Boltzmann equation. The very important subject of fluctuations and correlations (including the fluctuation-dissipation theorem) is mentioned only in passing. We also cannot treat out-of-equilibrium physics here (including the Green-Kubo relations, Onsager’s reciprocity theorem, Kramers-Kröning relations, linear response theory). All of these exciting subjects could be part of an advanced course on statistical physics.

Heidelberg, winter term 2017/18

Ulrich Schwarz
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1 Probability theory

1.1 Probability in physics

Classical physics (classical mechanics and electrodynamics) is deterministic, that means the governing equations (Newton’s and Maxwell’s equations, respectively) are differential equations that have a unique solution once we know the initial conditions (and boundary conditions for the case of Maxwell’s equations, which are partial differential equations). Quantum mechanics of course introduces probability into physics in the form of the statistical (Kopenhagen) interpretation, but still we solve a deterministic differential equation (Schrödinger’s equation for the wavefunction) and then probability follows as the squared modulus of the complex wavefunction.

In marked contrast, statistical physics directly brings the concept of probability into physics. Now the central concept is to calculate the probability of a certain macroscopic state, thus it is not a derived quantity, but the most elementary concept. For example, in the canonical ensemble the relevant statistics will be the Boltzmann distribution. Therefore we start our course on statistical physics with an introduction into probability theory. Later of course we have to ask how the probabilistic nature of statistical physics emerges from more microscopic descriptions, and we will see that both classical and quantum mechanics provide some justification for this (deterministic chaos and thermalization of the wavefunction, respectively).

1.2 Throwing dice

The history of probability theory is long and twisted. We start with a simple example (throwing dice) to illustrate what one would expect from a theory of probability. Possible outcomes are \{1, 2, 3, 4, 5, 6\}. For N throws the event \{i\} occurs \(N_i\) times. We then identify the probability \(p_i\) for event \{i\} with its frequency:

\[
p_i = \frac{\text{# favorable outcomes}}{\text{# possible outcomes}} = \frac{N_i}{N} \quad \text{in the limit } N \to \infty
\]

For an ideal die we expect \(p_i = \frac{1}{6} \approx 0.167\). Hence for 1000 throws \{6\} should occur around 167 times.

We first note that our definition is normalized:

\[
\sum_{i=1}^{6} N_i = N \quad \xRightarrow{1/N} \quad \sum_{i=1}^{6} p_i = 1
\]
We next consider events that are not directly an experimental outcome, but a more complicated question to ask about the system. E.g. what is the probability to get an odd outcome?

\[
p_{\text{odd}} = \frac{\text{# favorable outcomes}}{\text{# possible outcomes}} = \frac{N_1 + N_3 + N_5}{N_1 + N_3 + N_5} = p_1 + p_3 + p_5
\]

⇒ sum rule: summation of probabilities for simultaneous disjunct events

What is the probability to get twice \{6\} when throwing two times? We first throw \(N\) times and find \(N_6\) times a 6. We then throw \(M\) times and find \(M_6\) times a 6. Thus we count

\[
p_{66} = \frac{\text{# favorable outcomes}}{\text{# possible outcomes}} = \frac{N_6 \cdot M_6}{N \cdot M} = \frac{N_6}{N} \cdot \frac{M_6}{M} = p_6 \cdot p_6 = \frac{1}{36}
\]

⇒ product rule: multiplication of probabilities for subsequent independent events

Finally we note that we could either throw \(N\) dice at once or the same die \(N\) times - the result should be the same

⇒ ergodic hypothesis of statistical physics: ensemble average = time average

Identifying probability with frequency is called the classical or frequentist interpretation of probability. There are two problems with this. First there are some examples for which naive expectations of this kind fail and a more rigorous theory is required. Second there are many instances in which an experiment cannot be repeated. Consider e.g. the statistical distribution of galaxy sizes in the universe, for which we have only one realization in our hands. In order to address these two problems, the concept of probability can be approached by an axiomatic approach and with Bayesian theory, respectively.

### 1.3 Axiomatic approach

Above we described an empirical approach to measure probability for the dice throwing experiment and this sharpened our intuition what we expect from a theory of probability. We now construct a mathematical theory of probability by introducing an axiomatic system (Kolmogorov 1933). It has been shown that this approach allows to describe also complex systems without generating contradictions.\[1\]

Let \(\Omega = \{ \omega_i \}\) be a set of elementary events. The complete set of possible events is the sample space \(B\) defined by:

1. \(\Omega \in B\)
2. if \(A \in B\), then \(\overline{A} \in B\)

---

if \(A_1, A_2, \ldots \in B\), then \(\bigcup_{i=1}^{\infty} A_i \in B\)

By setting all \(A_i\) with \(i\) larger than a certain value to empty sets, the last point includes unions of a finite number of sets. We see that the event space is closed under the operations of taking complements and countable unions. This concept is also known as \(\sigma\)-algebra. In our case we actually have a Borel-algebra, because the \(\sigma\)-algebra is generated by a topology. The most important point is that we have to avoid non-countable unions, because this might lead to pathological situations of the nature of the Banach-Tarski paradoxon (which states that a sphere can be disassembled into points and that they then can be reassembled into two spheres because the set of real numbers is non-countable).

**Corollaries**

1. \(\emptyset \in B\)
2. \(A \cap B = \overline{A} \cup \overline{B} \in B\)

**Examples**

1. \(\Omega = \{1, \ldots, 6\}\) for the ideal die. This set of elementary events is complete and disjunct \((\omega_i \cap \omega_j = \emptyset\) if \(i \neq j\), \(\bigcup_{i=1}^{6} \omega_i = \Omega\)). This event space is discrete.

2. All intervals on the real axis, including points and semi-infinite intervals like \(x \leq \lambda\). Here \(x\) could be the position of a particle. This event space is continuous.

We now introduce the concept of probability. For each event \(A\) in the event space \(B\) we assign a real number \(p(A)\), such that

1. \(p(A) \geq 0\) \(\forall A \in B\)
2. \(p(\Omega) = 1\)
3. \(p(\bigcup_{i} A_i) = \sum_{i} p(A_i)\) if \(A_i \cap A_j = \emptyset\) for \(i \neq j\)

Note that the last assumption is the sum rule. Kolmogorov showed that these rules are sufficient for a consistent theory of probability.

**Corollaries**

1. \(p(\emptyset) = 0\)
2. \(p(A) + p(\overline{A}) = p(\Omega) = 1 \Rightarrow p(A) = 1 - p(\overline{A}) \Rightarrow 0 \leq p(A) \leq 1\)
Consider $A_1, A_2 \in B$:

\[
p(A_1) = p(A_1 \cap A_2) + p(A_1 \cap \overline{A_2}) := C_1
\]

\[
p(A_2) = p(A_2 \cap A_1) + p(A_2 \cap \overline{A_1}) := C_2
\]

\[
\Rightarrow p(A_1) + p(A_2) = p(C_1) + p(C_2) + 2p(A_1 \cap A_2)
\]

\[
= p(A_1 \cup A_2) + p(A_1 \cap A_2)
\]

\[
\Rightarrow p(A_1 \cup A_2) = p(A_1) + p(A_2) - p(A_1 \cap A_2)
\]

### 1.4 Continuous distributions and distribution function

Consider the event space containing the intervals and points on the real axis. $p(x \leq \lambda)$ is the probability that $x$ is smaller or equal to a given $\lambda$ (e.g., the position of a particle in 1D):

\[
P(\lambda) := p(x \leq \lambda) \text{ cumulative distribution function}
\]

If $P(\lambda)$ is differentiable, then

\[
P(\lambda) = \int_{-\infty}^{\lambda} p(x) dx
\]

where

\[
p(\lambda) = \frac{dP(\lambda)}{d\lambda} \text{ probability density or distribution function}
\]

We now can write the probability for $x \in [x_1, x_2]$ as $\int_{x_1}^{x_2} p(x) dx$. With $x_2 = x_1 + dx_1$, we can approximate the integral by a product and thus find that $p(x_1)dx_1$ is the probability to have $x \in [x_1, x_1 + dx_1]$. Thus $p(x)$ is the probability density and $p(x)dx$ is the probability to find a value around $x$.

### 1.5 Bayesian statistics

A multidimensional distribution $\vec{x} = (x_1, ..., x_n)$ is called a multivariate distribution, if

\[
p_2(\vec{x}') \, dx'_1 \ldots \, dx'_n \text{ is the probability for } x_i \in [x'_i, x'_i + dx'_i]
\]

We also speak of a joint distribution.
Examples

1. A classical system with one particle in 3D with position and momentum vectors has six degrees of freedom, thus we deal with the probability distribution $p(\vec{q}, \vec{p})$. For $N$ particles, we have $6N$ variables.

2. We measure the probability $p(a, i)$ for a person to have a certain age $a$ and a certain income $i$. Then we can ask questions about possible correlations between age and income.

3. Consider a collection of apples ($a$) and oranges ($o$) distributed over two boxes (left $l$ and right $r$). We then have a discrete joint probability distribution $p(F, B)$ where $F = a, o$ is fruits and $B = l, r$ is boxes.

Marginal probability: now we are interested only in the probability for a subset of all variables

$$p(x_1) = \int dx_2 \ldots dx_n p(x)$$

is the probability for $x_1 \in [x'_1, x'_1 + dx'_1]$ independent of the outcome for $x_2, \ldots, x_n$.

Examples

1. We integrate out the momentum degrees of freedom to focus on the positions.

2. We integrate $p(a, i)$ over $i$ to get the age structure of our social network.

3. We sum over the two boxes to get the probability to have an orange

$$p(o) = p(o, l) + p(o, r)$$

This example shows nicely that the definition of the marginal probability essentially implements the sum rule.

Conditional probability: we start with the joint probability and then calculate the marginal ones. From there we define the conditional ones. Consider two events $A, B \in \mathcal{B}$. The conditional probability for $A$ given $B$, $p(A|B)$, is defined by

$$p(A, B) = p(A|B) \cdot p(B)$$

joint probability for the outcome of $A$ and $B$ conditional probability for $A$ to occur if $B$ is certain

Thus the definition of the conditional probability essentially introduces the product rule.
Example

Consider a fair die and the events $A = \{2\}$ and $B = \{2, 4, 6\}$.

\[
p(A|B) = \frac{p(A,B)}{p(B)} = \frac{p(A)}{p(B)} = \frac{1}{3}
\]

\[
p(B|A) = \frac{p(A,B)}{p(A)} = \frac{p(A)}{p(A)} = 1
\]

Statistical independence: $p(A_1|A_2) = p(A_1)$  $A_1$ is independent of $A_2$

\[
\Rightarrow p(A_1,A_2) = p(A_1|A_2) \cdot p(A_2) = p(A_1) \cdot p(A_2)
\]

Thus we get the product rule (multiplication of probabilities) that we expect for independent measurements, compare the example of throwing dice discussed above. We also see that

\[
\Rightarrow p(A_2|A_1) = \frac{p(A_1,A_2)}{p(A_1)} = p(A_2)
\]

Statistic independence is mutual.

Bayes’ theorem: $p(A,B) = p(A|B) \cdot p(B) = p(B,A) = p(B|A) \cdot p(A)$

\[
p(B|A) = \frac{p(A,B) \cdot p(B)}{p(A)} = \frac{p(A|B) \cdot p(B)}{\sum_{B'} p(A|B') \cdot p(B')}
\]

Bayes’ theorem

where for the second form we have used the sum rule. Despite of its simplicity, this formula named after Thomas Bayes (1701-1761) is of extremely large practical relevance. It allows to ask questions about the data that are not directly accessible by measurements.

Examples

Consider again the fruits ($F = a,o$) in the boxes ($B = l,r$). We assume that left and right are selected with probabilites $p(l) = 4/10$ and $p(r) = 6/10$ (they sum to 1 as they should). We next write down the known conditional probabilities by noting that there are two apples and six oranges in the left box and three apples and one orange in the right box:

\[
p(a|l) = 1/4, p(o|l) = 3/4, p(a|r) = 3/4, p(o|r) = 1/4
\]

We now ask: what is the probability of choosing an apple?

\[
p(a) = p(a|l)p(l) + p(a|r)p(r) = 11/20
\]

Note that the result is not 5/12 that we would get if there was no bias in choosing boxes. The probability of choosing an orange is

\[
p(o) = 1 - p(a) = 9/20
\]
We next ask a more complicated question: if we have selected an orange, what is the probability that it did come from the left box? The answer follows by writing down the corresponding conditional probability:

\[ p(l|o) = \frac{p(o|l)p(l)}{p(o)} = \frac{2}{3} \]

Therefore

\[ p(r|o) = 1 - \frac{2}{3} = \frac{1}{3} \]

Above we have formulated the probability \( p(F|B) \) for the fruit conditioned on the box. We now have reverted this relation to get the probability \( p(B|F) \) for the box conditioned on the fruit. Our prior probability for the left box was \( p(l) = \frac{4}{10} < 0.5 \). Our posterior probability for the left box, now that we know that we have an orange, is \( p(l|o) = \frac{2}{3} > 0.5 \). Thus the additional information has reverted the bias for the two boxes.

A company produces computer chips in two factories:

- **factory**
  - events \( A \) and \( \overline{A} \)
    - 60% come from factory A
    - 40% come from factory B

- **defect or not**
  - events \( d \) and \( \overline{d} \)
    - 35% from factory A
    - 25% from factory B

What is the probability that a defect chip comes from factory A?

\[
p(A|d) = \frac{p(d|A) \, p(A)}{p(d)}
\]

\[
p(d) = p(d|A) \, p(A) + p(d|B) \, p(B)
\]

\[
p(A) = 0.6, \; p(B) = 0.4, \; p(d|A) = 0.35, \; p(d|B) = 0.25
\]

\[ \Rightarrow p(A|d) = 0.68 \]

We can design a webpage that makes offers to customers based on their income. However, the only data we are allowed to ask them for is age. So we buy the correlation data \( p(a,i) \) from the tax office and then estimate the income of our users from their age information. The more multivariate data sets we can use for this purpose, the better we will be with these estimates and the more accurate our offers will be.
1.6 Expectation and covariance

Both for discrete and continuous probability distributions, the most important operation is the calculation of the expectation of some function \( f \) of the random variable:

\[
\langle f \rangle = \sum_i f(i)p_i \quad \text{or} \quad \langle f \rangle = \int f(x)p(x)dx
\]

In particular, the average of the random variable itself is

\[
\mu = \langle i \rangle = \sum_i ip_i \quad \text{or} \quad \mu = \langle x \rangle = \int xp(x)dx
\]

**Examples**

1. Throwing the dice: \( \langle i \rangle = 21/6 = 3.5 \)
2. Particle with uniform probability for position \( x \in [-L, L] \): \( \langle x \rangle = 0 \)

The next important operation is the calculation of the mean squared deviation (MSD) or variance, which tells us how much the realization typically deviates from the average (now only for the discrete case):

\[
\sigma^2 = \langle (i - \langle i \rangle)^2 \rangle = \langle i^2 - 2i\langle i \rangle + \langle i \rangle^2 \rangle
\]
\[
= \langle i^2 \rangle - 2\langle i \rangle^2 + \langle i \rangle^2 = \langle i^2 \rangle - \langle i \rangle^2
\]

Here we have used the fact that averaging is a linear operation. \( \sigma \) is called the standard deviation.

For two random variables, the covariance is defined as

\[
\sigma_{ij}^2 = \langle (i - \langle i \rangle)(j - \langle j \rangle) \rangle = \langle ij \rangle - \langle i \rangle \langle j \rangle
\]

where the average has to be taken with the joint probability distribution if both variables are involved. If \( i \) and \( j \) are independent, then their covariance vanishes.

**Examples**

1. Throwing the dice: \( \sigma^2 = 35/12 = 2.9 \)
2. Particle with uniform probability for position \( x \in [-L, L] \): \( \sigma^2 = L^2/3 \)

1.7 Binomial distribution

The binomial distribution is the most important discrete distribution. We consider two possible outcomes with probabilities \( p \) and \( q \) (\( p + q = 1 \), binary process), respectively, and repeat the process \( N \) times.
Examples

1. flipping a coin \(N\) times, outcomes head or tail

\[\begin{array}{c}
0.5 \\
0.5 \\
0.5 \\
0.5 \\
0.5 \\
0.5 \\
0.5 \\
0.5 \\
\end{array}\]

Figure 1.1: lineage tree for the ideal coin experiment

2. following a ball falling through an ‘obstacle array’

\[\begin{array}{c}
\bullet \\
\bullet \\
\bullet \\
\bullet \\
\bullet \\
\bullet \\
\bullet \\
\bullet \\
\end{array}\]

Figure 1.2: obstacle array

3. stepping \(N\) times forward or backward along a line \(\Rightarrow\) 1D Brownian random walk (‘drunkard’s walk’)

\[\begin{array}{c}
x \\
| \Delta x \\
\end{array}\]

\[\begin{array}{c}
\Delta t \\
t \\
\end{array}\]

Figure 1.3: random walk: one possible path out of many

4. throwing the dice \(N\) times and counting \(\#\{6\}\) \(\Rightarrow p = \frac{1}{6}, q = \frac{5}{6}\)

5. \(N\) independent spins with magnetic moment \(\mu\) in an external magnetic field \(B\) pointing up:
\[ p_{up} = c \cdot e^{\mu B/k_B T}, \quad p_{down} = c \cdot e^{-\mu B/k_B T} \quad (c \text{ is determined by } p + q = 1.) \]

6 N gas atoms are in a box of volume \( V \) which is divided into subvolumes \( pV \) and \( qV \). On average \( \langle n \rangle = p \cdot N \) atoms are in the left compartment. What is the probability for a deviation \( \Delta n \)? Or the other way round: Can one measure \( N \) by measuring the frequencies of deviations \( \Delta n \) ?

![Figure 1.4: gas box with two compartments](image)

In the following we use the terms of example 1. What is the probability to get \( i \in \{0, 1, ..., N\} \) heads? Because every throw is independent we have to multiply the probabilities:

\[ p^i \cdot q^{N-i} \]

However, there is more than one sequence of head and tails to arrive at \( i \) heads. The number of realizations is given by the \textit{binomial coefficient}:

\[ \frac{N(N-1)\ldots(N-(i-1))}{i(i-1)\ldots1} = \frac{N!}{(N-i)!i!} = \binom{N}{i} \quad \text{binomial coefficient} \]

The binomial coefficient is the number of ways one can choose \( i \) objects out of \( N \). The numerator is the number of ways we can select \( i \) objects out of \( N \) without putting them back. However, here we assume that we have numbered the objects and care for their identify. We therefore have to correct for the number of ways to rearrange the \( i \) objects, which is the denominator.

Another way to understand that the binomial coefficient has to appear here is to write our procedure of repeating the experiment with the two possible outcomes \( N \) times:

\[ (p + q)^N = (p + q)(p + q)\ldots(p + q) = \sum_{i=0}^{N} \binom{N}{i} \cdot p^i q^{N-i} \]

where in the last step we have used the binomial formula \( (x + y)^N = \sum_{i=0}^{N} \binom{N}{i} x^i y^{N-i} \).

Thus the binomial coefficient simply gives the multiplicity that arises from multiplying out this expression. Remember Pascal’s triangle (Figure 1.5):

\[ \binom{N}{i} = \binom{N-1}{i-1} + \binom{N-1}{i} \]
In summary, we now have for the binomial distribution:

$$p_i = \binom{N}{i} \cdot p^i \cdot q^{N-i}$$

Note that normalization is ensured:

$$\sum_{i=0}^{N} p_i = \sum_{i=0}^{N} \binom{N}{i} \cdot p^i q^{N-i} = (p+q)^N = 1^N = 1$$

Obviously we have $2^N$ possible outcomes of the experiment, which we also see by considering

$$\sum_{i=0}^{N} \binom{N}{i} = \sum_{i=0}^{N} \binom{N}{i} 1^i \cdot 1^{N-i} = (1+1)^N = 2^N$$

**Example**

We plot the binomial distribution in Figure 1.6 for $p = \frac{1}{6}$ and $N = 10$. This is the probability to get $i$ times a 6 when we throw the dice 10 times. The average of this distribution is $N \cdot p = 10/6 = 1.67$ and close to the peak.

Next we want to characterise the binomial distribution. It typically looks like in Figure 1.6 with one clear peak. We first calculate the average $\mu$: 

![Figure 1.5: Pascal's triangle with sums on the right](image-url)
Figure 1.6: Binomial distribution for $p = \frac{1}{6}$, $N = 10$. Points are joined by lines to better show the shape of the distribution.

\[
\mu = \langle i \rangle = \sum_{i=0}^{N} i \cdot p_i = \sum_{i=0}^{N} i \cdot \frac{N!}{(N - i)!i!} p^i \cdot q^{N-i}
\]

\[
= N \cdot p \sum_{i=1}^{N} \frac{(N - 1)!}{(N - i)!(i - 1)!} p^{i-1} \cdot q^{N-i}
\]

\[
= N \cdot p \sum_{i=1}^{M} \frac{M!}{j!(M-j)!} p^j \cdot q^{M-j} = N \cdot p
\]

where we relabeled according to $M = N - 1$, $j = i - 1$ and used $(N - i) = (N - 1) - (i - 1) = M - j$.

A more elegant way to get the same result is:

\[
\langle i \rangle = \sum_{i=0}^{N} \binom{N}{i} (p \cdot \frac{d}{dp}) p^i \cdot q^{N-i}
\]

\[
= (p \frac{d}{dp}) (p + q)^N = N \cdot p(p + q)^{N-1} = N \cdot p
\]

The trick is to consider $p$ as a variable before using $p + q = 1$ in the final step.

We now use the same trick to calculate the second moment:
The mean squared deviation (MSD or variance) follows as:

$$\sigma^2 = \langle (i - \langle i \rangle)^2 \rangle = \langle i^2 \rangle - \langle i \rangle^2$$

$$= p \cdot N + p^2 \cdot N(N - 1) - p^2 \cdot N^2 = p \cdot N - p^2 \cdot N$$

$$= p \cdot N(1 - p) = N \cdot p \cdot q \quad \text{vanishes for } p = 0 \text{ or } q = 0$$

$$\Rightarrow \langle i \rangle = p \cdot N, \quad \sigma^2 = N \cdot p \cdot q$$

$\sigma$ is called ‘width’ or ‘standard deviation’ (SD). The ‘relative width’ or ‘coefficient of variation’ is then given as

$$\frac{\sigma}{\mu} = \sqrt{\frac{N \cdot p \cdot q}{N \cdot p}} = \sqrt{\frac{q}{p}} \cdot \frac{1}{\sqrt{N}} \quad \overset{N \rightarrow \infty}{\longrightarrow} 0$$

This is an example of the ‘law of large numbers’: For large $N$ the distribution becomes very sharp.

**Examples**

1. $10^{24}$ gas atoms in a box, divided into two compartments of equal size

   $$\Rightarrow p = q = 0.5$$

   $$\Rightarrow \mu = N \cdot p = N / 2 \quad \text{atoms on average on left side}$$

   The actual number deviates by

   $$\sigma = \sqrt{N \cdot p \cdot q} = 0.5 \cdot 10^{12}$$

   $$\Rightarrow \frac{\sigma}{\mu} = 10^{-12} \quad \text{the relative deviation is tiny! This is the reason why thermodynamics works!}$$

2. We can use the result for the standard deviation to check experimentally if a die is ideal. We throw $N = 10^5$ times and find $n = 1.75 \cdot 10^4$ times a $\{6\}$

   $$\Rightarrow p_6 = \frac{n}{N} = 0.175$$
This is not in agreement with the ideal value $p_6 = 0.167$. However, how relevant is the deviation? We calculate the expected deviation for $p_6$:

$$\frac{\Delta n}{N} = \frac{\sqrt{N \cdot q \cdot p}}{N} = \frac{\sqrt{5}}{6\sqrt{N}} = 0.001$$

where we have used $p = 1/6$ and $q = 5/6$ for the ideal die. Because the measured value is farther away from the ideal $p_6$ than this, we conclude that the die is not ideal. Note that for $N = 10^3$ the width $\sigma = 0.012$ would have been too large to draw this conclusion.

1.8 Continuum limit of the binomial distribution

![Figure 1.7: change of the binomial distribution with increasing N](image)

We now consider the case that we perform infinitely many realizations of the binary process. For $p = \text{const}$ the limit $N \to \infty$ implies:

$$\mu = p \cdot N \to \infty \quad \text{for } N \to \infty.$$  

However, the relative width $\frac{\sigma}{\mu}$ becomes smaller and smaller:

$$\frac{\sigma}{\mu} = \sqrt{\frac{1 - p}{p} \frac{1}{\sqrt{N}}} \to 0 \quad \text{for } N \to \infty.$$  

Where is the peak of the distribution?

$$p_i = \binom{N}{i} p^i q^{N-i}$$

A Taylor expansion around the peak is problematic, because $p_i = \binom{N}{i} p^i q^{N-i}$ is a sensitive function of $i$. Therefore it is better to expand its logarithm $\ln p_i$. In regard to the normalization, our method is an example of the saddle-point approximation or method of steepest descent.
We start by taking the logarithm:
\[
\ln p_i = \ln N! - \ln i! - \ln (N - i)! + i \ln p + (N - i) \ln q
\]

We need derivatives:
\[
\frac{d \ln i!}{di} \approx \frac{\ln(i + 1)! - \ln i!}{1} = \ln(i + 1) \approx \ln i \quad \text{for } i \gg 1
\]

Integration yields:
\[
\ln i! \approx i \ln i - i + O(\ln(i))
\]

This agrees with Stirling’s formula:
\[
\ln i! = i \ln i - i + O(\ln(i))
\]

Back to \( p_i \):
\[
\Rightarrow \frac{d \ln p_i}{di} = -i + \ln(N - i) + \ln p - \ln q
\]
\[
= \ln \left(\frac{(N - i)p}{i \cdot q}\right) = 0 \quad \text{at peak } i_m
\]
\[
\Rightarrow (N - i_m)p = i_m(1 - p)
\]
\[
\Rightarrow i_m = \frac{p \cdot N}{1 - p} \quad \text{at peak}
\]

We note that peak and average are the same for the binomial distribution.

We next consider the second derivative
\[
\frac{d^2 \ln(p_i)}{di^2} = -\frac{1}{i} - \frac{1}{N - i} = -\frac{N}{i(N - i)}
\]

which we then evaluate at the peak position as
\[
\Rightarrow \ln p_i = \ln p_\mu - \frac{1}{2} \frac{1}{\sigma^2} (i - \mu)^2 + ...
\]
\[
\Rightarrow p_i = p_\mu \cdot e^{-\frac{(i - \mu)^2}{2\sigma^2}}
\]

This is a Gaussian with average \( \mu = p \cdot N \) and variance \( \sigma^2 = N \cdot p \cdot q \).
Note that this does not work for $p \to 0$. We need $p = \text{const}$, hence $\mu = p \cdot N \to \infty$. Our expansion is valid for

$$\frac{i - \langle i \rangle}{N \cdot p \cdot q} \ll 1$$

that is for distances of the order of $\sigma$ around the peak at $\mu$. Farer away, the expansion is not valid, but absolute values are of the order $e^{-\sqrt{N}}$ and can be neglected. Thus our derivation works as long as $\sigma^2 = N \cdot p \cdot q \gg 1$. If we take the alternative limit

$$N \to \infty, \quad p \to 0, \quad p \cdot N = \mu = \text{const}$$

this yields the so called 'Poisson distribution' for rare events. This one-parameter distribution is given as

$$p_i = \frac{\mu^i}{i!} \cdot e^{-\mu} \quad \text{with } \sigma^2 = \mu$$

with variance and average being identical.

We now change from index $i$ to a spatial variable $x = N \cdot \Delta x$ with $\mu_x = \mu \cdot \Delta x$ and $\sigma_x = \sigma \cdot \Delta x_i$.

$$\Delta x \propto \frac{1}{N} \to 0 \quad \text{for } N \to \infty$$

$$\Rightarrow \mu_x = p \cdot N \cdot \Delta x = \text{const}$$

$$\Rightarrow p(x) = p_m \cdot e^{-\frac{(x-\mu)^2}{2\sigma^2}} \quad \text{continuous probability density}$$

The probability for the continuous random variable $x \in [x_1, x_2]$ is given by

$$\int_{x_1}^{x_2} dx \, p(x)$$

where we integrated over $p(x) \, dx$, the probability to find $x$ between $x$ and $x + dx$. The continuous probability distribution $p(x)$ is actually a probability density, because we have to integrate to turn it into a probability.

Regarding the normalization, we first note that it is independent of the average $\mu$, so we can take $\mu = 0$:

$$\int p(x) \, dx = 1 = p_m \int_{-\infty}^{\infty} dx \, e^{-x^2/(2\sigma^2)}$$

Thus we have to deal with the Gauss integral:

$$\int dx \, e^{-ax^2} = \left( \int dx \, e^{-ax^2} \int dy \, e^{-ay^2} \right)^{\frac{1}{2}}$$

$$= \left( \int_0^{2\pi} d\phi \int_0^{\infty} dr \, r \cdot e^{-ar^2} \right)^{\frac{1}{2}}$$

$$= \left( 2\pi \int_0^{\infty} \frac{1}{2} du \, e^{-au} \right)^{\frac{1}{2}}$$

$$= \left( \frac{\pi}{a} \right)^{\frac{1}{2}}$$
In the following, we often need the second moment of this distribution:

\[
\left( \frac{a}{\pi} \right)^{\frac{1}{2}} \int dx \, x^2 e^{-ax^2} = - \left( \frac{a}{\pi} \right)^{\frac{1}{2}} \frac{d}{da} \int dx \, e^{-ax^2} \\
= - \left( \frac{a}{\pi} \right)^{\frac{3}{2}} \cdot \frac{d}{da} \left( \frac{\pi}{a} \right)^{\frac{1}{2}} = \frac{1}{2a}
\]

In our case \( a = 1/(2\sigma^2) \) and thus \( p_m = (2\pi\sigma^2)^{-\frac{1}{2}} \)

\[
\Rightarrow p(x) = \frac{1}{(2\pi\sigma^2)^{\frac{1}{2}}} \cdot e^{-(x-\mu)^2/(2\sigma^2)} \quad \text{Gauss or normal distribution}
\]

Its variance is \( \langle x^2 \rangle = \frac{1}{2a} = \sigma^2 \). Thus the factor of 2 in the Gaussian is needed to get the correct variance.

![Gaussian with indicated 1σ-interval](image)

Figure 1.8: Gaussian with indicated 1σ-interval

The probability to find \( x \) within an interval of one, two or three standard deviations around \( \mu \) is

\[
\int_{\mu-m\sigma}^{\mu+m\sigma} dx \, p(x) = \begin{cases} 
0.683, & m = 1 \\
0.954, & m = 2 \\
0.997, & m = 3 
\end{cases}
\]

### 1.9 Random walks

As indicated in Figure 1.3, a random walk is the trajectory in which for each step we draw a random number to decide whether to step to the left or to the right. This has been compared to a drunkard walking home along the pavement. To make this more precise, we define the following quantities:

- \#right steps: \( n_1 = i \)
- \#left steps: \( n_2 = N - i \)
time: \( t = N \cdot \Delta t \)

position: \( x = m \cdot \Delta x \)

\[
m = n_1 - n_2 = i - (N - i) = 2i - N
\]

Note that at a given time step the particle can be only at an even or odd position. Our terms yield the following average:

\[
\Rightarrow \langle x \rangle = (2\langle i \rangle - N)\Delta x = (2p - 1)N \cdot \Delta x
\]

\[
= \left( \frac{\Delta x}{\Delta t} \right) \cdot t \quad \text{drift velocity } v
\]

\( p = 0.5 \) (symmetric random walk) \( \Rightarrow v = 0 \).

\[
\langle x^2 \rangle = \langle (2i - N)^2 \rangle \Delta x^2
\]

\[
= (4\langle i^2 \rangle - 4\langle i \rangle N + N^2)\Delta x^2
\]

\( p = 0.5 \rightarrow \langle x^2 \rangle = (N + N^2(1 - 2 + 1))\Delta x^2 = N\Delta x^2
\]

\[
= \frac{\Delta x^2}{\Delta t} \cdot t = 2 \cdot D \cdot t \quad \text{identifying the diffusion constant } D = \frac{\Delta x^2}{2\Delta t}
\]

\[
\sigma^2 = \langle x^2 \rangle = 2 \cdot D \cdot t
\]

\( \Rightarrow \sigma \propto \sqrt{t} \)

The ‘mean squared displacement’ (MSD) grows \( \propto t \), the ‘root mean squared displacement’ (RMSD) grows as \( \propto t^{0.5} \).

![Figure 1.9: ballistic versus diffusive movement](image)

A more general derivation for arbitrary dimensions \( d \) is as follows: We consider the end-to-end vector defined by

\[
\vec{R} = \sum_{i=1}^{N} \vec{r}_i
\]
For the mean squared displacement we get
\[ \langle \vec{R}^2 \rangle = 2 \cdot d \cdot D \cdot t \]

The most important aspect here is that two random vectors are uncorrelated if \( i \neq j \), so all off-diagonal terms vanish and only the diagonal terms survive. This creates the linear scaling with \( N \) and therefore also with \( t \).

\( d \) is the spatial dimension and we use Pythagoras and the fact that all dimensions are equivalent. In one dimension, \( d = 1 \), this result becomes the same as above. Note that if you identify time with contour length, this would be a model for a polymer (freely jointed chain).

**Rate equation**

Above we have derived the global properties of the random walk. Now we address its local properties and see that in the end we get the same results again.

We ask how the equation of motion looks like for a random walk particle. It turns out that this is a rate equation. In each time step the particle has to jump to the position \( m \) either from the left or from the right. Let \( p(m, N) \) be the probability to be at position \( m \) at time \( N \).
\[ p(m, N + 1) = p(m - 1, N) \cdot p + p(m + 1, N) \cdot q \]

\[ p = q = 0.5 \quad \Rightarrow \quad p(m, N + 1) - p(m, N) = \frac{p(m - 1, N) + p(m + 1, N) - 2p(m, N)}{2} \]

The term ‘derivative’ can be justified doing a Taylor expansion around \( x \):

\[
\begin{align*}
  f(x + \Delta x) &= f(x) + f'(x) \cdot \Delta x + \frac{1}{2} f''(x) \cdot \Delta x^2 + \\
  f(x - \Delta x) &= f(x) - f'(x) \cdot \Delta x + \frac{1}{2} f''(x) \cdot \Delta x^2 + 
\end{align*}
\]

Adding these two expressions and dividing by \( \Delta x^2 \) results in an expression for the second derivative:

\[ f''(x) = \frac{f(x + \Delta x) + f(x - \Delta x) - 2f(x)}{\Delta x^2} \]

Going back to our rate equation, we can write

\[
p(x, t + \Delta t) - p(x, t) = \frac{p(x - \Delta x, t) + p(x + \Delta x, t) - 2p(x, t)}{2} \cdot D \cdot \frac{2\Delta t}{\Delta x^2}
\]

We now use the expression for the second derivative and take the continuum limit:

\[ \Delta x, \Delta t \to 0 \quad \Rightarrow \quad \frac{\partial p(x, t)}{\partial t} = D \cdot p''(x, t) \quad \text{diffusion equation} \]

We note that the one-dimensional symmetric random walk obeys a diffusion equation, which in mathematical terms is a partial differential equation. For the initial condition

\[ p(x, t = 0) = \delta(x) \]

the solution is given by a Gaussian

\[ p(x, t) = \frac{1}{\sqrt{4\pi \cdot D \cdot t}} \cdot e^{-x^2/(4Dt)} \]
Note that by taking the continuum limit, we allow for arbitrary large values of $x$. In the discrete case, we have a binomial distribution on a finite domain.

Comparing with the Gaussian distribution, we see that $\sigma = \sqrt{2 \cdot D \cdot t}$ so as the global analysis, also the local considerations give us again the square root scaling of a random walk.

![Figure 1.12: Two distributions with different t values. The distribution’s width $\sigma = \sqrt{2 \cdot D \cdot t}$ increases with the root of time.](image)

How does this look if $p \neq \frac{1}{2}$, that is in the case of an asymmetric random walk?

$$p = -v \cdot p' + D \cdot p''$$

This equation has many names (Fokker-Planck equation, Smoluchowski equation, drift-diffusion equation, advection-diffusion equation, convection-diffusion equation, etc). It is very similar to the Schrödinger equation (the two convert into each other if we consider an imaginary time).

**Mean first passage time**

We finally consider the following question. A particle is performing a symmetric random walk in $d = 1$ with step size $\delta$ and jump time $\tau$ in the interval $x \in [0, b]$. We ask how long it will take to leave this boundary. Obviously this time will depend on the starting position $x$ and we call it $T(x)$, the mean first passage time. We now use a similar consideration as for the rate equation to write

$$T(x) = \tau + \frac{1}{2} [T(x + \delta) + T(x - \delta)]$$

We rearrange to get

$$\frac{1}{\delta^2} [T(x + \delta) + T(x - \delta) - 2T(x)] + \frac{2\tau}{\delta^2} = 0$$
We identify again a second spatial derivate and perform the continuum limit to get

\[ T''(x) + \frac{1}{D} = 0 \]

Thus we have obtained an ordinary differential equation for \( T(x) \). The solution has to be a polynomial of order 2 that depends on boundary conditions. For two absorbing boundaries we have \( T(0) = T(b) = 0 \) and the solution is

\[ T(x) = \frac{1}{2D}(2bx - x^2) \]

We assume that the position is released at a random position and therefore we average over \( x \):

\[ T = \frac{1}{b} \int_0^b T(x)dx = \frac{b^2}{12D} \]

Again we see that the time scales with the distance \( b \) squared. The inverse scaling with \( D \) is expected for dimensional reasons. The prefactor \( 12 \) can only be obtained by doing the full calculation. For a reflecting boundary at \( x = 0 \), one has to use the boundary condition \( T'(0) = 0 \).

1.10 Computation with random variables

Let \( x \) be some random variable with a continuous distribution \( p(x) \). We consider a coordinate transformation \( x \rightarrow y(x) \). Assuming that also the inverse transformation \( y \rightarrow x(y) \) exists, we want to know what the probability distribution \( p_y(y) \) is. This result is easily obtained using the transformation theorem.

\[ 1 = \int dx \ p_x(x) = \int dy \ \left| \frac{dx}{dy} \right| p_x(x(y)) \]

Examples

\[ \begin{align*}
    y &= c \cdot x \\
    \Rightarrow \quad p_y(y) &= \frac{1}{c} \cdot p_x \left( \frac{y}{c} \right)
\end{align*} \]

Another way to see this:

\[ p_y(y) = \int dx \ p_x(x)\delta(y - cx) \]

\[ = \int \frac{dz}{c} p_x \left( \frac{z}{c} \right) \delta(z - y), \quad \text{substituting } z = c \cdot x \]

\[ = \frac{1}{c} p_x \left( \frac{y}{c} \right) \]
Moments:

\[ \langle y \rangle = \int dy \ y \cdot p_y(y) = \int (c \ dx)(c \cdot x) \frac{1}{c} \cdot p_x(x) = c \langle x \rangle \]

\[ \langle y^2 \rangle = \int dy \ y^2 \cdot p_y(y) = c^2 \langle x^2 \rangle \]

\[ \sigma_y^2 = \langle (y - \langle y \rangle)^2 \rangle = \langle y^2 \rangle - \langle y \rangle^2 = c^2 \cdot \sigma_x^2 \]

2

\[ y = -\frac{1}{\omega} \ln(1 - x) \]

\[ \Rightarrow x = 1 - e^{-\omega y} \]

\[ \Rightarrow p_y(y) = \omega \cdot e^{-\omega y} \cdot p_x(x(y)) \]

Let's take \( x \) to be a uniformly distributed variable in \([0, 1]\) with \( p_x(x) := 1 \). We will need this later, eg for Monte Carlo simulations of the Boltzmann distribution.

\[ \Rightarrow p_x = 1 \Rightarrow y \text{ is exponentially distributed} \]

3

A similar procedure exists in higher dimensions. We have a look at an n-tupel \( \vec{x} = (x_1, ..., x_n) \). This tupel is transformed to another tupel \( y_i(\vec{x}) \) with the index \( i \) in the set \([1, ..., n]\):

\[ p_{\vec{y}}(\vec{y}) = \left| \frac{\partial (x_1, ..., x_n)}{\partial (y_1, ..., y_n)} \right| \cdot p_{\vec{x}}(\vec{x}(\vec{y})) \]

A standard method to obtain Gaussian random variables is the Box-Müller procedure:

\[ y_1 = \sqrt{-2 \ln x_1} \cos 2\pi x_2 \]

\[ y_2 = \sqrt{-2 \ln x_1} \sin 2\pi x_2 \]

\[ \Rightarrow x_1 = e^{-\frac{1}{2}(y_1^2 + y_2^2)} \]

\[ \Rightarrow x_2 = \frac{1}{2\pi} \arctan \frac{y_2}{y_1} \]

\[ \Rightarrow p_{\vec{y}}(\vec{y}) = \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}y_1^2} \cdot \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}y_2^2} \cdot p_{\vec{x}}(\vec{x}) \]

Both \( y_1 \) and \( y_2 \) are Gaussian distributed with \( \sigma = 1 \), if \( x_1 \) and \( x_2 \) are uniformly distributed in \([0, 1]\).
1.11 The central limit theorem

We next consider the addition of two random variables \( x \) and \( y \). Given \( p_x(x), p_y(y) \), we define \( z = x + y \) and write

\[
p_z(z) = \int dx dy \delta(z - (x + y)) p(x, y) = \int dx \ p(x, z - x) = \int dx \ p_x(x)p_y(z - x)
\]

where in the last step we have assumed that the two variables are independent. We see that the resulting probability distribution is a convolution. This suggests that it might be helpful to use Fourier transforms.

For a given probability distribution \( p(x) \), we define the following characteristic or generating function:

\[
G(k) = \langle e^{ikx} \rangle = \int dx \ p(x) e^{ikx}
\]

which is the Fourier transform of \( p(x) \).

If all moments exist, we can make a Taylor expansion:

\[
G(k) = \sum_{n=0}^{\infty} \frac{(ik)^n}{n!} \langle x^n \rangle
\]

\[
\Rightarrow \quad \langle x^n \rangle = \mu_n = \left. \frac{1}{i^n} \frac{d^n G(k)}{dk^n} \right|_{k=0}
\]

Hence if we know the characteristic function we can generate all moments \( \mu_n \).

Now let us do the same thing for the logarithm:

\[
\ln G(k) = \sum_{n=0}^{\infty} \frac{(ik)^n}{n!} \cdot \kappa_n
\]

The cumulants can be generated using the same trick as above:

\[
\kappa_n = \left. \frac{1}{i^n} \frac{d^n \ln G(k)}{dk^n} \right|_{k=0}
\]

Looking at the first few cumulants, we see that they are interesting quantities:

\[
\kappa_0 = \ln G(k)|_{k=0} = \ln 1 = 0
\]

\[
\kappa_1 = \frac{1}{i} \left. \frac{G'}{G} \right|_{k=0} = \langle x \rangle
\]

\[
\kappa_2 = \frac{1}{i^2} \left. \frac{G''G - G'^2}{G^2} \right|_{k=0} = \langle x^2 \rangle - \langle x \rangle^2 = \sigma^2
\]

The third cumulant looks more complicated:

\[
\kappa_3 = \frac{1}{i^3} \left. \left( G''' - 3G'G'' + 2G'^3 \right) \right|_{k=0} = \mu_3 - 3\mu_1\mu_2 + 2\mu_1^3
\]

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The cumulants are specific combinations of the moments. The relation can also be reversed:

\[
\begin{align*}
\mu_1 &= \kappa_1 \\
\mu_2 &= \kappa_2 + \kappa_1^2 \\
\mu_3 &= \kappa_3 + 3\kappa_2\kappa_1 + \kappa_1^3
\end{align*}
\]

A probability distribution is completely characterised by its moments or cumulants (except if its moments are not finite, as for the Lorentz distribution). A theorem of Marcinkiewicz from 1939 states that either all but the first two cumulants vanish or there are an infinite number of non-vanishing cumulants.

**Examples**

The most important example is the Gauss distribution. Its characteristic function is given as:

\[
G(k) = \int dx \ e^{ikx} \cdot \frac{1}{(2\pi\sigma^2)^\frac{1}{2}} \cdot e^{-(x-\mu)^2/(2\sigma^2)}
\]

\[
= \int dx \ \frac{1}{(2\pi\sigma^2)^\frac{1}{2}} \cdot e^{-(x-\mu-\frac{ik}{\sigma^2})^2/(2\sigma^2)}
\]

\[
= e^{-\frac{1}{2}k^2\sigma^2+ik\mu}
\]

\[\Rightarrow \ln G(k) = ik\mu - \frac{1}{2}k^2\sigma^2\]

\[\Rightarrow \kappa_1 = \frac{1}{i} \left. \frac{d \ln G}{dk} \right|_{k=0} = \mu
\]

\[\kappa_2 = \frac{1}{i^2} \left. \frac{d^2 \ln G}{dk^2} \right|_{k=0} = \sigma^2
\]

All other \(\kappa_i\) vanish. The Gauss distribution is the only one having just two non-zero cumulants.

Back to addition of two random variables \(x\) and \(y\):

\[z = x + y\]

\[\Rightarrow \quad p_z(z) = \int dx \ p_x(x) \cdot p_y(x-z)\]

Due to the convolution theorem this becomes

\[G_z(k) = G_x(k) \cdot G_y(k)\]

\[\Rightarrow \ln G_z(k) = \ln G_x(k) + \ln G_y(k)\]
Having in mind the definition of the cumulants this yields

\[ \kappa_n^{(z)} = \kappa_n^{(x)} + \kappa_n^{(y)} \]

By iteration, hence \( z = x_1 + \ldots + x_N \), it is possible to construct the \( n \)-th cumulant:

\[ \kappa_n^z = \sum_{i=1}^{N} \kappa_n^{(i)} \]

We are now in a state to formulate the central limit theorem:

***If a random variable is the sum of many independent random variables, then it has a Gaussian distribution.***

**Proof**

\[ Z = \frac{1}{N} (x_1 + \ldots + x_N) \]

\[ \Rightarrow \langle z \rangle = \frac{1}{N} \sum_{i}^{N} \langle x_i \rangle = \langle x \rangle \]

\[ \Rightarrow \sigma_z^2 = \left( \frac{1}{N} \right)^2 \sum_{i=1}^{N} \sigma_{x_i}^2 = \frac{1}{N} \sigma_x^2 = \frac{\sigma_x^2}{N} \]

\[ \kappa^z_n = \left( \frac{1}{N} \right)^n \sum_{i=1}^{N} \kappa_n^{(i)} = \frac{1}{N^{n-1}} \kappa_n^x \]

\[ \Rightarrow \text{for } N \to \infty \text{ all higher cumulants vanish, with finite average and variance } \propto \frac{1}{N} \]

\[ \Rightarrow p(z) \text{ is that of a Gaussian with variance } \sigma_z^2 / N \]

Actually the essence of the CLT becomes clearer if we define the new variable to be

\[ Z = \frac{1}{\sqrt{N}} (x_1 + \ldots + x_N) \]

and ask for \( \langle x_i \rangle = 0 \). Then \( \langle Z \rangle = 0, \sigma_Z^2 = \sigma_x^2 \) and all higher cumulants vanish in the limit of very large \( N \). However, the definition above is experimentally more relevant.

### 1.12 Information entropy

In 1948 Claude Shannon introduced a measure for uncertainty of a probability distribution which agrees with the thermodynamic definition of entropy. The relation between information theory and statistical physics was further discussed by Edwin Jaynes in 1957, who introduced the maximum entropy principle, which today is widely used in
statistical data analysis (e.g., image processing).

For a given discrete probability distribution $p_i$, we introduce a dimensionless measure for its disorder, the entropy:

$$S = -\sum_i p_i \ln p_i$$

**Comments**

1. $0 \leq p_i \leq 1 \implies S \geq 0$

![Graph](image)

Figure 1.13: $-x \cdot \ln x$ as a function of $x$

2. $\exists j: p_j = 1 \implies p_i = 0 \text{ for } i \neq j \implies S = 0$
   
The entropy is minimal, if outcome is certain.

3. For a given homogeneous distribution $p_i = \text{const} = \frac{1}{\Omega}$, with $\Omega = \#\text{states}$:

$$\sum_i p_i = \sum_{i=1}^\Omega \frac{1}{\Omega} = \Omega \cdot \frac{1}{\Omega} = 1$$

$$S_h = -\sum_{i=1}^\Omega \frac{1}{\Omega} \ln \frac{1}{\Omega} = \ln \Omega$$

Hence we see that entropy increases with the number of states.
Entropy is maximal for the homogeneous distribution.

\[ S_h - S = \sum_{i=1}^{\Omega} p_i \ln p_i + \ln \Omega \]

\[ = \sum_{i=1}^{\Omega} p_i \ln p_i + \sum_{i=1}^{\Omega} p_i \ln \Omega \]

\[ = \frac{1}{\Omega} \sum_{i=1}^{\Omega} (p_i \Omega) \ln (p_i \Omega) \]

Our aim is to minimize \( S_h - S \). Direct minimization gives us

\[ \delta (S_h - S) = \frac{1}{\Omega} \sum_{i=1}^{\Omega} (\ln x_i + 1) \delta x_i = 0 \Rightarrow x_i = e^{-1} \]

because \( x = 1/e \) is the position of the minimum of \( x \ln x \) and because each term has to be minimized by itself independent of the others. However, this result does not satisfy the normalization constraint \( \sum_{i=1}^{\Omega} x_i = \Omega \). We add this constraint to the target function with a Lagrange parameter \( \lambda \) and thus have

\[ \frac{1}{\Omega} \sum_{i=1}^{\Omega} (\ln x_i + 1 + \lambda) \delta x_i = 0 \Rightarrow x_i = e^{-(1+\lambda)} \]

Implementing the constraint specifies \( \lambda = -1 \) and thus \( x_i = 1 \) will be the correct solution. Hence the entropy (or disorder) is maximal for the (normalized) homogeneous distribution and all other distributions have smaller entropies.

The same result can also be obtained by using a small trick rather than a Lagrange parameter. Rather than introducing \( \lambda \), we add zero to the target function in a way that only works for the properly normalized distribution:

\[ S_h - S = \frac{1}{\Omega} \sum_{i=1}^{\Omega} x_i \ln x_i + \frac{1}{\Omega} \sum_{i=1}^{\Omega} (1 - x_i) \]

\[ = \frac{1}{\Omega} \sum_{i=1}^{\Omega} (x_i \ln x_i + 1 - x_i) \]

\[ \Rightarrow \text{The only minimum (Figure 1.14) is at } x_i = 1. \]

Thus we get the same result as for the calculation with the Lagrange parameter.

We consider two independent subsystems 1 and 2:

\[ p_{ij} = p_i^{(1)} \cdot p_j^{(2)} \]
$\Rightarrow S = - \sum_{i,j} p_{ij} \ln p_{ij}$

$= \sum_{i,j} p_i^{(1)} p_j^{(2)} \left[ \ln p_i^{(1)} + \ln p_j^{(2)} \right]$

$= - \sum_i \left( \sum_j p_j^{(2)} \right) p_i^{(1)} \ln p_i^{(1)} - \sum_j \left( \sum_i p_i^{(1)} \right) p_j^{(2)} \ln p_j^{(2)}$

$= S_1 + S_2$

Entropy is additive for independent subsystems.

6 A bit of information theory: How many ‘yes-or-no’ questions do we have to ask to find out which state $j$ is realized? We divide $\Omega$ into two disjunct domains $\Omega_1$ and $\Omega_2$ such that

$$\sum_{i \in \Omega_1} p_i = \sum_{i \in \Omega_2} p_i = \frac{1}{2}$$

Firstly we ask: Is $j$ in $\Omega_1$? We then choose the correct domain and scale the probability by 2 and repeat the dividing procedure. This has to be done $k$-times while $k$ is given by

$$2^k p_j = 1 \Rightarrow k = - \ln_2 p_j$$

On average, the number of questions required is

$$\sum_{i=1}^{\Omega} p_i (- \ln_2 p_i) = S + \text{const}$$

We conclude that entropy is not only a measure for disorder but also for uncertainty.
We now aim to maximize entropy with the additional constraint:

\[ U = \sum_i p_i E_i = \text{const} \]

Here \( E_i \) is some scalar property of each state (later this will be energy, thus \( U \) will be the average energy).

\[ \Rightarrow \delta S = -\sum_{i=1}^{\Omega} (\ln p_i + 1) \delta p_i = 0 \]

Auxiliary conditions:

1. \( \sum_i p_i = 1 \Rightarrow \sum_i \delta p_i = 0 \)
2. \( \sum_i p_i E_i = U \Rightarrow \sum_i E_i \delta p_i = 0 \)

Method of Lagrange multipliers:

\[-\sum_i (\ln p_i + 1 + \lambda_1 + \lambda_2 E_i) \cdot \delta p_i = 0\]

\[\Rightarrow p_i = e^{-(1+\lambda_1+\lambda_2 E_i)}\]

The auxiliary conditions then yield

1. \[ e^{-(1+\lambda_1)} \sum_i e^{-\lambda_2 E_i} = 1 \]
\[ e^{-(1+\lambda_1)} = \frac{1}{\sum_i e^{-\lambda_2 E_i}} := \frac{1}{Z} \]

2. \[ \frac{\sum_i E_i e^{-\lambda_2 E_i}}{\sum_i e^{-\lambda_2 E_i}} = U \]
\[ \Rightarrow \lambda_2 := \beta \text{ is a function of } U \]

\[\Rightarrow p_i = \frac{1}{Z} \cdot e^{-\beta E_i}\]

This exponential distribution later becomes the Boltzmann distribution.
Continuous distribution

In the case of a continuous distribution the entropy becomes:

$$S = - \int dx \, p(x) \ln p(x)$$

For a Gaussian distribution this yields

$$S = \int dx \, \frac{1}{\sqrt{2\pi} \sigma} e^{-(x-\mu)^2/(2\sigma^2)} \left( \frac{(x-\mu)^2}{2\sigma^2} + \frac{1}{2} \ln 2\pi \sigma^2 \right)$$

$$S = \frac{1}{2} \left( 1 + \ln(2\pi \sigma^2) \right)$$

The entropy increases with the variance: The broader the distribution, the larger the disorder or uncertainty.
2 The microcanonical ensemble

2.1 Thermodynamic equilibrium

It is a matter of experience that after some time (relaxation time) an isolated physical system arrives at a state of macroscopic rest (thermodynamic equilibrium). Then a few macroscopic quantities (such as volume $V$, pressure $p$ and temperature $T$) are sufficient to completely characterise the system (state variables). If external conditions are changed, the system adopts a new equilibrium state. If we change external conditions very slowly, the system is going through a series of equilibrium states (quasi-stationary process). Even if a system is in macroscopic equilibrium, its constituents move on a microscopic level as long as temperature is finite. This becomes evident when observing dust particles in gas or liquid, or to be more specific, aerosols in the atmosphere or colloids in a fluid solvent: they all undergo Brownian motion. Therefore many microscopic states correspond to the macroscopic state. The essence of equilibrium statistical physics is to calculate the macroscopic properties of equilibrium states from our knowledge of the underlying microscopic physics.

Examples

1. Consider a gas container with two compartments, of which only one is filled. If the wall is removed, the gas expands until it fills the whole space (Figure 2.1).

2. Again we consider a box with two compartments, this time with two different fluids (black and white). After the separating wall is removed, the fluids mix due to diffusion. A grey final state is established (Figure 2.2).
2.2 Micro- and macrostates

Talking about many \( \approx 10^{23} \) particles, it is neither possible nor desirable to follow their trajectories. Moreover we could be never certain about the initial conditions to assume for such a calculation. Therefore the statistical description aims at averaging or projecting the microstates onto the macrostates without going into the issue of time evolution. The solution to this challenge is a central postulate which will allow us to perform such a procedure. For the averaging procedure, we need a statement about the probability \( p_i \) that a certain microstate \( i \) occurs.

In thermodynamic equilibrium, the microstates are visited one after the other (‘time average’) or occur simultaneously in equivalent realizations (‘ensemble average’). The equivalence of time and ensemble averages is called ‘ergodicity’.

In statistical physics, we first have to identify the relevant microstates. In general, they are characterised by their quantum numbers resulting from the solution of Schrödinger’s equation. Each state \( i \) then has a distinct probability \( p_i \).

**Examples**

Consider a spin-\( \frac{1}{2} \) particle with spin \( |\uparrow\rangle \) and \( |\downarrow\rangle \), hence this is a two state system. For an electron we have the magnetic moment \( \mu = e\hbar /2mc \), energy \( E = -2\mu Hm_z \) and spin \( m_z = \pm 1/2 \). \( H \) is the external magnetic field.
N non-interacting spin-$\frac{1}{2}$ particles. Now the system has $2^N$ possible states. The energy of the system is then given as $E = \sum E_i$.

1D harmonic oscillator $E_n = \hbar \omega (n + \frac{1}{2})$, $n = 0, 1, ...$. This system has infinitely many but countable states.

N atoms in a crystal, each vibrating around its mechanical equilibrium state ("harmonic crystal"). In three dimensions, a simple model is to consider this is a collection of 3N non-interacting harmonic oscillators ("Einstein model"). Although these are infinitely many states, they can be counted easily.

A particle in a box. The Schrödinger equation then is:

$$\frac{-\hbar^2}{2m} \Delta \Psi = E \Psi$$

$$\Rightarrow \Psi(t) = \sin \frac{\pi n_x x}{L_x} \cdot \sin \frac{\pi n_y y}{L_y} \cdot \sin \frac{\pi n_z z}{L_z}$$

$$E = \frac{\pi^2 \hbar^2}{2m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

This system has infinitely many but countable states $(n_x, n_y, n_z)$.

Now consider N such particles in a box without interaction ("ideal gas"). Like for the harmonic crystal, this will be infinitely many states, but they can be counted.

### 2.3 Density of states

We see that in quantum mechanics we can easily count the number of states. The question now is how to deal with classical systems. We clarify this issue using the 1D harmonic oscillator.
In quantum mechanics the energy levels are given as:

$$E_n = \hbar \omega (n + \frac{1}{2})$$

The number of states with $E_n \leq E$ is then obtained as

$$N_E \approx \frac{E}{\hbar \omega}$$

In the classical case it is a bit more complicated:

$$m \ddot{x} + kx = 0 \Rightarrow \omega^2 = \frac{k}{m}$$

$$p = \dot{x}m, \ q = x$$

$$\Rightarrow \ H(q, p) = \frac{1}{2} m \omega^2 q^2 + \frac{p^2}{2m} = E$$

Defining the quantities:

$$a := \sqrt{2mE} \quad b := \sqrt{\frac{2E}{m\omega^2}}$$

$$\Rightarrow \ (p/a)^2 + (q/b)^2 = 1$$

This is the equation of an ellipse in phase space with area $A = \pi a b$ which represents the number of states with energy $\leq E$.

Figure 2.5: The classical 1D harmonic oscillator corresponds to a movement in 2D phase space on the elliptical path that corresponds to energy conservation. The enclosed area $A$ represents all states with equal or lower energy. In quantum mechanics, state space is divided into small boxes of size $\hbar$. Thus $A/\hbar$ is the number of states corresponding to the classical system.
\[ V_E = \pi ab = \frac{2\pi E}{\omega} \]

Comparing this result with the quantum mechanics one gets

\[ N_E = \frac{V_E}{\hbar} \]

Hence we see that the number of classical states is obtained by dividing the phase space volume through the Planck constant \( \hbar \).

This example suggests to count states in a classical system by dividing phase space into boxes of size \( \hbar \). Another argument leading to the same conclusion comes from wave mechanics. According to de Broglie, for a single particle with mass \( m \) we have \( p = \hbar k = mv = h/\lambda \), therefore \( v = h/(m\lambda) \), where \( \lambda \) is the wavelength of the particle. For a wave packet with size \( l \), the uncertainty in position is \( \delta x = l \). The relative uncertainty in wavelength is \( \delta\lambda/\lambda = \lambda/l \). Therefore \( \delta p = m\delta v = h\delta\lambda/\lambda^2 = h/l \) and we finally get the Heisenberg uncertainty relation \( \delta x\delta p = \hbar \), because \( l \) drops out. Therefore in quantum mechanics it is meaningless to choose a smaller box size in phase space and it becomes possible to count the number of states by dividing classical phase space volume by the Planck constant \( \hbar \) (for one particle).

### 2.4 The fundamental postulate

For both classical and quantum mechanical systems, energy \( E \) is a conserved quantity for an isolated system. For a system at rest, \( E \) is the only relevant integral of motion, as suggested by Noether’s theorem (energy conservation follows from invariance to translation in time, and this is always valid). We now consider the ensemble of microstates corresponding to a macrostate with state variables \( E, V, N \) given (‘microcanonical ensemble’). For a system at rest, there is no physical reason to single out any other features of the system as being relevant on the macroscopic level. Let’s assume that the value of \( E \) can be determined with an uncertainty \( \delta E \). We look at the quantum mechanical number of microscopic states between \( E - \delta E \) and \( E \) (‘microcanonical partition sum’):

\[ \Omega(E) = \sum_{n: E - \delta E \leq E_n \leq E} 1 \]

For a classical multiparticle system, one has to correct not only for the microscopic box size as explained above for a single particle, but also for the fact that in quantum mechanics particles are indistinguishable (the wavefunction is invariant under particle exchange) - which yields a factor of \( 1/N! \) due to \( N! \) being the number of possible permutations:

\[ \Omega(E, \delta E) = \frac{1}{h^{3N} N!} \int_{E - \delta E \leq H(\vec{q}, \vec{p}) \leq E} d\vec{q} \, d\vec{p} \]
if we count the number of microscopic states in classical phase space (counting from quantum mechanics is straightforward and does not need any further comments).

What is the probability density $\rho$ for the microcanonical ensemble? First we know that $\rho$ has to vanish outside the energy hypersurface in phase space. Second we expect that the system smears out its presence in phase space as it goes towards equilibrium. Several reasons have been evoked for this expectation, including deterministic chaos and spreading of the wavefunction in a system that is not perfectly isolated. Also one can use Liouville’s and von Neumann’s equations to motivate this (see below). Here however we take this expectation as our fundamental postulate and show that the whole machinery of statistical mechanics and thermodynamics follows from this one postulate:

For an isolated system at equilibrium, all microstates are equally probable.

$$p_i(E) = \begin{cases} \frac{1}{\Omega(E)} = \text{const} & E - \delta E \leq E_i \leq E \\ 0 & \text{otherwise} \end{cases}$$

Due to its huge success, there is no doubt that the fundamental postulate is correct. We note that the homogeneous distribution maximizes entropy

$$S = -k_B \sum_{i=1}^{\Omega} p_i \ln p_i = k_B \ln \Omega$$

This is "Boltzmann's postulate" after whom the physical constant $k_B$ is named which we introduce here such that later it gives us a temperature scale. Thus the fundamental postulate immediately suggests an extremum principle, which in many physics theories is the most convenient and elegant way to solve problems (e.g. in analytical mechanics). Note that the maximum entropy principle does not require any more physical reasoning, it is simply a mathematical consequence of the fundamental postulate, as shown in the section on information entropy in the first chapter.

Examples for the microcanonical ensemble

1. three spin-$\frac{1}{2}$ particles
   Possible states are:
\[
\begin{array}{cccc}
\text{\textit{n}} & \text{\textit{m}_1} & \text{\textit{m}_2} & \text{\textit{m}_3} & \text{energy } E \\
1 & + & + & + & -3 \mu H \\
2 & + & + & - & -1 \mu H \\
3 & + & - & + & -1 \mu H \\
4 & - & + & + & -1 \mu H \\
5 & + & - & - & +1 \mu H \\
6 & - & + & - & +1 \mu H \\
7 & - & - & + & +1 \mu H \\
8 & - & - & - & +3 \mu H \\
\end{array}
\]

If we know that \( E = -\mu H \), then the corresponding microcanonical ensemble is
\[
\{(++-), (+++), (-++)\} \implies \Omega = 3.
\]

Each state is equally likely with
\[
p_n = \frac{1}{\Omega} = \frac{1}{3}
\]

\( \text{ideal gas} \)

\[
\Omega(E, \delta E) = \frac{1}{h^{3N} N!} \int_{E-\delta E \leq \mathcal{H}(\vec{q}, \vec{p}) \leq E} \frac{d\vec{q} \; d\vec{p}}{6N}\text{-dimensional integral}
\]

\[
\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m_i} = \frac{\vec{p}^2}{2m} = E
\]

\[
\implies \Omega = \frac{1}{h^{3N} N!} V^N f(R, \delta R)
\]

where \( f(R, \delta R) \) is the volume of a spherical shell with radius \( R = \sqrt{2mE} \) and thickness \( \delta R = \frac{1}{2} \sqrt{2m/E} \delta E \) in \( 3N \)-dimensional space.

From analysis we know the expression for the volume of a sphere with radius \( R \) in \( D \)-dimensional space:

\[
V(R) = \frac{\pi^{D/2}}{(D/2)!} R^D
\]
Taking $D = 3$ we recover the well known formula:

$$V = \frac{4\pi}{3} R^3$$

because $(3/2)! = \Gamma(3/2) = 3\sqrt{\pi}/4$.

$$\Rightarrow f(R, \delta R) = V(R) - V(R - \delta R)$$

$$= \frac{\pi^{D/2}}{(D/2)!} \left[ R^D - (R - \delta R)^D \right]$$

For $D = \text{const}$, we could expand this expression in $\frac{\delta R}{R}$ and got $\frac{D \delta R}{R}$ for the square bracket. Here however we are interested in the limit $D \to \infty$ for $\frac{\delta R}{R} \ll 1$:

$$(1 - \frac{\delta R}{R})^D = e^D \ln(1 - \frac{\delta R}{R}) \approx e^{-D} \frac{\delta R}{R} \quad D \to \infty$$

$$\Rightarrow f(R, \delta R) = \frac{\pi^{D/2}}{(D/2)!} R^D = V(R)$$

$\delta R$ drops out; in high dimensions the volume of the sphere is manly at its surface.

$$\Rightarrow \Omega(E) = \frac{V^N \pi^{3N/2} (2mE)^{3N/2}}{h^{3N} N! (\frac{3N}{2})!}$$ microcanonical partition sum for an ideal gas

The entropy of an ideal gas then becomes:

$$S = k_B \ln \Omega = k_B \left\{ N \ln V + \frac{3N}{2} \ln\left(\frac{2\pi mE}{\hbar^2}\right) - \ln N! - \ln\left(\frac{3N}{2}\right)! \right\}$$

expression A

Considering $N \gg 1$ and applying two times Stirling’s formula, expression A becomes:

$$- \ln N! - \ln\left(\frac{3N}{2}\right)! = - \left[ N (\ln N - 1) + \frac{3N}{2} (\ln \frac{3N}{2} - 1) \right]$$

$$= -N \left[ -\frac{5}{2} + \frac{3}{2} \ln \frac{3}{2} + \frac{5}{2} \ln N \right]$$

$$= N \left[ \frac{5}{2} - \ln \left( \left(\frac{3}{2}\right)^{3/2} N^{5/2} \right) \right]$$

$$\Rightarrow S = k_B N \left\{ \ln \left[ \frac{V}{N} \right] \left( \frac{4\pi mE}{3h^2 N} \right)^{3/2} + \frac{5}{2} \right\}$$
Comments

1. $S, V, E, N$ are all extensive and occur only in the combinations $s = \frac{S}{N}, v = \frac{V}{N}, \ e = \frac{E}{N}$ ('specific quantities').

2. The exponent $\frac{3}{2}$ reflects the fact, that each particle has 3 degrees of freedom.

3. With $\lambda := \left( \frac{3h^2}{4\pi me} \right)^\frac{1}{2}$ ('thermal de Broglie' wavelength) we get:

   $$s = k_B \left\{ \ln \left( \frac{v}{\lambda^3} \right) + \frac{5}{2} \right\}$$

4. This first non-trivial result from statistical physics has been known before in thermodynamics as 'Sackur-Tetrode-equation'. It has been impressively verified in experiments.

2.5 Equilibrium conditions

We consider two isolated systems to form a composite isolated system. The entropy then is given as:

$$S = k_B \ln(\Omega_1 \cdot \Omega_2)$$
$$= k_B \ln \Omega_1 + k_B \ln \Omega_2$$
$$= S_1 + S_2$$

The quantities $E, V$ and $N$ are also additive ('extensive').

Thermal contact

We next bring the systems in thermal contact, such that they can exchange energy, but not volume or particles:

Figure 2.6: Thermal contact allows for heat exchange between the two systems.

In the new equilibrium state, energy will be $E_1'$ and $E_2'$, with:

$$E = E_1 + E_2 = E_1' + E_2'$$
In equilibrium, $S = k_B \ln \Omega$ must be maximal:

$$\Rightarrow \, dS = \frac{\partial S_1}{\partial E_1'} dE_1' + \frac{\partial S_2}{\partial E_2'} dE_2' = 0$$

$$= \left( \frac{\partial S_1}{\partial E_1'} - \frac{\partial S_2}{\partial E_2'} \right) dE_1' = 0$$

We define a new state variable $T$ ('temperature') by:

$$\frac{\partial S(E,V,N)}{\partial E} := \frac{1}{T(E,V,N)}$$

$$\Rightarrow \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dE_1' = 0$$

$$\Rightarrow [T_1 = T_2]$$

The two systems exchange energy until their temperatures are the same. Before equilibrium is reached, entropy grows:

$$dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 > 0$$

$$T_1 > T_2 \Rightarrow dE_1 < 0$$

Hence we see that energy flows to the cooler system. Temperature defined this way agrees with our intuitive understanding of temperature.

If the two systems only exchange energy, then:

$$dE_i = T_i \, dS_i$$

$$\Rightarrow dS_2 = \frac{dE_2}{T_2} = -\frac{dE_1}{T_2} = -\frac{T_1}{T_2} \, dS_1$$

$$\Rightarrow dS = dS_1 + dS_2$$

$$= dS_1 \left( 1 - \frac{T_1}{T_2} \right) > 0 \quad \text{before equilibrium is reached}$$

$$T_1 > T_2 \Rightarrow dS_1 < 0, \, dS_2 > 0, \, |dS_2| > |dS_1|$$

The warmer system loses entropy, the cooler system gains entropy. Overall more entropy is generated.

$$\Rightarrow \, \text{entropy is not conserved (unlike energy } E)$$

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Contact with volume exchange

We now assume that the wall is also mobile, thus volume can be exchanged:

\[
dS = \frac{\partial S_1}{\partial E_1} dE_1 + \frac{\partial S_2}{\partial E_2} dE_2 + \frac{\partial S_1}{\partial V_1} dV_1 + \frac{\partial S_2}{\partial V_2} dV_2 = -dE_1 + \frac{\partial S_1}{\partial V_1} dV_1 + \frac{\partial S_2}{\partial V_2} dV_2
\]

We define another new state variable (‘pressure’) by:

\[
\frac{\partial S(E, V, N)}{\partial V} = \frac{p(E, V, N)}{T(E, V, N)}
\]

\[
\Rightarrow dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 + \left( \frac{p_1}{T_1} - \frac{p_2}{T_2} \right) dV_1 = 0
\]

\[
T_1 = T_2, \ p_1 = p_2
\]

Volume is exchanged until the pressures are the same.

If temperatures are equal:

\[
dS = \frac{p_1 - p_2}{T} dV_1 > 0
\]

The system with larger pressure increases its volume.

Contact with exchange of particle number

Finally let’s assume a permeable membrane and define a new state variable (‘chemical potential’) by:

\[
\frac{\partial S(E, V, N)}{\partial N} = -\frac{\mu(E, V, N)}{T(E, V, N)}
\]

The equilibrium condition becomes:

\[
\mu_1(E_1, V_1, N_1) = \mu_2(E_2, V_2, N_2)
\]

Assume \( T_1 = T_2 \), but \( \mu_2 > \mu_1 \):

\[
\Rightarrow dS = (-\mu_1 + \mu_2) \frac{dN_1}{T} > 0
\]

\[
dN_1 > 0 \Rightarrow \mu_2 > \mu_1
\]

\Rightarrow\ \text{particles flow from large to small chemical potential}
Equations of state

We note that the three newly introduced variables:

\[ T = T(E, V, N), \quad p = p(E, V, N), \quad \mu = \mu(E, V, N) \]

defined by

\[ dS = \frac{1}{T} \, dE + \frac{p}{T} \, dV - \frac{\mu}{T} \, dN \]

are intensive, that is their values do not change if the system is doubled, because otherwise \( S \) could not be extensive.

Rearranging the equation above for \( dE \) gives:

\[ dE = T \, dS - p \, dV + \mu \, dN \]

The pairs \((T, S), ((-p, V))\) and \((\mu, N)\) are ‘conjugate’ variables in regard to energy. We identify the three types of energies as heat, mechanical energy and chemical energy.

\( S = S(E, V, N) \) is the ‘fundamental equation’, containing the complete information on the system. The three equations for \( T, p \) and \( \mu \) are ‘equations of state’. Each by itself contains only incomplete information on the system. Typically the equations of state are experimentally accessible and thus ground our theory in experiments. If only some of them are known, the others have to be guessed based on some additional information (e.g. a model). Moreover thermodynamic relations give strong additional constraints on possible equations of state (see other chapter).

2.6 Equations of state for ideal gas

\[ S = k_B \, N \left[ \ln \left( \frac{V}{N\lambda^3} \right) + \frac{5}{2} \right] \quad \text{fundamental equation} \]

\[ \lambda \propto \left( \frac{N}{E} \right)^{\frac{1}{2}} \]

\[ \Rightarrow \quad \frac{1}{T} = \frac{\partial S}{\partial E} \bigg|_{V,N} = k_B \, N \frac{\partial}{\partial E} \ln E^3 = \frac{3}{2} \frac{k_B \, N}{E} \]

\[ \Rightarrow \quad E = \frac{3}{2} \, N \, k_B \, T \quad \text{caloric equation of state} \]

\[ \Rightarrow \quad e = \frac{E}{N} = \frac{3}{2} \, k_B \, T \]

Hence each degree of freedom carries energy \( \frac{1}{2} k_B \, T \). We also note for the specific heat:

\[ c_v = \frac{dE}{dT} = \frac{3}{2} N k_B \]
thus the specific heat is independent of temperature. In fact this result is the classical high-temperature limit for the quantum mechanical fluids we are discussing later.

\[
\frac{p}{T} = \frac{\partial S}{\partial V}_{E,N} = k_B N \frac{1}{V} \Rightarrow pV = Nk_B T 
\]

thermal equation of state

The thermal equation of state is also known as the ideal gas law (combining the two laws of Gay-Lussac and Boyle-Mariotte).

\[
\frac{-\mu}{T} = \frac{\partial S}{\partial N}_{E,V} = k_B \left[ \ln \left( \frac{V}{N\lambda^3} \right) + \frac{5}{2} \right] + k_B N \frac{\partial}{\partial N} \ln N^{-\frac{1}{2}}
\]

\[
\Rightarrow \mu = k_B T \ln \left( \frac{N\lambda^3}{V} \right)
\]
equation of state for chemical potential

Defining density \( \rho = \frac{N}{V} \), \( p \) becomes:

\[
p = \rho k_B T
\]

\[
[p] = \frac{J}{m^3} = \frac{N}{m^2} = Pa
\]

Pressure can be interpreted as force per area or as energy density. For the chemical potential we can write

\[
\mu = k_B T \ln \rho \lambda^3 = k_B T \ln \frac{p}{p_0} \text{ with } p_0 = \frac{k_B T}{\lambda^3}
\]

Thus for an ideal (=dilute) gas chemical potential is grows logarithmically with pressure.

The following numbers are quite instructive:

At room temperature: \( T \approx 300K \).

\[
\Rightarrow k_B T = 4.1 \cdot 10^{-21} J = 4.1 \ pN \cdot nm = \frac{1}{40} eV = 25 \ meV \text{ thermal energy}
\]

\[
p_0 = \frac{4.1 \cdot 10^{-21}}{(10^{-10} m)^3} = 4.1 \ GPa
\]

Because ambient pressure \( p = 1 \ atm = 10^5 \ Pa \), the chemical potential \( \mu \) is usually negative. We calculate the volume of one mole ideal gas at ambient pressure:

\[
V = \frac{N k_B T}{p} = 6.022 \cdot 10^{23} \cdot 4.1 \cdot 10^{-21} \frac{J}{10^5 \ Pa} \approx 24 \cdot 10^{-3} \ m^3 = 24 \ l
\]
2.7 Two-state system

We now consider other important examples for the microcanonical ensemble. We first consider an 'atom' which can either be in its ground (zero energy) or excited state (energy $\epsilon$).

As the total energy $E$ and the number of particles $N$ are fixed, we know exactly how many atoms are in the excited state:

$$N_e = \frac{E}{\epsilon} \quad \text{number of atoms in excited state}$$
$$N_0 = N - N_e \quad \text{atoms in ground state}$$

The number of microstates is the number of ways one can choose $N_e$ out of $N$:

$$\Omega = \frac{N!}{N_e! (N - N_e)!}$$

The entropy then becomes, using Stirling’s formula:

$$S = k_B \ln \Omega$$
$$\approx k_B \left[ (N \ln N - N) - (N_e \ln N_e - N_e) - ((N - N_e) \ln(N - N_e) - (N - N_e)) \right]$$
$$= k_B \left[ -N_e \ln \frac{N_e}{N} - (N - N_e) \ln \left(1 - \frac{N_e}{N}\right) \right]$$

$$\Rightarrow \quad \bar{s} = -k_B \left[ \rho_\epsilon \ln \rho_\epsilon + (1 - \rho_\epsilon) \ln(1 - \rho_\epsilon) \right]$$

where $\rho_\epsilon = \frac{N_e}{N} = \frac{E}{\epsilon N}$, $0 \leq \rho_\epsilon \leq 1$ is the density of the excited state and $1 - \rho_\epsilon = \frac{N - N_e}{N}$ is the density of the ground state. Note that this result make a lot of sense. It basically is Shannon’s formula, $S = -\sum_i p_i \ln p_i$, with $i$ running over the two possible states, ground and excited. We note that the fundamental equation is independent of volume and depends only on $E$ and $N$.

Thermal equation of state:

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_N = -k_B N \left[ \frac{1}{e N} \ln \frac{E}{e N} + \frac{1}{e N} - \frac{1}{e N} \ln \left(1 - \frac{E}{e N}\right) - \frac{1}{e N} \right] = \frac{k_B}{e} \ln \left(\frac{N \epsilon}{E} - 1\right)$$
\[ E = \frac{N \epsilon}{1 + e^{\epsilon/(k_B T)}} = \frac{N \epsilon}{1 + e^\beta} \]

where we have introduced a dimensionless inverse temperature \( \beta = \epsilon / (k_B T) \).

We consider the two limits:

1. **High \( T \), small \( \beta \):**
   
   \[ E = \frac{N \epsilon}{2}, \quad \rho_\epsilon = \frac{E}{\epsilon N} = \frac{1}{2}, \quad 1 - \rho_\epsilon = \frac{1}{2} \]
   
   \[ \Rightarrow \text{both states have equal density.} \]

2. **Low \( T \), large \( \beta \):**
   
   \[ E = 0, \quad \rho_\epsilon = 0, \quad 1 - \rho_\epsilon = 1 \]
   
   \[ \Rightarrow \text{only the ground state is populated.} \]

Here we see a very general principle of statistical physics: at low \( T \), energy wins (everybody is in the ground state), and at high \( T \), entropy wins (all states are equally populated).

![Figure 2.8: Energy and specific heat of the two-state model as a function of temperature.](image)

The energy approaches \( \frac{N \epsilon}{2} \) asymptotically. The capacity peaks at the temperature \( T_{\text{max}} = \frac{0.42 \epsilon}{k_B} \).

We finally calculate the specific heat:

\[ c_v = \frac{dE}{dT} = N \epsilon \left( \frac{1}{1 + e^\beta} \right)^2 \frac{e^\beta}{k_B} \frac{1}{T^2} \]

\[ = N k_B \beta^2 \frac{1}{(e^{-\beta/2} + e^{+\beta/2})^2} \]

We see that the heat capacity vanishes both for low and high \( T \). It peaks at a finite temperature \( T = \frac{0.42 \epsilon}{k_B} \). Such a ‘Schottky hump’ reveals the existence of two low lying energy states in a spectrum.
Alternative derivation

We consider an alternative way to calculate $\Omega(E)$. For each atom we introduce an occupation (or occupancy) number $n_j \in \{0, 1\}$ for the external state:

$$\Omega(E) = \sum_{n_1=0}^{1} \ldots \sum_{n_N=0}^{1} \delta \left( E - \epsilon \sum_{i=1}^{N} n_i \right)$$

sum over $2^N$ states

$$= \sum_{n_1=0}^{1} \ldots \sum_{n_N=0}^{1} \int \frac{dk}{2\pi} e^{i k (E - \epsilon \sum_{i=1}^{N} n_i)}$$

$$= \int \frac{dk}{2\pi} e^{i k E} \left( \sum_{n=0}^{1} e^{-ik\epsilon n} \right)^{N}$$

$$= \int \frac{dk}{2\pi} \exp \left\{ N \left[ \frac{ik}{N} + \ln \left( \frac{1 + e^{-i k \epsilon}}{1} \right) \right] \right\}$$

In the limit $N \to \infty$, we solve this integral with the ‘saddle point approximation’:

$$\Omega(E) = \frac{1}{2\pi} \int dk \ e^{N f(k)} = \frac{1}{2\pi} e^{N f(k_0)} \int dk \ e^{N f(k) \left( \frac{2\pi}{N f''(k_0)} \right)^{1/2}}$$

where $f(k)$ has a maximum at $k_0$. 

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We define \( \gamma = \frac{E}{N} \):

\[
\begin{align*}
  f'(k) &= i\gamma + \frac{e^{-ike}(-ie)}{1 + e^{-ike}} = i\gamma - \frac{ie}{e^{ike} + 1} = 0 \\
  \Rightarrow \quad k_0 &= \frac{1}{ie} \ln \frac{e - \gamma}{\gamma} \\
  \Rightarrow \quad f(k_0) &= \frac{T}{e} \ln \frac{e - \gamma}{\gamma} - \ln \frac{e - \gamma}{e} \\
  f''(k_0) &= \frac{(ie)^2 e^{ik_0e}}{(e^{ik_0e} + 1)^2} = (\gamma - e) \gamma \\
  \Rightarrow \quad \Omega(E) &= e^{Nf(k_0)} \left( \frac{1}{2\pi N f''(k_0)} \right)^\frac{1}{2} \\
  &= \exp \left\{ \frac{Nf(k_0)}{\alpha N} - \frac{1}{2} \ln \frac{2\pi Nf''(k_0)}{\alpha \ln N \to \text{neglect in limit } N \to \infty} \right\} \\
  \Rightarrow \quad \Omega(E) &= e^{Nf(k_0)}
\end{align*}
\]

\[
\begin{align*}
  \Rightarrow \quad S &= k_B N f(k_0) = k_B N \left\{ \rho_e \ln \left( \frac{1}{\rho_e} - 1 \right) - \ln(1 - \rho_e) \right\} \\
  &= -k_B \left[ \rho_e \ln \rho_e + (1 - \rho_e) \ln(1 - \rho_e) \right]
\end{align*}
\]

because \( \rho_e = \gamma / \epsilon \).

Thus we recovered the same result as above with the combinatorial approach.

### 2.8 Einstein model for specific heat of a solid

In 1907, Einstein introduced a simple model for the vibrational modes in a crystal. From this, we can calculate the specific heat of a solid, which is one of the central questions in solid state physics. Later this model was improved by Debye as we will see later. The Einstein model is also of fundamental importance because it is the microcanonical treatment of a collection of harmonic oscillators. It assumes that each atom in the crystal vibrates with a natural frequency \( \omega \) around its equilibrium position. Thus for \( N_A \) atoms in three dimensions, we have a collection of \( N = 3N_A \) harmonic oscillators, each with two degrees of freedom. In quantum mechanics, each harmonic oscillator is quantized and can carry an integral number of quanta \( \hbar \omega \). Together with the zero energy we have

\[
E = \hbar \omega \left( \frac{N}{2} + Q \right)
\]
where $Q$ is the overall number of quanta. Therefore

$$Q = \left( \frac{E}{\hbar \omega} - \frac{N}{2} \right)$$

These $Q$ quanta are distributed over $N$ states. That’s the same as distributing $Q$ marbles over $N$ boxes or as placing $Q$ marbles and $N - 1 \approx N$ match sticks in a row:

$$\Omega(E, N) = \frac{(Q + N)!}{Q!N!}$$

There is no role for $V$ in this model.

We calculate the entropy using Stirling’s formula:

$$S = k_B \Omega = k_B \left[ (Q + N)(\ln(Q + N) - 1) - Q(\ln Q - 1) - N(\ln N - 1) \right]$$

$$= k_B \left[ Q \ln \frac{Q + N}{Q} + N \ln \frac{Q + N}{N} \right]$$

$$= k_B N \left[ (e + \frac{1}{2}) \ln(e + \frac{1}{2}) - (e - \frac{1}{2}) \ln(e - \frac{1}{2}) \right]$$

with $e = E/E_0$ and $E_0 = N\hbar \omega$. We next calculate temperature:

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{1}{E_0} \frac{\partial S}{\partial e} = \frac{k_B N}{E_0} \ln \left( \frac{e + \frac{1}{2}}{e - \frac{1}{2}} \right)$$

We define $\beta = \hbar \omega/k_B T$ and invert this equation:

$$2e = \frac{e^\beta + 1}{e^\beta - 1} \Rightarrow E = \frac{N\hbar \omega}{2} \frac{e^\beta + 1}{e^\beta - 1} = N\hbar \omega \left( \frac{1}{2} + \frac{1}{e^\beta - 1} \right)$$

For $T \to 0$, $E \to N\hbar \omega/2$, the zero energy. For $T \to \infty$, $E \to Nk_B T = 6N_A(k_B T/2)$, the classical limit for $6N_A$ degrees of freedom. We also calculate the specific heat:

$$c_v = \frac{dE}{dT} = Nk_B \beta^2 \frac{1}{(e^{\beta/2} - e^{-\beta/2})^2}$$

For $T \to 0$, $c_v$ vanishes. It then rises exponentially and plateaus at $3N_A k_B$ for $T \to \infty$. This classical limit is also known as the law of Dulong-Petit. The crossover takes place at $T = \hbar \omega/k_B$.

It is very instructive to compare these results with the two-state system, for which we found

$$c_v = \frac{dE}{dT} = Nk_B \beta^2 \frac{1}{(e^{\beta/2} - e^{-\beta/2})^2}$$

where we now define dimensionless inverse temperature as $\beta = \epsilon/k_B T$. Thus the result is essentially the same, except for the minus sign, which however makes a huge difference. Later we will see that this is typical for the difference between fermionic
systems (each state can be occupied either once or not at all) and bosonic systems (each
state can be filled with arbitrarily many quanta, like the harmonic oscillator).

The theoretical curve fits the experimental data qualitatively, but if one zooms in around
\( T = 0 \), one finds that the experimental curve rises as \( T^3 \) rather than exponentially. The
reason for this discrepancy is that atoms do not vibrate by themselves at a fixed fre-
quency, but in groups of variable frequencies. We will consider this important fact later
in the Debye model.

![Energy and specific heat of the Einstein model as a function of temperature.](image)

**Figure 2.9:** Energy and specific heat of the Einstein model as a function of temperature.

**Alternative derivation**

Again we consider an alternative way to calculate \( \Omega(E) \) by using occupation numbers:

\[
\Omega(E) = \sum_{n_1=0}^{\infty} \cdots \sum_{n_N=0}^{\infty} \delta \left( E - \hbar \omega \sum_{i=1}^{N} (n_i + \frac{1}{2}) \right)
\]

\[
= \sum_{n_1=0}^{\infty} \cdots \sum_{n_N=0}^{\infty} \int \frac{dk}{2\pi} e^{ik(E - \hbar \omega \sum_{i=1}^{N} (n_i + \frac{1}{2}))}
\]

\[
= \int \frac{dk}{2\pi} e^{ikE} \sum_{n_1=0}^{\infty} \cdots \sum_{n_N=0}^{\infty} e^{-ik\hbar \omega \sum_{i=1}^{N} (n_i + \frac{1}{2})}
\]

\[
= \int \frac{dk}{2\pi} e^{ikE} \left( e^{-ik\hbar \omega /2} \sum_{n=0}^{\infty} e^{-ik\hbar \omega n} \right)^N
\]

\[
= \int \frac{dk}{2\pi} e^{ikE} \left( e^{-ik\hbar \omega /2} \right)^N \left( 1 - e^{-ik\hbar \omega} \right)
\]

\[
= \int \frac{dk}{2\pi} e^{ikE} [k \xi - \ln(2i \sin(k\hbar \omega /2))]
\]

Note that this time the occupation number is not restricted, but runs over all possible
numbers. Therefore in the last step we have used the geometrical sum to achieve a
closed formula. It is a non-trivial question why this series converges in our case. Be-
cause the Delta-function is a distribution, in principle one has to apply the formula
above to a test function. If this test function is sufficiently well-behaved, then one can regularize the exponent by adding a small and real $\epsilon$ to the exponent. Then the series converges and one can send $\epsilon$ to zero in the end.

The remaining integral can again be solved using the method of steepest decent with \[ f(k) = ikE/N - \ln(2i \sin(k\hbar\omega/2)) \]

Again the Gaussian integral can be neglected and only the first term in the Taylor expansion matters, with \[ k_0 = \frac{1}{2i\hbar\omega/2} \ln \frac{E/N + \hbar\omega/2}{E/N - \hbar\omega/2} \]

After a lengthy calculation, one then gets the same result as above.

### 2.9 Entropic elasticity of polymers

We consider a chain-like polymer molecule consisting of $N$ monomers of size $a$ in one dimension.

![Figure 2.10: A one-dimensional polymer consisting out of monomers of size $a$. The sequences to the right and left are indicated by arrows. $L$ is the effective or projected length and $L_0 = Na$ the contour length.](image)

$N_+ : \#$segments to right

$N_- : \#$segments to left
\[ N_+ - N_- = \frac{L}{a} \]
\[ N_+ + N_- = N \]
\[ \Rightarrow N_+ = \frac{1}{2} \left( N + \frac{L}{a} \right) \]
\[ N_- = \frac{1}{2} \left( N - \frac{L}{a} \right) \]
\[ \Rightarrow \Omega = \frac{N!}{N_+! \cdot N_-!} \]
\[ \Rightarrow S = -k_B \left( N_+ \ln \frac{N_+}{N} + N_- \ln \frac{N_-}{N} \right) \]
\[ \Rightarrow S = -k_B N \left( \rho_+ \ln \rho_+ + \rho_- \ln \rho_- \right) \]

Here we defined \( \rho_\pm = \frac{N_\pm}{N} = \frac{1}{2} \left( 1 \pm \frac{L}{L_0} \right) \) with the ‘contour length’ \( L_0 = Na \) in the last step.

We have a look at two limits:

\( \rho_+ \to 1, \rho_- \to 0 \Rightarrow S \to 0 \)

There is only one possible configuration for the polymer.

\[ \frac{S}{k_B N} = -\frac{1}{2} \ln \frac{1}{2} - \frac{1}{2} \ln \frac{1}{2} \]

Figure 2.11: \( S/(k_B N) \) as a function of \( x \). For \( x_0 = 0 \) the function is maximal with \( f(x_0) = \ln 2 \approx 0.7 \).

\( L \to 0, \rho_+ \to \frac{1}{2}, \rho_- \to \frac{1}{2} \Rightarrow S \to N k_B \ln 2 \)

We see that the entropy is maximal for \( L = 0 \), hence the polymer coils up (2.3)

Stretching the polymer decreases its entropy. Therefore an entropic restoring force exists which pulls against an external stretching force.

Note that we cannot define temperature in the usual way, \( 1/T = \partial S/\partial E \), because \( S(N, L) \) does not depend on \( E \). However, there should be a conjugate quantity to length.
$L$, and this should be a force $F$ and at the same time defines temperature $T$:

$$\frac{F}{T} = \frac{\partial S}{\partial L}$$

$$x = \frac{L}{L_0} \Rightarrow \frac{1}{L_0} \frac{\partial S}{\partial x} = -\frac{N k_B}{2L_0} \ln \left( \frac{1+x}{1-x} \right) \approx -\frac{N k_B L}{L_0^2}$$

$$L_0 = \frac{N a}{k_B T}$$

$$F = \frac{k_B T L}{N a^2}$$

Figure 2.12: $f(x) = \ln \left( \frac{1+x}{1-x} \right)$ as a function of $x$.

The entropic restoring force corresponds at small extension to a harmonic potential:

$$U = \frac{k_B T L^2}{2 N a^2}$$

Most materials expand with temperature (e.g., ideal gas: $pV = N k_B T$). For the polymer, in contrast, increasing temperature causes a raise in restoring force and thus the system contracts. Note that this is a purely entropic effect (our polymer has no energy). In analogy with mechanics, $k = \frac{k_B T}{N a^2}$ is called the ‘entropic spring constant’ and it increases with $T$.

**2.10 Statistical deviation from average**

For two systems in thermal contact, our equilibrium condition $T_1 = T_2$ followed from the maximal entropy principle. We now investigate how sharp this maximum is. As an instructive example, we consider two ideal gases in thermal contact:

$$S_i = \frac{3}{2} k_B N_i \ln E_i + \text{terms independent of } E_i \ (i \in \{1, 2\})$$
\[ S = S_1 + S_2 \]

Maximal entropy:
\[ dS = 0 \quad \Rightarrow \quad \frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} \]

\[ \Rightarrow \frac{3}{2} k_B \frac{N_1}{E_1} = \frac{3}{2} k_B \frac{N_2}{E_2} \quad \text{corresponding to} \quad T_1 = T_2 \]

\[ \Rightarrow \bar{E}_1 = \frac{N_1}{N_2} \bar{E}_2 = \frac{N_1}{N - N_1} (E - \bar{E}_1) \quad \Rightarrow \quad \bar{E}_1 = \frac{N_1}{N} E \]

We check for maximum:
\[ \frac{\partial^2 S}{\partial E_1^2} = -\frac{3}{2} k_B \left( \frac{N_1}{E_1^2} + \frac{N_2}{E_2^2} \right) < 0 \]

We now consider a small deviation:
\[ E_1 = \bar{E}_1 + \Delta E, \quad E_2 = \bar{E}_2 - \Delta E \]

\[ \Rightarrow S(\bar{E}_1 + \Delta E) = \frac{3}{2} k_B \left[ N_1 \ln \left( \bar{E}_1 \left( 1 + \frac{\Delta E}{\bar{E}_1} \right) \right) + N_2 \ln \left( \bar{E}_2 \left( 1 - \frac{\Delta E}{\bar{E}_2} \right) \right) \right] \]

\[ \approx \frac{3}{2} k_B \left[ N_1 \ln \bar{E}_1 + N_2 \ln \bar{E}_2 + \left( \frac{N_1}{\bar{E}_1} - \frac{N_2}{\bar{E}_2} \right) \Delta E - \frac{N_1}{2} \left( \frac{\Delta E}{\bar{E}_1} \right)^2 - \frac{N_2}{2} \left( \frac{\Delta E}{\bar{E}_2} \right)^2 \right] \]

\[ \Rightarrow \Omega = \bar{\Omega} \exp \left[ -\frac{3}{4} \left( \frac{\Delta E}{E} \right)^2 N^2 \left( \frac{1}{N_1} + \frac{1}{N_2} \right) \right] \]

Plugging in a typical number \( N_i = 10^{27} \):

\[ \Rightarrow \quad \Omega \text{ drops dramatically away from the maximum } \bar{E}_1 \]

<table>
<thead>
<tr>
<th>( \frac{\Delta E}{E} )</th>
<th>( e^{-\frac{3}{4} \left( \frac{\Delta E}{E} \right)^2 N^2 \left( \frac{1}{N_1} + \frac{1}{N_2} \right)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^{-10} )</td>
<td>( e^{-600} \approx 10^{-260} )</td>
</tr>
<tr>
<td>( 10^{-11} )</td>
<td>( e^{-6} )</td>
</tr>
<tr>
<td>( 10^{-12} )</td>
<td>( e^{-0.06} \approx 1 )</td>
</tr>
</tbody>
</table>

We see that macrostates with \( \bar{E}_1(1 \pm 10^{-12}) \) and \( \bar{E}_2(1 \mp 10^{-12}) \) are equally likely. Fluctuations in energy are of the order \( 10^{-12} \), hence tiny.
2.11 Foundation of the fundamental postulate

There is a long and twisted history of justifying the fundamental postulate. The main problem here is that on a microscopic basis, dynamics is governed by Newton’s equations, which are reversible, while macroscopic systems decay irreversibly into a unique equilibrium state. A rigorous derivation of the drive towards equilibrium from microscopic principles does still not exist and several mechanisms are discussed that somehow smooth out phase space density, such that a homogeneous distribution over the energy shell is achieved. One has to state clearly that statistical mechanics works very well for most physical systems of interest, but it is notoriously difficult to establish a microscopic derivation. This is why we still have to speak of a fundamental postulate.

A very instructive approach to this question is to consider Hamiltonian dynamics. In classical systems with N particles, each microstate is a point in 6N-dimensional ‘phase space’ \((\vec{r}_1, \ldots, \vec{r}_n, \vec{p}_1, \ldots, \vec{p}_n) = (\vec{q}, \vec{p})\). In statistical mechanics, we consider many particle systems and therefore cannot say in which state the system is exactly located, but rather use a statistical ensemble of states. The probability distribution is continuous and the probability that the system is in state \((\vec{q}(t), \vec{p}(t), t)\) is

\[
\rho(\vec{q}(t), \vec{p}(t), t) \, d\vec{q} \, d\vec{p}
\]

where \(\rho\) is the phase space probability density. For initial conditions \((\vec{q}(0), \vec{p}(0))\) the system evolves according to Hamilton’s equations:

\[
\dot{q}_i = -\frac{\partial H}{\partial \dot{q}_i}, \quad \dot{p}_i = \frac{\partial H}{\partial q_i}
\]

For an isolated system at rest, energy is conserved due to the time invariance (Noether theorem):

\[
\mathcal{H} = \text{const} = E
\]

The solutions to the system of ordinary differential equations are unique and do not intersect. Energy conservation reduces phase space to a \((6N - 1)\)-dimensional hypersurface, the energy surface or energy shell.

We now define a phase space velocity

\[
\vec{\sigma} := (\dot{q}, \dot{p})
\]

and the corresponding current

\[
\vec{j} = \rho \, \vec{\sigma}
\]

For an arbitrary region of phase space, we have a balance equation:

\[
\int_{\Omega} d\vec{A} \cdot \vec{j} = -\frac{\partial}{\partial t} \int_{V} d\vec{q} \, d\vec{p} \, \rho(\vec{q}, \vec{p}, t)
\]

\[
\Rightarrow \int_{V} d\vec{q} \, d\vec{p} \left[ \frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} \right] = 0
\]
\begin{align*}
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) &= 0 \quad \text{continuity equation} \\
\Rightarrow V \arbitrary 
\end{align*}

Thus the system evolves like a hydrodynamic system, with a probability fluid streaming through state space. We now use Hamilton’s equation to show that

\begin{align*}
0 &= \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left( \frac{\partial \rho q_i}{\partial q_i} + \frac{\partial \rho p_i}{\partial p_i} \right) \\
&= \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left( \frac{\partial \rho q_i}{\partial q_i} + \frac{\partial \rho p_i}{\partial p_i} \right) + \rho \sum_{i=1}^{3N} \left( \frac{\partial q_i}{\partial q_i} + \frac{\partial p_i}{\partial p_i} \right) \\
&= \frac{d \rho}{dt} = 0 \quad \text{Liouville’s theorem}
\end{align*}

The total derivative of the probability density vanishes. The probability fluid is ‘incompressible’ and \( \rho(\vec{q}(t), \vec{p}(t), t) = \rho(\vec{q}(0), \vec{p}(0), 0) \).

Let \( V_0 \) be the volume of some initial region \( R_0 \) of phase space. At some time \( t \) afterwards, this region can have evolved to some region \( R_t \) with complicated shape, but its volume is unchanged: \( V_t = V_0 \) (Figure 2.13).

![Figure 2.13: The phase space volume stays constant, although its shape may change.](image)

At this point, we can draw two important conclusions. First the number of occupied microstates does not change, because phase space volume is conserved. More general, entropy does not change, because the system evolves deterministically and thus information content is not changed. Second the fact that the phase space volume is conserved does not mean that its shape does not change. In fact for many systems of interest, one finds that a well-defined region of phase space quickly distorts into a very complex shape, especially for chaotic systems. When viewed from a coarse-grained perspective (like in a real world experiment with limited resolution), we will see a smooth
distribution. This has been compared with the stirring of oil and water, which keep distinct domains on the microscale (oil and water do not mix), but appear to be uniform on a macroscopic scale. A more rigorous way to deal with the coarse-graining issue in a classical framework is the BBGKY-hierarchy (after Bogoliubov, Born, Green, Kirkwood, Yvon). On the quantum level, one also could argue that completely isolated systems never exist and that coupling to the environment, even if very weak, will eventually lead to smoothing in state space.

In order to learn more about the equilibrium state, we next rewrite Liouville’s theorem:

\[
\frac{\partial \rho}{\partial t} = - \sum_{i=1}^{3N} \left[ \dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} \right]
\]

\[
= - \sum_{i=1}^{3N} \left[ \frac{\partial H}{\partial p_i} \frac{\partial \rho}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} \right]
\]

\[
= - \{H, \rho\} \quad \text{Liouville’s equation}
\]

Here we used the notation of ‘Poisson brackets’ in the last step. Liouville’s equation is also known as the collisionless Boltzmann equation because it describes the streaming part for the probability fluid in phase space.

Let us now assume that \( \rho(\vec{q}, \vec{p}, t) \) only depends on the conserved value of energy \( E \).

\[
\rho(\vec{q}, \vec{p}, t) = \Phi(E), \quad \frac{dE}{dt} = 0
\]

We now get

\[
\frac{\partial \rho}{\partial t} = - \{H, \rho\}
\]

\[
= - \sum_{i=1}^{3N} \left[ \frac{\partial H}{\partial p_i} \frac{\partial \rho}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} \right]
\]

\[
= - \sum_{i=1}^{3N} \left[ \frac{\partial H}{\partial p_i} \frac{\partial \rho}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} \right] \frac{\partial \Phi}{\partial E} = 0
\]

\[
\{H, H\} = \frac{\partial^2 \Phi}{\partial E^2} = 0
\]

This result is also known as Jean’s theorem. Thus in this case the state space probability density is constant and has the same value for a given energy. We conclude that once the microcanonical equilibrium state is reached, the system will stay there for ever.

We next consider an observable \( A \) which depends on time only through phase space:

\[
A(t) = A(q(t), \vec{p}(t))
\]

\[
\Rightarrow \frac{dA}{dt} = \sum_{i=1}^{3N} \left[ \frac{\partial A}{\partial q_i} \dot{q}_i + \frac{\partial A}{\partial p_i} \dot{p}_i \right] = \{H, A\}
\]
In equilibrium the ensemble average of an observable

$$\langle A \rangle = \int d\vec{q} \ d\vec{p} \ \rho(\vec{q}, \vec{p}) \ A(\vec{q}, \vec{p})$$

will be time-independent. In particular we expect this to apply to all state variables. Equivalent results can be derived for quantum mechanical systems. However, in this case we cannot use a scalar probability density, because phase space coordinates do not commute. Instead we need to introduce a density operator.

For a given state $|\Psi\rangle$, the observable has the average (projection):

$$\langle A \rangle = \langle \Psi | A | \Psi \rangle$$

We define the density operator or density matrix:

$$\rho = |\Psi\rangle \langle \Psi|$$

This then yields

$$\langle A \rangle = \langle \Psi | A | \Psi \rangle = \sum_n \langle \Psi | A | n \rangle \langle n | \Psi \rangle$$

$$= \sum_n \langle n | \Psi \rangle \langle \Psi | A | n \rangle = \sum_n \langle n | \rho A | n \rangle$$

$$= tr \{ \rho A \} \quad \text{average over quantum mechanical distribution of states}$$

If we now turn to statistical mechanics, we superimpose a second layer of probability over the quantum mechanical probabilities. We call the states that follow the Schrödinger equation pure states and then consider mixed states by adding up several of the pure states in an incoherent manner (no superposition, so probability is not transferred from one qm state to the other and the weights stay constant).

Using an extended definition of the density matrix:

$$\rho = \sum_i p_i \ |\Psi_i\rangle \langle \Psi_i|$$

$$\Rightarrow \langle A \rangle = \sum_i p_i \langle \Psi_i | A | \Psi_i \rangle$$

$$= \sum_i \sum_n p_i \langle \Psi_i | A | n \rangle \langle n | \Psi_i \rangle$$

$$= \sum_i \sum_n p_i \langle n | \Psi_i \rangle \langle \Psi_i | A | n \rangle$$

$$= \sum_n \langle n | \rho A | n \rangle = tr(\rho A)$$

Again stationary distributions result if $\rho$ is a function of the stationary ensemble in energy representation:

$$\mathcal{H} |n\rangle = E_n |n\rangle$$
\[
0 = \partial_t \rho = [\mathcal{H}, \rho]
\]

\[
\Rightarrow 0 = \langle m | \mathcal{H} \rho - \rho \mathcal{H} | n \rangle = (E_m - E_n) \rho_{mn}
\]

\[
\Rightarrow \rho_{mn} = 0 \text{ for } E_m \neq E_n
\]

without degeneracy: \( \rho = \sum_n \rho(E_n) |n\rangle \langle n | \)

We now derive the quantum mechanical analogue of Liouville’s equation:

Schrödinger equation: \( i\hbar \partial_t |\Psi\rangle = \mathcal{H} |\Psi\rangle \)

adjoint Schrödinger equation: \( i\hbar \partial_t \langle \Psi | = \langle \Psi | \mathcal{H} \)

\[
\Rightarrow i\hbar \partial_t \rho = i\hbar \sum_i p_i (|\Psi_i\rangle \langle \Psi_i| + |\Psi_i\rangle \langle \Psi_i|)
\]

\[
= \sum_i p_i (\mathcal{H} |\Psi_i\rangle \langle \Psi_i| - |\Psi_i\rangle \langle \Psi_i| \mathcal{H})
\]

\[
= [\mathcal{H}, \rho] \text{ commutator}
\]

\[
\partial_t \rho = -\frac{i}{\hbar} [\mathcal{H}, \rho] \text{ von Neumann equation}
\]

Like Liouville’s equation, von Neumann’s equation (also called the quantum Liouville equation) suggests that in equilibrium, probability distributions and state variables are constant.
3 The canonical ensemble

3.1 Boltzmann distribution

We consider a system in contact with a ‘thermal reservoir’ or ‘heat bath’. Then it is temperature $T$ rather than energy $E$ that is fixed. A simple example would be a bottle of beer in a large lake, which eventually will cool down to the temperature of the lake. To qualify as a thermal reservoir, the surrounding system has to be much larger such that its temperature does not change as energy is exchanged with the system of interest. Together the two systems form an isolated system for which energy is fixed at $E_{\text{tot}}$.

![Figure 3.1: Two systems in thermal contact. System 2 is considerably larger than system 1 and serves as a ‘thermal reservoir’. Together the two systems are again a microcanoncial ensemble.](image)

We now consider one specific microstate $i$ in system 1. This microstate comes with an energy $E_i$. Its probability to occur is

$$p_i = \frac{\Omega_{\text{res}}(E_{\text{tot}} - E_i)}{\Omega_{\text{tot}}(E_{\text{tot}})} = \frac{e^{S_{\text{res}}(E_{\text{tot}} - E_i)/k_B}}{e^{S_{\text{tot}}(E_{\text{tot}})/k_B}}$$

Here we used that the composite system is microcanonical and that we have fixed the microstate in system 1; then the number of accessible microstates is determined by system 2 (the reservoir) only.

We next introduce the average energy of system 1 as the reference energy:

$$U = \langle E \rangle = \sum_i p_i E_i$$

We now Taylor-expand the entropy of the heat bath:

$$S_{\text{res}}(E_{\text{tot}} - E_i) = S_{\text{res}}(E_{\text{tot}} - U + U - E_i) = S_{\text{res}}(E_{\text{tot}} - U) + \frac{U - E_i}{T}$$
Here we have used $\frac{\partial S}{\partial E} = 1/T$. Note that higher order terms do not appear because a reservoir has a constant temperature (first derivative constant, thus the second and the higher order derivatives vanish). We also can use additivity of the entropy to write

$$S_{tot}(E_{tot}) = S(U) + S_{res}(E_{tot} - U)$$

Defining the inverse temperature

$$\beta := \frac{1}{k_B T}$$

we thus get

$$p_i = \frac{e^{\beta U_i} e^{-\beta E_i} e^{S_{res}(E_{tot} - U_i)}/k_B}{e^{S(U)}/k_B e^{S_{res}(E_{tot} - U)}/k_B} = e^{\beta F_i} e^{-\beta E_i}$$

where $F = U - TS$ and where the terms with $S_{res}$ have canceled out. We note that $p_i \sim e^{-\beta E_i}$ and that the prefactor $e^{\beta F}$ has the role of a normalization factor. In order to normalize, we use $\sum_i p_i = 1$ to write

$$p_i = \frac{1}{Z} e^{-\beta E_i}$$

Boltzmann distribution

with

$$Z = \sum_i e^{-\beta E_i}$$

partition sum

We conclude that the probability for a microstate decreases exponentially with its energy. The newly defined quantity $Z$ is the central concept of the canonical ensemble and plays a similar role as the phase space volume $\Omega$ in the microcanonical ensemble.

**Comments:**

1. We note that the expansion around $E_{tot} - U$ is not required to get the Boltzmann factor $e^{-\beta E_i}$. We would have obtained this result also by expanding simply around $E_{tot}$, because the derivative would also have given $1/T$. The normalization is ensured anyway by the new quantity $Z$. The expansion used here becomes important later because only in this way we get the prefactor $e^{\beta F}$. As we will discuss below in more detail, this leads to the important relation $F = -k_B T \ln Z$ connecting thermodynamics (F) and statistics (Z).

2. For classical Hamiltonian systems we have

$$p(\mathbf{q}, \mathbf{p}) = \frac{1}{Z N! h^{3N}} e^{-\beta H(\mathbf{q}, \mathbf{p})}$$

with the Hamiltonian $H$ and the partition sum (or, better, the partition function) is

$$Z = \frac{1}{N! h^{3N}} \int d\mathbf{q} d\mathbf{p} e^{-\beta H(\mathbf{q}, \mathbf{p})}$$
3. From Liouville’s theorem it follows that the Boltzmann distribution is a stationary distribution as $\rho = \rho(\mathcal{H})$. Like for the microcanonical distribution, it is reasonable to associate it with equilibrium.

4. The Boltzmann distribution can also be motivated by information theory. In chapter 1 we showed that it maximizes entropy under the condition that:

$$U = \langle E \rangle = \text{const}$$

### 3.2 Free energy

The Boltzmann factor $e^{-\beta E}$ means that a microstate is the less likely the higher its energy. However, if we ask for the probability that the system has energy $E$, we have to consider all microstates with energy $E$:

$$p(E) = \frac{1}{Z} \frac{\Omega(E)}{\Omega} e^{-\beta E} = \frac{1}{Z} e^{-\beta E + S(E)/k_B}$$

This probability is maximal, if the quantity:

$$F(E, V, N) = E - T S(E, V, N)$$

has a minimum with respect to $E$. This is the case when:

$$0 = \frac{\partial F}{\partial E} = 1 - T \frac{\partial S}{\partial E} = \frac{1}{T}$$

that is when the system is at the temperature of the heat bath.

We conclude that not the smallest energy (like for vanishing $T$) or the highest entropy (like for very high $T$) is achieved in equilibrium, but the smallest $F$, which is a combination of energy and entropy with the relative importance determined by temperature. The smaller weight of the Boltzmann factor for higher energy is compensated by the fact that the number of microstates usually increases with energy. For example, for the ideal gas we have $\Omega \sim E^{3N/2}$ and therefore $S \sim \ln E$. Therefore $F = E - T S(E)$ diverges logarithmically at low $E$ and linearly at high $E$, with a minimum somewhere inbetween (note that for this argument, we have to keep $T$ fixed and cannot replace it be $E$, because this is the temperature of the heat bath given from outside).

Because in the canonical ensemble we fix $T$ rather than $E$, we actually should write $F(T, V, N)$ using the caloric equation of state to convert $E$ into $T$. This quantity is called the ‘Helmholtz free energy’ or simply the ‘free energy’. Its appearance in the canonical ensemble provides a direct link to thermodynamics, which derives the extremum principle for the free energy solely from macroscopic arguments. We conclude:
In the canonical ensemble, equilibrium corresponds to the minimum of the free energy $F(T, V, N)$.

We can construct $F(T, V, N)$ from $S(E, V, N)$ (entropy representation of the microcanonical ensemble) in the following way:

1. introduce a new variable $T = \frac{\partial S(E, V, N)}{\partial E}$
2. eliminate $E$ in favor of $T$ by solving for $E = E(T, V, N)$
3. construct $F(T, V, N) = E(T, V, N) - T S(E(T, V, N), V, N)$

Alternatively we can start from the energy representation of the microcanonical ensemble:

1. $T(S, V, N) = \frac{\partial E}{\partial S}$
2. $S = S(T, V, N)$
3. $F(T, V, N) = E(S(T, V, N), V, N) - T S(T, V, N)$

Mathematically, such procedures are known as ‘Legendre transformations’, when a function is rewritten such that it becomes a unique function of its derivative. Legendre transforms also occur in analytical mechanics:

\[
\mathcal{L} = \mathcal{L}(q, \dot{q}, t) \quad \rightarrow \quad \mathcal{H} = \mathcal{H}(q, p, t) = -(\mathcal{L} - \dot{q} p) \quad \text{with} \quad p = \frac{\partial \mathcal{L}}{\partial \dot{q}}
\]

where the Legendre transform of the (negative) Lagrange function gives the Hamiltonian function. The free energy $F$ is in fact the Legendre transform of energy $E$ with the argument changing from entropy $S$ to temperature $T$, which is defined as a derivative of $E$.

We now consider the total differential of $F(T, p, V)$:

\[
dF = dE + d(TS) = TdS - pdV + \mu N - TdS - SdT = -SdT - pdV + \mu N
\]

This is the fundamental equation of the canonical ensemble and leads to three equations of state:

\[
S = -\frac{\partial F}{\partial T} \\
p = -\frac{\partial F}{\partial V} \\
\mu = \frac{\partial F}{\partial N}
\]
How do we calculate $F$? In principle, we can start from the microcanonical ensemble and calculate it as explained above. However, this will be quite tedious or even impossible for many cases. There is a much simpler way to do it. We recall that

$$p_i = e^{\beta F} e^{-\beta E_i} = \frac{1}{Z} e^{-\beta E_i}$$

and therefore we simply have

$$\Rightarrow \quad F(T, V, N) = -k_B T \ln Z(T, V, N)$$

Thus the free energy follows directly from the partition sum and there is no need to go through the microcanonical ensemble.

A similar comment applies to the average energy $U = \langle E \rangle$. In principle, it follows from the microcanonical ensemble. However, if we work in the canonical ensemble, we can calculate it directly from the partition sum:

$$\langle E \rangle = \sum_i p_i E_i = \frac{1}{Z} \sum_i E_i e^{-\beta E_i} = \frac{1}{Z} (-\partial_\beta \sum_i e^{-\beta E_i} = -\partial_\beta \ln Z(\beta) = \langle E \rangle)$$

We can check consistency with the definition of the free energy:

$$\langle E \rangle = -\partial_\beta \ln Z(\beta) = \partial_\beta (\beta F) = F + \beta \frac{\partial F}{\partial \beta} = F - \frac{k_B T^2}{k_B T} \frac{\partial F}{\partial T} = F + TS$$

as it should.

For the variance of the energy we find:

$$\sigma_E^2 = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

$$= \frac{1}{Z} \partial_\beta^2 Z - \left( \frac{1}{Z} \partial_\beta Z \right)^2$$

$$= \partial_\beta \left( \frac{1}{Z} \partial_\beta Z \right) = \partial_\beta \ln Z$$

$$= -\partial_\beta \langle E \rangle = k_B T^2 \partial_T \langle E \rangle$$

$$= k_B T^2 \frac{c_v(T)}{\text{specific heat}}$$

Thus the second moment is related to a material property. Note that this implies $c_v(T) \geq 0$. We note that this equation connects to physical quantities that naively are unrelated: a measure for fluctuations on the left hand side and a material property or response function on the right hand side. Such surprising relations constitute the big success of thermodynamics. In the context of statistical physics, they are examples of the fluctuation-dissipation theorem.
We finally comment on the sharpness of the energy distribution. For the microcanonical ensemble, we showed that in the macroscopic limit \( N \to \infty \) the distribution becomes very sharp around the value \( E \). For the canonical ensemble, the same holds true for \( \langle E \rangle \).

We note that \( c_v \approx N k_B \) and \( \langle E \rangle \approx k_B T N \) and therefore

\[
\frac{\sigma_E}{\langle E \rangle} = \frac{1}{\sqrt{N}} = 10^{-10}
\]

for a macroscopic system with \( 10^{20} \) particles. In contrast, the single particle with \( N = 1 \) experiences very strong fluctuations.

![Figure 3.2: The energy distribution of a canonical system. \( \langle E \rangle \) scales with \( N \) while \( \sigma_E / \langle E \rangle \) is proportional to \( 1/\sqrt{N} \).](image)

### 3.3 Non-interacting systems

The canonical formalism is especially convenient if the energy of the system is a sum over the energies of \( N \) independent elements (e.g., atoms in a gas or solid). We denote by \( \epsilon_{ij} \) the \( j^{th} \) energy state of the \( i^{th} \) element:

\[
Z = \sum_{j_1} \sum_{j_2} \cdots \sum_{j_N} e^{-\beta \sum_{i=1}^{N} \epsilon_{ij}}
\]

\[
= \left( \sum_{j_1} e^{-\beta \epsilon_{1j_1}} \right) \left( \sum_{j_2} e^{-\beta \epsilon_{2j_2}} \right) \cdots \left( \sum_{j_N} e^{-\beta \epsilon_{Nj_N}} \right)
\]

\[
= z_1 \cdot z_2 \cdots z_N = \prod_{i=1}^{N} z_i
\]

\[
\Rightarrow F = -k_B T \sum_{i=1}^{N} \ln z_i = -k_B T \ln Z
\]
Thus the partition sum factorises and the free energy is additive over the elements. For \( N \) identical elements we simply have:

\[
Z = z^N, \quad F = -k_B T N \ln z
\]

where \( z \) is the ‘single particle partition sum’.

**Example:**

1. **Two-state system**
   We consider a two state system as discussed above. As all particles are identical, we only have to calculate the single particle partition sum.

\[
z = 1 + e^{-\beta \epsilon} \Rightarrow E = -\partial_\beta \ln z^N = \frac{N e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}} = \frac{N \epsilon}{1 + e^{\beta \epsilon}}
\]

This is exactly the result we obtained in two complicated calculations from the microcanonical ensemble.

Remember: \( c = \frac{dE}{dT} \) gives the Schottky-hump.

Consider again the two limits:

1. \( T \to \infty (\beta \epsilon \ll 1) : z \to 2 \)

\[
\begin{align*}
p_0 &= \frac{1}{z} = \frac{1}{2} \\
p_e &= \frac{e^{-\beta \epsilon}}{z} = \frac{1}{2}
\end{align*}
\]

Both states are equally likely.

2. \( T \to 0 (\beta \epsilon \gg 1) : z \to 1 \)

\[
\begin{align*}
p_0 &= \frac{1}{z} = 1 \\
p_e &= \frac{e^{-\beta \epsilon}}{z} = 0
\end{align*}
\]

Only the ground state is occupied.

2. **Harmonic oscillator (Einstein model)**

\[
E_n = \hbar \omega \left(n + \frac{1}{2}\right), \quad n = 0, 1, ...
\]
Again we only need the single particle partition sum:

\[ z = \sum_{n=0}^{\infty} e^{-\beta E_n} = e^{-\frac{1}{2} \beta \hbar \omega} \left( 1 + e^{-\beta \hbar \omega} + e^{-2\beta \hbar \omega} + \ldots \right) \]

\[ = e^{-\frac{1}{2} \beta \hbar \omega} \frac{1}{1 - e^{-\beta \hbar \omega}} \quad \text{using the geometrical sum} \]

\[ \Rightarrow E = -\partial_{\beta} \ln z^N = N \left\{ \frac{\hbar \omega}{2} - \frac{e^{-\beta \hbar \omega} \hbar \omega}{1 - e^{-\beta \hbar \omega}} \right\} \]

\[ = N \hbar \omega \left\{ \frac{1}{e^{\beta \hbar \omega} - 1} + \frac{1}{2} \right\} \]

Again this is the same result as the one we obtained from microcanonical calculations.

\[ T \to 0 \ (\beta \hbar \omega \to \infty): \quad E \to \frac{N \hbar \omega}{2} \quad \text{Each oscillator is in its ground state.} \]

\[ T \to \infty \ (\beta \hbar \omega \to 0): \quad E \to Nk_B T \to \infty \quad \text{Each of the two modes carries energy } k_B T / 2. \]

Figure 3.3: Harmonic oscillator: For \( T \) large, the energy of an harmonic oscillator (blue curve) increases linearly with temperature as in the classical case.
Figure 3.4: Harmonic oscillator: The heat capacity $c$ asymptotically approaches a constant value at high temperature.

3 Ideal gas

$$Z = \frac{1}{N! \hbar^{3N}} \int d\vec{q} \int d\vec{p} \, e^{-\beta p^2 / (2m)} = \frac{1}{N! \hbar^{3N}} \, V^N \left( \frac{2\pi m}{\beta} \right)^{\frac{3N}{2}}$$

$$F = -k_B T \ln Z = -k_B T N \left[ \ln V + \frac{3}{2} \ln \left( \frac{2\pi m k_B T}{\hbar^2} \right) - \frac{\ln N!}{N} \right] \approx -k_B T N \left[ \ln \left( \frac{V N}{\lambda^3} \right) + \frac{3}{2} \ln \left( \frac{2\pi m k_B T}{\hbar^2} \right) + 1 \right] = F(T, V, N)$$

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z = \frac{3N}{2} \frac{1}{\beta} = \frac{3}{2} \, N \, k_B \, T = E \quad \text{caloric equation of state}$$

We see that we get the same result as for the microcanonical ensemble.

$$p = -\frac{\partial F}{\partial V} = k_B \, T \, N \, \frac{1}{V} \Rightarrow p \, V = N \, k_B \, T \quad \text{thermal equation of state (ideal gas law)}$$

$$S = \frac{\partial F}{\partial T} = k_B \, N \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{2\pi m k_B T}{\hbar^2} \right) + 1 + \frac{3}{2} \right]$$

Replacing $T = \frac{2E}{3Nk_B}$ and using the thermal wavelength $\lambda = \left( \frac{3\hbar^2 N}{4\pi m E} \right)^{\frac{1}{4}}$, we recover the result from the microcanonical ensemble:

$$S = k_B \, N \left\{ \ln \left( \frac{V}{N \lambda^3} \right) + \frac{5}{2} \right\}$$

One can easily check that $F(T, V, N)$ also follows as Legendre transform from this expression for $S(E, V, N)$. 68
Maxwell distribution

For a classical gas with \( \mathcal{H} = \frac{p^2}{2m} + V(q) \), we ask for the probability \( dW \) to find some particle, e.g. \( i = 1 \), in the momentum interval

\[ p \leq |p_1| \leq p + dp. \]

Thus we simply integrate out all other degrees of freedom: \( \vec{p}_2, \ldots, \vec{p}_N, \vec{q}_1, \ldots, \vec{q}_N \).

\[ \Rightarrow \quad dW = \frac{1}{\tilde{Z}} 4\pi e^{-\beta p^2/(2m)} p^2 dp \]

![Maxwell distribution](image)

Figure 3.5: Maxwell distribution: The probability density \( \rho \) as a function of \( p \).

The normalization constant is

\[ \tilde{Z} = (2\pi m k_B T)^\frac{3}{2} \]

such that \( \int dW = 1 \). This result is valid for any type of gas (arbitrary interaction potential \( V \)). For an ideal gas, the average energy is the average kinetic energy:

\[ E = N \left\langle \frac{p^2}{2m} \right\rangle = \frac{3}{2} N k_B T \]
as expected.

One can easily calculate that the most likely velocity is \( v_{max} = \sqrt{2k_B T / m} \). For air, we use the mass of an oxygen molecule, \( 32 \text{ g} / N_A \) with the Avogadro number \( N_A = 6 \times 10^{23} \) (nitrogen or a mixture of oxygen and nitrogen would give us the same order of magnitude, because their molecular weights are so similar). With \( k_B T = 4 \times 10^{-21} J \), we then get \( v_{max} = \sqrt{2k_B T / m} = 400 m/s \). However, the mean free path length is only \( 10^{-7} \) m and the mean collision time \( 2 \times 10^{-10} \) s, so the molecules do not get far. One also can calculate that the coefficient of variation \( \sigma_v / \langle v \rangle \approx 0.67 \), which shows that the distribution is very broad.
Barometric formula
For an ideal gas in the gravitational field of the earth we have

$$\mathcal{H} = \sum_{i=1}^{N} \left\{ \frac{\mu_i^2}{2m} + m g h_i \right\}$$

where $h_i$ is the height of particle $i$. To get the probability that a particle is at height $h$, we arbitrarily choose one particle and integrate out all other degrees of freedom:

$$\Rightarrow \quad dW = \frac{e^{-mg h/(k_B T)}}{Z} \, dh$$

Thus the density will decrease exponentially with distance. The length scale for this will be $(k_B T)/(mg)$. Using the mass of oxygen molecules, $32g/N_A$ with the Avogadro number $N_A = 6 \times 10^{23}$, gravitational acceleration $g = 9.8m/s^2$, and $k_B T = 4 \times 10^{-21}J$, we get 7.5 km, in good agreement with the experimental scale. Because of the ideal gas law, the pressure will also decay exponentially on the same scale. Note that this model neglects the fact that temperature decreases with height (typically one degree by 100 m).

![Figure 3.6: Barometric formula: The probability density $\rho$ as a function of $h$. Assuming constant $T$, the density decays exponentially. For $T \downarrow$ the particles come down, while for $T \uparrow$ they go up.](image)

3.4 Equipartition theorem
We define $f$ to be the degrees of freedom (DOFs) that can be excited by thermal energy. We have a look at the heat capacities for the harmonic oscillators and the ideal gas:

- **harmonic oscillator**: $f = 2N$, each oscillator has kinetic and potential energy
  $$T \to \infty : \quad c_v = N k_B = f \frac{1}{2} k_B$$
ideal gas: \( f = 3N \), each particles has three degrees of translation, but there is not interaction potential

\[
c_v = \frac{3}{2} N k_B = f \frac{1}{2} k_B
\]

Such a result was not obtained for the two-state system. Obviously it is related to harmonic terms in the Hamiltonian.

Consider a harmonic Hamiltonian with \( f = 2 \): 

\[
H = A q^2 + B p^2
\]

\[
z \propto \int dq \, dp \, e^{-\beta H} = \left( \frac{\pi}{A \beta} \right)^{\frac{1}{2}} \cdot \left( \frac{\pi}{B \beta} \right)^{\frac{1}{2}} \propto \left( T^\frac{1}{2} \right)^f
\]

We conclude:

\[
\text{For sufficiently high temperature (classical limit), each quadratic term in the Hamiltonian contributes a factor } T^{\frac{1}{2}} \text{ to the partition sum ('equi}partition theorem').\]

This then leads to the following terms in other quantities:

\[
\begin{align*}
\text{free energy: } F &= -k_B T \ln z = -f \frac{1}{2} k_B T \ln T \\
\text{entropy: } S &= -\frac{\partial F}{\partial T} = \frac{f}{2} k_B (\ln T + 1) \\
\text{internal energy: } U &= -\frac{\partial}{\partial} \ln z = \frac{f}{2} k_B T \\
\text{heat capacity: } c_v &= \frac{dU}{dT} = \frac{f}{2} k_B
\end{align*}
\]

all extensive, scale with \( f \)

Examples

\[
\text{monoatomic ideal gas A monoatomic ideal gas has three translational (kinetic) degrees of freedom.}
\]

\[
\Rightarrow \quad c_v = \frac{3}{2} N k_B
\]

The positional degrees of freedom do not have quadratic energy. However, special wall potentials can give similar contributions. For the ideal gas, the wall only leads to the volume term.
2. Diatomic ideal classical gas (e.g., H-H)

The molecule has 6 modes, but different modes have different degrees of freedom. We consider a classical Hamiltonian in the center of mass system and look at relative rotational motions:

\[ H = \frac{1}{2M} \left( p_x^2 + p_y^2 + p_z^2 \right) + \frac{1}{2I} \left( \frac{p_\phi^2}{\sin^2 \Theta} + p_\Theta^2 \right) + \left( \frac{p_r^2}{2\mu} + \frac{\mu \omega^2 r^2}{2} \right) \]

Here \( I \) denotes moment of inertia and \( \mu \) the reduced mass. The total number of degrees of freedom then is

\[ f = f_t + f_r + f_v = 7 \]

\[ c_v = \frac{7}{2} N k_B \]

By only measuring the heat capacity \( c_v \), we can already infer some far-reaching statements about the architecture of the molecule. Note that this measurement does not work at room temperature, when the vibrational modes are not populated yet. At room temperature, one only measures \( c_v = (5/2)Nk_B \).

3. Triatomic molecules

Here one has to differ between triangular and linear shaped molecules. Each have \( 3 \times 3 = 9 \) modes, but the degrees of freedom \( f \) are different. For the triangular shaped molecules, we have three rotational modes and three vibrations, giving \( f = 3 + 3 + 2 \times 3 = 12 \). For the linear molecule, we have only two rotational modes but four vibrational ones, giving \( f = 3 + 2 + 2 \times 4 = 13 \).

**Virial theorem**

We consider a classical Hamiltonian system. Let \( x_i = q_i, p_i \) be position or momentum.

\[ \left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{1}{Z} \int \text{d}\Gamma \left( x_i \frac{\partial H}{\partial x_j} \right) e^{-\beta H} = \frac{x_i}{x_i} \left( e^{-\beta H} \right)_{\frac{1}{\beta}} = k_B T \delta_{ij} \]

Here we used partial integration and considered no contributions at infinity.

Specify to position and harmonic potential:

\[ V_i = \frac{1}{2} m \omega^2 q_i^2 \]
\[ \Rightarrow \langle q_i \frac{\partial V}{\partial q_i} \rangle = \langle q_i (m\omega^2 q_i) \rangle = 2 \langle V_i \rangle \]
\[ \Rightarrow \langle V_i \rangle = \frac{k_B T}{2} \]

Application to momentum and kinetic energy instead yields:
\[ T_i = \frac{p_i^2}{2m} \]
\[ \Rightarrow \langle p_i \frac{\partial T_i}{\partial p_i} \rangle = \langle p_i \frac{p_i}{m} \rangle = 2 \langle T_i \rangle = k_B T \]
\[ \Rightarrow \langle T_i \rangle = \frac{k_B T}{2} \]

Thus we obtain the same results as from the canonical ensembles. In classical mechanics, we derived a virial theorem for time rather than ensemble average:
\[ \langle T \rangle = \frac{1}{2} \langle \vec{q} \cdot \nabla V \rangle = \langle V \rangle \]
where the last step only works for harmonic systems and the average denote time averages.

3.5 Molecular gases

Each molecule can be thermally excited in many ways. Apart from the three translational modes, there are vibrational, rotational, electronic and nuclear ones. Often one can assume that they are independent:
\[ Z = Z_{\text{trans}} \cdot Z_{\text{vib}} \cdot Z_{\text{rot}} \cdot Z_{\text{elec}} \cdot Z_{\text{nuc}} \]

With respect to the \( N \) molecules in a gas we have:
\[ Z_x = z_x^N \]
where \( x \) stands for the different mode types. \( Z_{\text{trans}} \) is special, because it includes the effect of interaction potential, but we will postpone this for now and treat it later in relation to phase transitions. For a vanishing interaction potential or dilute gas, \( Z_{\text{trans}} \) is the one of the ideal gas, with a factor \( 1/N! \) accounting for exchange of particle identities. Only \( Z_{\text{trans}} \) depends on volume and thus contributes to pressure. In the following we mainly discuss diatomic molecules like molecular hydrogen \( H_2 \). Important applications include plasma physics (fusion) and astrophysics (star formation from interstellar clouds).
Vibrational modes

Intermolecular vibrations are often described by the ‘Morse potential’:

\[ V(r) = E_0 \left( 1 - e^{-\alpha (r-r_0)} \right)^2 \]

Figure 3.7: The Morse potential (blue) and its harmonic approximation (red) as a function of the interatomic distance \( r \).

An exact solution of the Schrödinger equation gives

\[ E_n = \hbar \omega_0 \left( n + \frac{1}{2} \right) - \frac{\hbar^2 \omega_0^2}{4E_0} \left( n + \frac{1}{2} \right)^2 \]

\[ \omega_0 = \frac{\alpha}{2\pi} \sqrt{\frac{2E_0}{\mu}}, \quad \mu = \frac{m_1m_2}{m_1+m_2} \text{ reduced mass} \]

For \( \hbar \omega_0 \ll E_0 \) (small anharmonic contribution, valid for \( E_0 \) large or \( \alpha \) small) we can use the harmonic approximation (anharmonic corrections can be calculated with perturbation theory):

\[ z_{vib} = e^{-\beta \hbar \omega_0/2} \frac{1}{1 - e^{-\beta \hbar \omega_0}} \]

Excitation of this mode occurs at:

\[ T_{vib} \approx \frac{\hbar \omega_0}{k_B} \approx 6.140 \text{ K} \quad \text{for } H_2 \]

Rotational modes

The standard approximation is the one of a rigid rotator. The moment of inertia for a rotator is given as

\[ I = \mu r_0^2 \]
Figure 3.8: The heat capacity $c_v$ as a function of temperature $T$. Around $T = T_{vib}$ the capacity increases and then levels off at $k_B$.

Figure 3.9: For $N_{vib}$ vibrational modes, the heat capacity raises in a step-wise manner. Here the heat capacity $c_v$ is plotted as a function of $T$ for $N_{vib} = 3$.

The rotation around the horizontal axis does not matter, because the corresponding quantum mechanical wave function is rotationally symmetric. The eigenfunctions obtained from the Schrödinger equation are the spherical harmonics $Y_{ml}$.

$$E_l = \frac{\hbar^2}{2I} l(l + 1)$$

with degeneracy $g_l = 2l + 1$.

The internal rotation contributes to the heat capacity of the diatomic molecule as shown in Figure 3.10 (small bump before the plateau). For $H_2$, the rise occurs for 85.4 K. Together with the vibrational contribution, this yields a specific heat with two rising parts as schematically shown in Figure 3.11. Below 20 K, the gas condensates into a liquid. Around 10,000 K, it starts to dissociate into atoms.
Figure 3.10: Rigid rotator: Sketch showing the contribution of internal rotation to the heat capacity of a diatomic molecule. For e.g. $H_2$: $T_{rot} = \frac{\hbar^2}{(I k_B)} \approx 85.4$ K.

Figure 3.11: Sketch showing the specific heat of a diluted gas of $H_2$ as a function of temperature.

**Nuclear contributions: ortho- and parahydrogen**

Due to the existence of a covalent bound, the spins of the electrons are coupled to $S_{elec} = 0$. However, the spins of the protons can have variable coupling. The two protons are fermions (spin-$\frac{1}{2}$ particles). For spin coupling $S = 1$ (parallel spins), there are three possible spin states:

$|\uparrow \uparrow\rangle, \frac{1}{\sqrt{2}}(|\uparrow \downarrow\rangle + |\downarrow \uparrow\rangle), |\downarrow \downarrow\rangle$ triplet state with degeneracy 3:‘orthohydrogen’

For spin coupling $S = 0$ (anti-parallel spins), there is only one possible spin state:

$\frac{1}{\sqrt{2}}(|\uparrow \downarrow\rangle - |\downarrow \uparrow\rangle)$ singlet state, no degeneracy:‘parahydrogen’
Under exchange of the two protons, the total wave function has to be anti-symmetric:

\[ \Psi(1, 2) = \Psi_0(r) \ Y_{l m}(\Theta, \Phi) \ |S,S_z\rangle \]

\[ \Rightarrow \ P_{12} \ \Psi(1, 2) = (-1)^{l+S+1} \ \Psi(1, 2) = -\Psi(1, 2) \]

\[ \Rightarrow \ S = 1 \ (ortho) : \ l = 1, 3, 5... \ only \ odd \ l \ are \ allowed \]
\[ S = 0 \ (para) : \ l = 0, 2, 4... \ only \ even \ l \ are \ allowed \]

As for low \( T \) (\( T \ll T_{rot} \)) only the ground state (\( l = 0 \)) is occupied, we conclude that only parahydrogen can exist at low temperatures. For high temperatures (\( T \gg T_{rot} \)), all four spin states are equally likely and ortho- and parahydrogen hence exist in a ratio of 3 : 1.

Importantly, the relaxation time to equilibrium is one year due to a very weak interaction energy. Below this time scale, the system has a memory and the specific heat depends on the preparation history.

Restricted partition sums:

\[ z_{ortho} = \sum_{l=1,3,5,...} (2l + 1) e^{-\frac{l(l+1)T_{rot}}{T}} \]
\[ z_{para} = \sum_{l=0,2,4,...} (2l + 1) e^{-\frac{l(l+1)T_{rot}}{T}} \]

After a long time, we have \( z_{rot} = 3z_{ortho} + z_{para} \). Figure 3.12 shows schematically how the two different contributions to \( c_v \) and their equilibrium mixture behave as a function of temperature.

Figure 3.12: Heat capacity as a function of temperature for ortho- and parahydrogen (blue). The red curve indicates the equilibrium ratio as obtained at high temperature.
3.6 Specific heat of a solid

We consider a solid to be a collection of masses and springs (harmonic solid). We only focus on the $3N$ vibrational modes and disregard electronic or nuclear modes. Translational and rotational modes obviously do not contribute in a solid. As we discussed before, the simplest approach is the so-called ‘Einstein solid’, consisting of $3N$ oscillators with frequency $\omega_0$ vibrating around their equilibrium positions. However, this model does not predict the experimentally measured low temperature dependence correctly ($c \propto T^3$). What is obviously missing here is the fact that the atoms do not oscillate by themselves, but collectively.

![Figure 3.13: Simple model of a solid: The regularly distributed atoms are connected by springs forming a large coupled system.](image)

**Debye model (1912)**

We first consider a one-dimensional crystal (linear chain).

![Figure 3.14: Debye model in one dimension: Atoms are arranged in a linear chain and coupled with springs. $q_i$ denotes the elongation away from equilibrium for the $i$-th atom.](image)

Each atom is displaced by $q_n(t)$ from its equilibrium position $x_n = n a$. We write down the equation of motion:

$$m \ddot{q}_n = F_n = \kappa (q_{n+1} - q_n) - \kappa (q_n - q_{n-1})$$

$$= \kappa \left( q_{n+1} + q_{n-1} - 2q_n \right)$$

discretized second derivative
In the continuum limit, this gives a wave equation $\ddot{q} - c_s^2 q'' = 0$ with the wave velocity $c_s = (\kappa a^2 / m)^{1/2}$ (velocity of sound). We stay in the discrete picture but use the fact that we expect wave-like solutions:

$$q_n(t) = A e^{i(\omega t + kna)}$$

$$\omega = \frac{2\pi}{T} \text{ frequency, } \quad k = \frac{2\pi}{\lambda} \text{ wave number}$$

$$\Rightarrow -m\omega^2 = \kappa \left[ e^{ika} + e^{-ika} - 2 \right] = -2\kappa \left[ 1 - \cos(ka) \right] = -4\kappa \sin^2 \left( \frac{ka}{2} \right)$$

$$\Rightarrow \omega(k) = \left( \frac{4\kappa}{m} \right)^{1/2} \left| \sin \left( \frac{ka}{2} \right) \right|$$

The frequency is not constant, but depends on the wave number. Since the solution is $2\pi$-periodic, we restrict it to the interval $-\pi / a < k < +\pi / a$ (first Brillouin zone). We note that for $k = 0$ (center of Brillouin zone), the phase difference between two neighbors is $e^{ika} = 1$ and they oscillate in phase. For $k = \pi / a$ (boundary of Brillouin zone), we have a phase difference of $e^{\pi a} = -1$ and neighbors oscillate against each other. The oscillation at small frequency defines the same velocity of sound as identified above because both cases correspond to the continuum limit:

$$c_s = \frac{d\omega}{dk} \bigg|_{k=0} = \sqrt{\frac{\kappa}{m} a}$$

Figure 3.15: The dispersion relation of the Debye model (blue) and its linear approximation for small values of $k$ (red).
We next consider a finite system size, that is $N$ atoms and a chain length $L = N a$. We choose periodic boundary conditions (Born-von Karman boundary conditions):

$$q_n = q_{n+N}$$

$$\Rightarrow \quad e^{i k Na} = 1 \quad \Rightarrow \quad k_j = \frac{2\pi}{a N} j, \quad j = 0, \pm 1, \ldots, \pm \frac{N}{2}$$

Only discrete $k-$values are allowed in the first Brillouin zone. As a result we have $N$ degrees of freedom, thus only $N$ oscillators are possible. Their $k-$values are separated by:

$$\Delta k = \frac{2\pi}{L}$$

which is the density of states in $k-$space.

Going to a three-dimensional system, waves are now written as:

$$\vec{A} e^{i(\vec{k} \cdot \vec{r} + \omega t)}$$

with wave vector $\vec{k}$. In addition to the longitudinal wave discussed in one dimension, we also have two transversal waves. The number of modes then becomes:

$$\# \text{modes} = \sum_{\vec{k}} 3 = 3 \prod_{i=x,y,z} \int_{-\pi/a}^{\pi/a} \frac{dk_i}{\Delta k}$$

$$= 3 \left( \frac{2\pi}{a} \right)^3 = \frac{3V}{a^3} = 3N$$

Here we introduced the volume $V = L^3$ in the penultimate step.

We now transfer the summation over modes from $\vec{k}$-space to $\omega$-space. This implies that we now switch from Cartesian to spherical coordinates. As an approximation we assume a linear dispersion relation:

$$\omega = c_s |k|$$

We also assume that longitudinal and transversal modes have the same velocity and and that all directions are equally probable.

$$\Rightarrow \quad \# \text{modes} = 3 \int \frac{d^3k}{(\Delta k)^3} = \frac{3V}{(2\pi)^3} \int_{0}^{k_{\text{max}}} 4\pi k^2 dk$$

$$= \frac{3V}{2\pi^2 c_s^3} \int_{0}^{\omega_D} d\omega \omega^2 = \frac{V}{2\pi^2 c_s^3} \omega_D^3 \approx 3N$$

The maximal or Debye frequency follows as:

$$\omega_D = c_s \left( \frac{6\pi^2 N}{V} \right)^{\frac{1}{3}} \approx 3.9 \frac{c_s}{a}$$
where we used \( V = N a^3 \). This agrees approximately with our earlier statement:

\[
k_{\text{max}} = \frac{\omega_D}{c_s} = \frac{\pi}{a}
\]

In summary, the Debye model assumes the following (normalized) density of states in \( \omega \)-space:

\[
D(\omega) = \begin{cases} 
\frac{3}{\omega_D^2} \omega^2 & \text{for } \omega \leq \omega_D \\
0 & \text{for } \omega > \omega_D 
\end{cases}
\]

![Figure 3.16: The density of states \( D \) for the Debye model as a function of \( \omega \).](image)

We now know how to count modes in frequency-space:

\[
\sum_{\text{modes}} (\ldots) = 3 \sum_k (\ldots) = 3N \int_0^{\omega_D} d\omega \ D(\omega) (\ldots)
\]

We now combine the spectrum with Einstein’s concept that each mode is a harmonic oscillator to arrive at the partition sum:

\[
z(\omega) = \frac{e^{-\beta \omega/2}}{1 - e^{-\beta \omega}}
\]
\[ Z = \prod_{\text{modes}} z(\omega) \]
\[ E = -\partial_\beta \ln Z = \sum_{\text{modes}} \hbar \omega \left( \frac{1}{e^{\beta \hbar \omega} - 1} + \frac{1}{2} \right) \]
\[ E = E_0 + 3N \int_0^{\omega_D} d\omega \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \frac{3\omega^2}{\omega_D^3} \]
\[ c_v(T) = \frac{\partial E}{\partial T} = \frac{-1}{k_B T^2} \frac{\partial E}{\partial \beta} \]
\[ c_v(T) = \left. \frac{\hbar^2}{k_B T^2} \sum_{\text{modes}} e^{\beta \hbar \omega} \omega^2 \right|_{e^{\beta \hbar \omega} - 1} \]
\[ c_v(T) = 3\hbar^2 N \int_0^{\omega_D} d\omega \frac{3\omega^2}{\omega_D^3} e^{\beta \hbar \omega} \omega^2 \]

The constant contribution \( E_0 \) from the rest energy drops out for the specific heat. We change the integration variable to \( u = \beta \hbar \omega \):

\[ c_v(T) = \frac{9Nk_B}{u_m^3} \int_0^{u_m} \frac{e^u u^4}{(e^u - 1)^2} du \]

Unfortunately this integral cannot be solved analytically.

We consider two limits:

1. \( k_B T \gg \hbar \omega_D, \ u \ll 1: \)
   \[ u \approx 1 \Rightarrow c_v(T) = 3Nk_B \] classical limit for 6N degrees of freedom

2. \( k_B T \ll \hbar \omega_D, \ u \gg 1: \)
   \[ u_m \rightarrow \infty \]

The integral becomes a constant and the only temperature dependence comes from the factor \( 1/u_m^3 \).

\[ c_v(T) = \frac{12\pi^4}{5} Nk_B \left( \frac{T}{T_D} \right)^5 \]

Here we defined the ‘Debye temperature’ \( T_D = \hbar \omega_D / k_B \). Note that if you replace \( T_D \) by \( \omega_D \) and then this by the formula derived for it above, then \( N \) drops out and \( c_v \) scales simply as \( V \), as it should, because there is not spatial aspect to the model.
Figure 3.17: The heat capacity as a function of temperature for two limits of the Debye model (blue) compared with the Einstein model (red). For the Debye model $c_v(T) \propto T^3$ at low temperatures in agreement with experimental results.

Typical experimental values are:

$$c_s = 5.000 \frac{m}{s}$$ (eg iron)
$$a = 2 \text{ Å}$$
$$\omega_D \approx \frac{4c_s}{a} = 10^{14} \text{ Hz}$$
$$T_D = \frac{\hbar \omega_D}{k_B} \approx \frac{10^{-34} Js 10^{14} \text{ Hz}}{\frac{3}{2} 10^{-23} J K} \approx 700 \text{ K}$$

**Summary**

1. At high $T$, we have the classical limit:

$$3N \text{ oscillators} \times 2 \text{ degrees of freedom each} \times \frac{k_B T}{2} \text{ energy}$$

2. At low $T$, all modes with $\hbar \omega \leq k_B T$ are excited.

$$\Rightarrow \# \text{modes} \propto \int d\vec{k} \propto k^3 \propto \omega^3 \propto T^3$$

**Final comments on solid state physics**

1. The excitations of the lattice can be considered as quasi-particles with energy $\hbar \omega$ ('phonons') in analogy to photons, which have similar statistics ('Bose statistics').
The three polarities of a wave with wave vector $\vec{k}$ can be interpreted as spins $(0, \pm 1)$.

2. The excitations discussed here are known as \textit{acoustic} modes (typically excited by sound). Electronic excitations lead to \textit{optical} modes (typically excited by electromagnetic radiation).

3. The standard way to measure the dispersion relation (or phonon spectrum) of a crystal is neutron scattering. X-rays also work, but this is much harder. One typically works around $k = 0$ in the Brillouin zone, which also satisfies the Bragg criterion for a strong reflection. One then looks for small side peaks (Stokes and anti-Stokes lines) that either come from acoustic phonons (Brillouin scattering) or from optical phonons (Raman scattering).

### 3.7 Black body radiation

The black body is a cavity filled with electromagnetic radiation in equilibrium with a thermal reservoir of temperature $T$. In the particle picture of quantum mechanics, we deal with a gas of photons. The dispersion relation for photons is

$$\epsilon(k) = h\omega(k) = hck$$

with the velocity of light $c \approx 3 \cdot 10^8 \text{ m/s}$. This relation is linear in $k$ as for the Debye model. In contrast to the Debye model, however, there is no cutoff in the frequency
spectrum. Moreover there are only two possible polarizations (dictated by Maxwell equations - in contrast to lattice vibrations there is no longitudinal mode). Like for the Debye model, each k-mode is a quantum mechanical oscillator:

\[ \epsilon_{k,m} = \hbar \omega(k) \left( n_{k,m} + \frac{1}{2} \right) \]

\[ \Rightarrow E = \sum_{k,m} \epsilon_{k,m} = 2 \sum_{k} \epsilon(k)n_k + E_0 \]

While for the Debye model the ground state contribution \( E_0 \) is finite, this is not the case for photons. We disregard it as it is an unobservable constant.

\[ \Rightarrow E = 2 \left( \frac{1}{\Delta k} \right)^3 \int \frac{d\tilde{k}}{4\pi} \frac{ e^{\beta \epsilon(k)} - 1}{e^{\beta \epsilon(k)} - 1} \]

\[ = \frac{2V}{(2\pi)^3} \int k^2 \frac{dk}{4\pi} \frac{\hbar c k}{e^{\beta \hbar c k} - 1} \]

\[ = \frac{V}{\pi^2 \beta^4 \hbar^4 c^3} \int_0^\infty \frac{u^3}{e^u - 1} du \]

\[ = \sum_{n=1}^\infty \frac{1}{n^4} \int_0^\infty \frac{u^3}{e^u - 1} du = 6 \sum_{n=1}^\infty \frac{1}{n^4} \pi^4 \]

\[ \Rightarrow E = \frac{4\sigma}{c} VT^4 \quad \text{with Stefan-Boltzmann constant} \quad \sigma = \frac{\pi^2 k_B^4}{60 \hbar^4 c^2} \]

For the heat capacity of a black body this implies:

\[ c_V = \frac{16\sigma}{c} VT^3 \]

The \( c_V \propto T^3 \) scaling is the same as for the low temperature limit of the Debye model. However, for the photon gas this result is rigorous as no linearization of the dispersion relation is required. Furthermore it is valid for all temperatures.

How much power \( P \) (energy/time) is emitted by a black body cavity with an opening of size \( A \) (Figure 3.19)? The energy flux \( J \) (energy/time · area) in direction of a photon is

\[ J = \frac{E}{A \Delta t} = \frac{E \Delta x}{(A \Delta x) \Delta t} = \frac{Ec}{V} \]

Photons move in all directions, but only the component perpendicular and outward to the opening contributes.

\[ \Rightarrow P = \frac{Ec}{V} A \frac{1}{4\pi} \int_0^{2\pi} d\Phi \int_0^1 d(\cos \Theta) \cos \Theta \]

\[ = \frac{P}{A} = \sigma T^4 \quad \text{Stefan-Boltzmann law} \]
We return to the energy integral and note that it can be written as an integral over
frequencies:
\[
\frac{E}{V} = \int_0^\infty d\omega \ u(\omega)
\]
Here we defined:
\[
 u(\omega) := \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/(k_B T)} - 1}
\]
Planck’s law for black body radiation

Figures 3.20 and 3.21 show the spectral radiance as a function of frequency and wave-
length respectively.

Figure 3.20: The spectral radiance \( u \) as a function of \( \omega \). For small or large \( \omega \) Planck’s law can be approximated by the Rayleigh-Jeans or Wien limits, respectively. Both limits were known to Max Planck when he derived his formula in 1900. For higher temperatures the spectral maximum is shifted to higher frequencies.
Figure 3.21: The spectral radiance $u$ as a function of wavelength $\lambda$. For higher temperatures the spectral maximum is shifted to shorter wavelengths.

The Planck distribution has a maximum at

$$\frac{du}{d\omega} \bigg|_{\omega=\omega_m} = 0 \quad \Rightarrow \quad \beta \hbar \omega_m = 3 \left( 1 - e^{-\beta \hbar \omega_m} \right)$$

$$\Rightarrow \quad \hbar \omega_m = 2.82 k_B T$$ Wien’s displacement law

For example, heating an iron from 1.000 to 2.000 K shifts its spectrum from red to white due to a larger contribution in the blue range.

The Planck distribution and the Stefan-Boltzmann law are very general and usually apply if matter and radiation are in thermodynamical equilibrium. The Planck distribution and Wien’s displacement law can be used to extract the temperature of such a system:

1. **sun:** $T = 5.800 \text{ K} \Rightarrow \lambda_m$ in the visible und UV range

2. **earth or human body:** $T = 300 \text{ K} \Rightarrow \lambda_m$ in the infrared range; this is why we can see people and heated houses so well with infrared cameras.

3. **cosmic background radiation:** $T = 2,73 \text{ K} \Rightarrow \lambda_m \approx \text{cm (microwaves)}$ discovered by Penzias and Wilson 1964 (Nobel Prize in physics 1978)

The ideal photon gas depends on volume only through its dispersion relation (no particle interactions):

$$\epsilon(k) = \hbar c k \propto \frac{1}{L} = \frac{1}{V}$$

$$E = 2 \sum_k \epsilon(k) n_k$$

$$p = -\frac{\partial E}{\partial V} = \frac{1}{3} \frac{E}{V} = \frac{1}{3} c E = \frac{1}{3} \frac{J}{c}$$
We note that the sun’s radiation pressure on earth is much smaller than the atmospheric pressure.

**Solar energy and the greenhouse effect**

Our earth is heated by the sun. Because we know its temperature, radius and distance, we can calculate how much energy should arrive here and how much it should warm up the earth. The sun radiates an energy flux \( J = \sigma T^4 \) due to its temperature \( T = 5.800 \text{ K} \). We have to multiply this by \( 4\pi R_s^2 \) with \( R_s = 696.000 \text{ km} \) being the radius of the sun to get the overall output. Because of energy conservation, at the distance \( r = 1.5 \times 10^8 \text{ km} \) where the earth is located, we have to divide by \( 4\pi r^2 \) to get the flux onto the earth:

\[
J = \sigma T_s^4 \left( \frac{R_s}{r} \right)^2 = 1.37 \text{ kW/m}^2
\]

which is known as the solar constant.

In thermal equilibrium, the earth should emit as much as it receives:

\[
J_{\text{in}} = \sigma T_s^4 \left( \frac{R_s}{r} \right)^2 = J_{\text{out}} = 4\sigma T_e^4
\]

where the factor 4 represents the fact that while the sun is so far away that it appears to be an emitter with parallel rays to us, the earth radiates in all directions, see the calculation above between the factor 4 difference between radiation in all directions and in one direction only. We conclude

\[
T_e = T_s \left( \frac{R_s}{2r} \right)^{1/2} = 280 \text{K} = 7^\circ \text{C}
\]

If we take into account that 30 percent of the sun’s radiation is actually reflected by the atmosphere (albedo), the estimate gets even worse:

\[
T_e = T_s 0.7^{1/4} \left( \frac{R_s}{2r} \right)^{1/2} = 256 \text{K} = -17^\circ \text{C}
\]

Thus everything should be frozen and life was not possible on earth.

The explanation for the discrepancy to the observed temperature is the famous greenhouse effect. Because the earth has a temperature of the order of 300 K, it emits in the infrared according to Planck (see above). While being relatively transparent in the visible and UV range, water vapor, \( \text{CO}_2 \) and \( \text{CH}_4 \) in the atmosphere strongly absorb in the infrared. Therefore they let radiation from the sun in but absorb radiation from the earth (ozone \( \text{O}_3 \) absorbs in the UV and therefore protects us from excessive DNA-damage). 40% of the outgoing radiation is absorbed, so only 60% is radiated away. A better estimate therefore is

\[
T_e = T_s \frac{0.7^{1/4}}{0.6^{1/4}} \left( \frac{R_s}{2r} \right)^{1/2} = 290 \text{K} = 17^\circ \text{C}
\]
which agrees well with our observations. Without any atmosphere, the earth would be around 30 degrees Celsius colder. Without clouds, it would be colder by 10-15 degrees. Interestingly, the power radiated by the sun was 25% weaker when life started on earth four billion years ago. While the sun got stronger, the amount of CO$_2$ in the atmosphere decreased because life started to generate oxygen and luckily the two effects balanced each other such that a relatively constant temperature of 15 degrees Celsius and a pressure of 1 atm was maintained on earth. Today, the amount of CO$_2$ increases again because we burn so much coal and gas, thus freeing carbon stored in the earth. Other reasons for the increasing CO$_2$ levels are the destruction of forest and increased land use. On Venus, which has a similar size and composition as the earth, but did not develop life, the greenhouse effect went out of control (too much CO$_2$ in the atmosphere), so the water oceans evaporated and today life is not possible there with 470 degrees Celsius and a pressure of 90 atm. In 2016 average atmospheric CO$_2$ concentrations have surpassed 400 parts per million, a level that has been last reached 3 million years ago, when temperatures were 2 – 3$^\circ$C warmer and sea levels 10-20 meters higher; even more recently this concentration has in fact shown in increasing rate of change, which is very alarming.

Eruptions of volcanos release sulphur dioxide into the atmosphere that absorb sun light and therefore cool the earth. 74,000 years ago the eruption of Toba in Indonesia possibly triggered a new ice age. Only thousands of humans survived as evidenced from their small genetic diversity at that time. When Tambora erupted in Indonesia in 1815, the following year was without summer in Europe and the population suffered from hunger. In 1991, Pinatubo erupted in the Philippines and temperature went down by half a degree for two years. In principle these effects could be used for climate engineering, by spraying vapor or sulphur dioxide into the atmosphere, but this might be
very difficult to control. Finally some history on climate research. Joseph Fourier in 1824 published his "Remarques Generales Sur Les Temperatures Du Globe Terrestre Et Des Espaces Planetaires", in which he concluded that the atmosphere must somehow isolate the earth. In 1859 John Tyndall found that water vapor and CO$_2$, but not oxygen or nitrogen in the atmosphere absorb and gives away heat. Climate research finally started fully in 1896 when Svante Arrhenius (Nobel Price 1903 for Physical Chemistry) published his treatise "On the Influence of Carbonic Acid in the Air Upon the Temperature of the Ground". He even calculated that temperature increases logarithmically with CO$_2$ concentration in the atmosphere, correctly predicting that a doubling leads to an increase of temperature of a few degrees.
# 4 The grandcanonical ensemble

## 4.1 Probability distribution

We now consider a reservoir for both energy and particle number. In this ‘grandcanonical ensemble’ the equilibrium conditions are $T_1 = T_2$ and $\mu_1 = \mu_2$. Thus now temperature $T$ and chemical potential $\mu$ are fixed. An example would be a open bottle lying on the ground of a lake. Now not only heat, but also particle number can be exchanged with the environment.

The derivation of the corresponding probability distribution is similar as for the canonical ensemble. We consider one specific microstate $i$ that then comes with an energy $E_i$ and a particle number $N_i$. Then its probability to occur is

$$p_i = \frac{\text{# favorable outcomes}}{\text{# possible outcomes}} = \frac{\Omega_{\text{res}}(E_{\text{tot}} - E_i, \ N_{\text{tot}} - N_i)}{\Omega_{\text{tot}}(E_{\text{tot}}, \ N_{\text{tot}})} = \frac{e^{\frac{S_{\text{res}}(E_{\text{tot}} - E_i, N_{\text{tot}} - N_i)}{k_B}}}{e^{\frac{S_{\text{tot}}(E_{\text{tot}}, N_{\text{tot}})}{k_B}}}$$

We next introduce the average energy $\bar{E}$ and the average particle number $\bar{N}$ as reference values and Taylor-expand the entropy of the reservoir:

$$S_{\text{res}}(E_{\text{tot}} - E + E_i, N_{\text{tot}} - N + N_i) = S_{\text{res}}(E_{\text{tot}} - E_i, N_{\text{tot}} - N_i) + \frac{E - E_i}{T} - \mu \frac{(N - N_i)}{T}$$

Here we have used $\frac{\partial S}{\partial E} = \frac{1}{T}$ and $\frac{\partial S}{\partial N} = \mu / T$. Note that higher order terms do not appear for a reservoir. We also can use additivity of the entropy to write

$$S_{\text{tot}}(E_{\text{tot}}, N_{\text{tot}}) = S(E, N) + S_{\text{res}}(E_{\text{tot}} - E_i, N_{\text{tot}} - N_i)$$

Together we therefore get

$$p_i = e^{\beta \Psi} e^{-\beta E_i + \beta \mu N_i}$$

where

$$\Psi = E - TS - \mu N$$

Thus the overall structure of the result is similar as for the canonical ensemble: there is a Boltzmann-factor $e^{-\beta E_i + \beta \mu N_i}$ for the weight of the microstate as a function of its energy $E_i$ and its particle number $N_i$, and there is a normalization factor $e^{\beta \Psi}$.

We can make this derivation shorter if we make the normalization only at the end. In this case we do not even have to specify around which reference values we expand. We simply write

$$p_i \propto e^{S_{\text{res}}(E_{\text{tot}} - E_i, N_{\text{tot}} - N_i)/k_B} \propto e^{-\beta E_i + \beta \mu N_i}$$
where now the expansion could also be around $E_{tot}, N_{tot}$ for simplicity. We therefore get
\[
p_i = \frac{1}{Z_G} e^{-\beta(E_i - \mu N_i)} \quad \text{grandcanonical prob. distribution}
\]
where
\[
Z_G = \sum_i e^{-\beta(E_i - \mu N_i)} \quad \text{grandcanonical partition sum}
\]
Note that we could have derived the same result through information theory by maximizing Shannon entropy with the two constraints of given average energy and given average particle number. From above we also can conclude that
\[
\Psi = -k_B T \ln Z_G
\]
must be the relevant thermodynamic potential.
Obviously our result is closely related to the canonical result. To make this clearer, we write $i = (N, j)$, where $j$ are all quantum numbers besides $N$:
\[
Z_G = \sum_{N=0}^{\infty} \left( \sum_j e^{-\beta E_j} \right) e^{\beta \mu N} = \sum_{N=0}^{\infty} Z(T, V, N) e^{\beta \mu N}
\]
Thus $Z_G$ follows by another summation from the canonical partition sum $Z$.

### 4.2 Grandcanonical potential

The probability to have a macroscopic value $(E, N)$ is:
\[
p(E, N) = \frac{1}{Z_G} \Omega(E, N) e^{-\beta(E - \mu N)} = \frac{1}{Z_G} e^{-\beta(E - TS - \mu N)} = \frac{1}{Z_G} e^{-\beta \Psi(T, V, \mu)}
\]
Here we defined the ‘grandcanonical potential’ that also appeared above: $\Psi(T, V, \mu) := E - TS - \mu N$.

$p$ is maximal, if $\Psi$ is minimal. We note:

- microcanonical ensemble: $S$ maximal
- canonical ensemble: $F$ minimal
- grandcanonical ensemble: $\Psi$ minimal
\[ \Psi = E [T, \mu] \] is the two-dimensional Legendre transform of energy from the extensive variables \((S, N)\) to the intensive variables \((T, \mu)\).

Total differential:

\[
d\Psi = d(E - TS - \mu N) = TdS - p dV + \mu dN - d(TS + \mu N) = -SdT - pdV - N d\mu
\]

Equations of state:

\[
S = -\frac{\partial \Psi}{\partial T}, \quad p = -\frac{\partial \Psi}{\partial V}, \quad N = -\frac{\partial \Psi}{\partial \mu}
\]

### 4.3 Fluctuations

Average and variance of the internal energy \(E\) can be calculated as before for the canonical ensemble. We now calculate average and variance of the particle number \(N\):

\[
\langle N \rangle = \sum_i p_i N_i = \frac{1}{Z_G} \sum_i N_i e^{-\beta(E_i - \mu N_i)} = \frac{1}{Z_G} \frac{1}{\beta} \partial_\mu \sum_i N_i e^{-\beta(E_i - \mu N_i)} = \frac{1}{\beta} \partial_\mu \ln Z_G
\]

\[
\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta^2} \frac{1}{Z_G} \partial_\mu \langle N \rangle = \frac{1}{\beta^2} \partial_\mu^2 \ln Z_G
\]

One can show with thermodynamic considerations (Maxwell relations):

\[
\frac{\partial N}{\partial \mu} \bigg|_{T,V} = -\frac{N^3}{V^2} \frac{\partial v}{\partial p} \bigg|_{N,T} \quad \left( v = \frac{V}{N} \right)
\]

\[
\Rightarrow \quad \kappa_T := -\frac{N}{V} \frac{\partial v}{\partial p} \bigg|_{N,T} = \frac{V}{N^2 k_B T} \sigma_N^2 \geq 0 \quad \text{as} \quad \sigma^2 \geq 0
\]

Here we defined the ‘isothermal compressibility’ \(\kappa_T\).
Like for the canonical ensemble, where we found

\[ c_v = \frac{\sigma_E^2}{k_B T^2} \geq 0 \]

again the variance is related to a material property:

\[ \sigma_N^2 = \frac{N^2 k_B T \kappa T}{V} \quad \text{intensive} \quad \Rightarrow \quad \sigma_N^2 \propto N \]

\[ \Rightarrow \quad \frac{\sigma_N}{\langle N \rangle} \propto \frac{1}{N^2} \]

Particle fluctuations are small for large systems as expected based on the law of large numbers.

Note that calculation of the average energy is a bit more tricky now than in the canonical ensemble because there are two terms related to \( \beta \). If we want to get only the energy part, we have to keep the chemical potential part constant:

\[ \langle E \rangle = -\partial_\beta \ln Z_G \bigg|_{\beta \mu} \]

A simpler solution is to do the derivative for \( \beta \) without constraint and then to subtract the part which is not wanted:

\[ \langle E \rangle = -\partial_\beta \ln Z_G + \mu \langle N \rangle = -\partial_\beta \ln Z_G + \frac{\mu}{\beta} \partial_\mu \ln Z_G \]

### 4.4 Ideal gas

For the canonical partition sum we had:

\[ Z(T, V, N) = \frac{1}{N!} \left( \frac{V}{\lambda^3} \right)^N \quad \text{with} \quad \lambda = \frac{\hbar}{(2\pi mk_B T)^{\frac{1}{2}}} \]

\[ Z_G = \sum_{N=0}^{\infty} Z(T, V, N) \ e^{\beta \mu N} = \sum_{N=0}^{\infty} \frac{1}{N!} \left( e^{\beta \mu} \frac{V}{\lambda^3} \right)^N \]

\[ = e^{z \frac{V}{\lambda^3}} \quad \text{with fugacity} \quad z := e^{\beta \mu} \]

\[ \Rightarrow \quad \langle N \rangle = \frac{1}{\beta} \partial_\mu \ln Z_G \]

\[ = \frac{1}{\beta} \partial_\mu \left( z \frac{V}{\lambda^3} \right) = \frac{V}{\lambda^3} e^{\beta \mu} \]

\[ \mu = k_B T \ln \left( \frac{NA^3}{V} \right) \]
This result is identical with the one we derived from the microcanonical ensemble. The variance then becomes:

\[ \sigma_N^2 = \frac{1}{\beta} \partial_{\mu} \langle N \rangle = \frac{1}{\beta} \partial_{\mu} \left( \frac{e^{\beta \mu} V}{\lambda^3} \right) = N \]

\[ \kappa_T = \frac{VN}{N^2 k_B T} = \frac{1}{p} \] which also follows from \( pV = Nk_B T \)

### 4.5 Molecular adsorption onto a surface

We consider a gas in contact with a solid surface (e.g. argon on graphene or molecular nitrogen on iron, as in the Haber-Bosch synthesis). The gas molecules can be adsorbed at \( N \) specific adsorption sites while one site can only bind one molecule. The energies of the bound and unbound state are \( \epsilon \) and 0, respectively. \( \epsilon \) can be negative or positive.

The gas acts as a reservoir fixing \( T \) and \( \mu \).

The partition sum is:

\[ Z_G = z_G^N \]

where we considered a non-interacting system with single particle partition sum:

\[ z_G = 1 + e^{-\beta(\epsilon - \mu)} \]

The mean number of absorbed particles per site follows as:

\[ \langle n \rangle = \frac{0 + 1 \cdot e^{-\beta(\epsilon - \mu)}}{Z_G} = \frac{1}{e^{-\beta(\mu - \epsilon)} + 1} \]

Figure 4.1: A gas at \((T, \mu)\) in contact with a solid surface. The solid contains \( N \) specific adsorption sites each able to bind one or none gas molecule.

The mean energy per site is:

\[ \langle \epsilon \rangle = \frac{0 + \epsilon \cdot e^{-\beta(\epsilon - \mu)}}{Z_G} = \epsilon \langle n \rangle \]

This model can be easily generalized to more complicated situations, e.g. if more than one molecule can be adsorbed.
Figure 4.2: The mean number of absorbed particles $\langle n \rangle$ as a function of the chemical potential $\mu$. Half-occupancy occurs at $\mu = \epsilon$.

If the adsorbate is an ideal gas:

$$\mu = k_B T \ln \frac{p}{p_0}$$

$$\Rightarrow e^{\beta \mu} = \frac{p}{p_0}$$

$$\Rightarrow \langle n \rangle = \frac{p}{p_0 e^{\beta \epsilon} + p}$$

The number of adsorbed particles first rises linearly with pressure (or, equivalently, with concentration) and then plateaus. This is known as the Langmuir isotherm.
Figure 4.3: The mean number of absorbed (ideal gas) particles $\langle n \rangle$ as a function of pressure $p$. 
5 Quantum fluids

5.1 Fermions versus bosons

For multi-particle systems, experiments have shown that the rules of single-particle quantum mechanics have to be extended by one more principle (generalized Pauli principle):

| Particles with half-integer (integer) spin are called fermions (bosons). Their total wave function (space and spin) must be antisymmetric (symmetric) under the exchange of any pair of identical particles. |

Comments

1. For electrons (spin = \( \frac{1}{2} \), fermions), we get the Pauli principle (antisymmetric wave function) and the Pauli exclusion principle (no two electrons can occupy the same state). If two electrons have opposite spins (singlet), their spin wave function is antisymmetric (\( \frac{1}{\sqrt{2}} (\hat{\uparrow}\downarrow - \hat{\downarrow}\uparrow) \)) and the spatial wave function can be symmetric. If two electrons have the same spin (triplet), their spin wave function is symmetric and the spatial wave function hence has to be antisymmetric:

\[
\Phi(1, 2) = a(1)b(2) - a(2)b(1)
\]

Since \( a = b \) for identical particles and thus \( \Phi(1, 2) = 0 \), two electrons can not be at the same position. This is the basis of atomic stability.

2. Fermions are the quantum mechanical analogues of classical particles (matter can not penetrate itself). Bosons, in contrast, are the quantum mechanical analogue of classical waves, which can be superimposed freely and thus transfer lots of information. The standard example are photons which can be freely created and annihilated and which are the exchange particles of the electromagnetic interaction.

Consequences for counting

We consider a system of two identical particles, each of which can exist in either of two states.

We see from Figure 5.1 that all cases differ in their outcome for the number of states. Both ‘classical’ and ‘corrected classical’ counting are incorrect. The rules of quantum
mechanics imply more than simply saying that identical particles cannot be distinguished. They actually mean that we have to do the calculation separately for fermions and bosons. However, at high temperature the particles are distributed over all states, the probability of two particles being in one state becomes very small and corrected classical counting becomes valid. All quantum fluids become ideal gases at high temperature.

**Grand canonical ensemble**

Quantum fluids are best treated in the grand canonical formalism. Thus we fix $T$ and $\mu$. For a non-interacting system, the partition sum for a single energy state for a fermion (only two states in regard two occupancy) is:

$$z_F = 1 + e^{-\beta(\epsilon - \mu)}$$

The average occupation number $n_F$ becomes:

$$n_F = \frac{0 \times 1 + 1 \times e^{-\beta(\epsilon - \mu)}}{1 + e^{-\beta(\epsilon - \mu)}} = \frac{e^{-\beta(\epsilon - \mu)}}{1 + e^{-\beta(\epsilon - \mu)}}$$

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

Fermi function

$$n_F(\epsilon = \mu, T) = \frac{1}{2}$$

$n_F(\epsilon, T)$ (compare Figure 5.2) is symmetric under inversion through the point $\epsilon = \mu$. Figure 5.1: Table of states for a system of two identical particles from a point of view of different statistics. Each particle can be either in state one or two.
Figure 5.2: The Fermi function as a function of $\epsilon/\mu$ for different temperature values.

For $T_0 \to 0$ the function becomes step-like with the 'Fermi edge' at $\epsilon = \mu$. At this point the probability for one state to be occupied is $\frac{1}{2}$. $\mu$ at $T = 0$ is called the 'Fermi energy'.

$\mu, n_F = \frac{1}{2}$. For $T \to 0$, the Fermi function approaches a step function:

$$n_F = \begin{cases} 1 & \epsilon < \mu \\ 0 & \epsilon \geq \mu \end{cases} = \Theta(\mu - \epsilon)$$

Here $\Theta$ is the Heaviside step function. For vanishing temperature, the fermions fill up all energy states up to the chemical potential $\mu$.

For bosons we have:

$$z_B = 1 + e^{-\beta(\epsilon - \mu)} + e^{-\beta(2\epsilon - 2\mu)} + \ldots = \sum_{n=0}^{\infty} \left(e^{-\beta(\epsilon - \mu)}\right)^n = \frac{1}{1 - e^{-\beta(\epsilon - \mu)}}$$

The average occupation number is:

$$n_B = \frac{e^{-\beta(\epsilon - \mu)} + 2e^{-\beta(2\epsilon - 2\mu)} + \ldots}{z_B} = \frac{1}{\beta} \partial_\mu \ln z_B$$

$$= \frac{e^{-\beta(\epsilon - \mu)}}{1 - e^{-\beta(\epsilon - \mu)}} = \frac{1}{e^{\beta(\epsilon - \mu)} - 1}$$
The result differs only by a minus sign from the fermion result, but this difference has dramatic consequences because this distribution diverges at $\epsilon = \mu$ (Figure 5.3). For $T \to 0$, the Bose-Einstein function vanishes everywhere except for the lowest energy state.

\[ n_B(\epsilon, T) \]

\[ n_B(\epsilon, T_1) > n_B(\epsilon, T_2) \]

Figure 5.3: These curves are schematic with $T_1 > T_2$ and $\mu_1 < \mu_2$. They diverge as $\epsilon \to \mu$. For a system with a finite number of particles, we therefore must have $\mu \leq \epsilon$. At low temperature, all particles accumulate in the state of lowest energy.

In summary we have found a dramatic difference between fermions and bosons at low temperature:

\[ \Rightarrow \] Fermions tend to fill up energy states one after the other.

\[ \Rightarrow \] Bosons tend to condense all into the same low energy state.

We finally compare the three statistics in form of the occupation number (Figure 5.4).

\[ n(\epsilon, T) \]

\[ n(\epsilon, T_1) > n(\epsilon, T_2) \]

Figure 5.4: A schematic sketch of the occupation number $n$ for the three statistics: Bose-Einstein (blue), Fermi-Dirac (red) and Maxwell-Boltzmann (black).
Examples of physical fluids

1. Fermi fluids
   a) electrons in a metal or in a white dwarf
   b) neutrons in the atomic nuclei or in neutron stars
   c) helium three (\(^3\)He: 2 protons, 1 neutron, 2 electrons, half-integer spin)

2. Bose fluids
   a) photons (black body radiation)
   b) quasi-particles like phonons (lattice vibrations), polaron (polarization waves), magnons (spin waves)
   c) helium-four (\(^4\)He: 2 protons, 2 neutrons, 2 electrons, integer spin)
   \(^4\)He becomes ‘superfluid’ below the critical temperature \(T_{\text{crit}} = 2.17\, \text{K}\).
   d) BCS-theory: Two electrons can form a bosonic pair in certain materials due to the interaction with the crystal lattice of ions. These become ‘superconducting’ below \(T_{\text{crit}}\).
   e) \(^{87}\text{Rb}\)-atoms are bosons. In 1995 rubidium atoms have been used to realize a ‘Bose-Einstein condensate’ in atomic traps at very low temperatures (\(T_{\text{crit}} \approx 10^{-7}\, \text{K}\)).

5.2 The ideal Fermi fluid

We consider \(N\) particles, but for simplicity work in the grand canonical ensemble. The spatial states are characterized by the wave vector \(\vec{k}\) of the wave function. The spin of each particle can be up or down \((m_S = \pm \frac{1}{2})\). Considering no additional interaction apart from the intrinsic one due to the particles being fermions, this implies:

\[
Z_{\text{G}} = \prod_{\vec{k},m_S} z_{\vec{k},m_S}
\]

\[
z_{\vec{k},m_S} = 1 + e^{-\beta(\epsilon_{\vec{k},m_S} - \mu)}
\]

\[
n_{\vec{k},m_S} = \frac{1}{e^{\beta(\epsilon_{\vec{k},m_S} - \mu)} + 1}
\]

For the dispersion relation, we have the classical relation for a massive particle combined with the de Broglie relation:

\[
\epsilon_{\vec{k},m_S} = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}
\]
In the following we will use a factor 2 for the spin degrees and replace the sums by integrals:

\[
\sum_{\vec{k},m_S} ... = 2 \frac{V}{h^3} \int d\vec{p} ... = 2 \frac{V}{h^3} \int dp p^2 4\pi ...
\]

\[
= 2 \frac{V}{h^3} \int_0^\infty d\epsilon 4\pi m^3 (2\epsilon)^{1/2} ...
\]

\[
= N \int_0^\infty d\epsilon \frac{V}{2\pi^2 N} \left( \frac{2m}{h^2} \right)^{1/2} \sqrt{\epsilon} ...
\]

The concepts used here are the same ones as used before for the Debye solid and the black body radiation. While here \(D \propto \sqrt{\epsilon}\), for the phonons and photons we had \(D \propto \epsilon^2\) due to the linear dispersion relation.

**Fermi energy**

For given particle number \(N\), the chemical potential \(\mu\) has to be determined from:

\[
N = \sum_{\vec{k},m_S} n_{\vec{k},m_S} = N \int_0^\infty d\epsilon\ D(\epsilon) \frac{1}{e^{\beta (\epsilon - \mu)} + 1}
\]

We first consider the limit \(T \to 0\):

\[
n(\epsilon) \to 1 - \Theta(\epsilon - \mu) = \Theta(\mu - \epsilon)
\]

The value of \(\mu\) at \(T = 0\) is called ‘Fermi energy’:

\[
\epsilon_F = \frac{p_F^2}{2m} = \mu \left( T = 0, v = \frac{V}{N} \right)
\]

\[
\Rightarrow N = \sum_{\vec{k},m_S \ for \ p \leq p_F} 1 = 2 \frac{V}{h^3} \int_{p \leq p_F} d\vec{p} = 2V \frac{4\pi}{3} p_F^3
\]

Here we integrated over the ‘Fermi sphere’.

\[
\Rightarrow \epsilon_F = \left( \frac{3\pi^2}{2} \right)^{2/3} \frac{\hbar^2}{2m v^2} = \left( \frac{3\pi^2}{2} \right)^{2/3} \frac{\hbar^2 \rho^2}{2m^2}
\]

Typical values for the Fermi energy:

\[
\epsilon_F = \begin{cases} 
10^{-4} \text{ eV} & 3\text{He} \\
10 \text{ eV} & \text{electrons in metal} \\
1 \text{ MeV} & \text{electrons in white dwarf} \\
35 \text{ MeV} & \text{neutrons in atomic nucleus}
\end{cases}
\]
Since $k_BT_R = eV/40$, for electrons in metals at room temperature $T_R$ we typically have $\epsilon_F \gg k_BT_R$. We evaluate the occupancy around the Fermi-edge (compare Figure 5.5):

\[
    n(\epsilon) = 0.5 \pm 0.23 \quad \text{for } \epsilon = \mu \mp k_BT \\
    n(\epsilon) = 0.5 \pm 0.45 \quad \text{for } \epsilon = \mu \mp 3k_BT
\]

We see that the width of the step at finite $T$ is only a few $k_BT$. Therefore only a few of the $N$ electrons in the 'Fermi sea' are thermally excited above $\epsilon_F$.

![Figure 5.5: The occupation number $n$ as a function of $\epsilon$ at finite temperature (blue) and the difference of the curve with respect to the one at $T = 0$ (red and red-dashed above blue).](image)

**Specific heat**

We use this result to calculate the specific heat based on the 'Sommerfeld method'. We consider an arbitrary function $f(\epsilon)$ (e.g. $f(\epsilon) = \epsilon^2$):

\[
    I = \int_0^\infty d\epsilon f(\epsilon) n(\epsilon) = \int_0^\mu d\epsilon f(\epsilon) + \int_0^\infty d\epsilon f(\epsilon) \left[ n(\epsilon) - \Theta(\mu - \epsilon) \right] \\
    \neq 0 \text{ only in small region around } \mu
\]

Expansion of $f(\epsilon)$ around the Fermi edge:

\[
    f(\epsilon) = f(\mu) + f'(\mu)(\epsilon - \mu) + ...
\]

We introduce $x = \beta(\epsilon - \mu)$:

\[
    \Rightarrow \eta(x) = n(\epsilon) - \Theta(\mu - \epsilon) = \frac{1}{e^x + 1} - \Theta(-x) \\
    = \left( \frac{1}{e^x + 1} - (1 - \Theta(x)) \right) = -\left( \frac{1}{e^{-x} + 1} - \Theta(x) \right) = -\eta(-x)
\]
\( \eta(x) \) being odd in \( x \) implies that all even terms on the Taylor expansion vanish.

\[
\Rightarrow \quad I = \int_0^\mu \de \epsilon f(\epsilon) + \frac{1}{\beta} \int_{-\beta\mu}^\infty \de x \left[f(\mu) + f'(\mu) \frac{x}{\beta} + \ldots\right] \eta(x)
\]

For low temperatures: \( \beta \mu \to \infty \):

\[
= \int_0^\mu \de \epsilon f(\epsilon) + \frac{f'(\mu)}{\beta^2} \int_{-\infty}^\infty \de x \ x \ \eta(x)
\]

\[
= 2 \int_0^\infty \de x \ \eta(x) = 2 \int_0^\infty \de x \ \frac{1}{\sqrt{\beta}} \pi^2 = \frac{\pi^2}{\beta^2}
\]

\[
= \int_0^\mu \de \epsilon f(\epsilon) + \frac{\pi^2}{6\beta^2} f'(\mu)
\]

We now apply this result to our normalization condition:

\[
1 = \int_0^\infty \de \epsilon D(\epsilon) n(\epsilon)
\]

with \( D(\epsilon) \propto \epsilon^{\frac{3}{2}} \) (compare Figure 5.6) to determine the chemical potential \( \mu(T, v) \).

Figure 5.6: The average occupancy \( n \) (blue) as a function of \( \epsilon \) next to the density of states \( D \propto \epsilon^{\frac{3}{2}} \) (red).

\[
1 = \int_0^\mu \de \epsilon D(\epsilon) + \frac{\pi^2}{6\beta^2} D'(\mu)
\]

\[
= \int_0^{\epsilon_F} \de \epsilon D(\epsilon) + \int_{\epsilon_F}^\mu \de \epsilon D(\epsilon)
\]

\[
= 1 + (\mu - \epsilon_F) D(\bar{\epsilon})
\]

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Here 1 is the result for $T = 0$ and $\bar{\epsilon}$ some value between $\mu$ and $\epsilon_F$ according to the mean value theorem.

$$
\mu - \epsilon_F = -\frac{\pi^2}{6\beta^2} \frac{D'(\mu)}{D(\bar{\epsilon})} \approx -\frac{\pi^2}{6\beta^2} \frac{D'(\epsilon_F)}{D(\epsilon_F)} \quad \text{using } \mu - \epsilon_F \propto T^2
$$

$$
\Rightarrow \quad \mu = \epsilon_F \left[ 1 - \frac{\pi^2}{12} \left( \frac{k_B T}{\epsilon_F} \right)^2 \right]
$$

for $T \ll \frac{\epsilon_F}{k_B}$ (Figure 5.7)

Figure 5.7: The chemical potential $\mu(T, v)$ decreases with increasing temperature. For $T \ll \frac{\epsilon_F}{k_B}$ it can be taken to be $\mu = \text{const} = \epsilon_F$.

We note that in general the chemical potential $\mu$ has to go down with temperature because for fixed particle number the joint integral with the density of states has to stay constant, compare Figure 5.8. Therefore higher order term in this expansion are not expected to change the general picture.

We next evaluate the energy:

$$
\frac{E}{N} = \int_0^\infty d\epsilon D(\epsilon) \epsilon n(\epsilon) \\
= \int_0^{\epsilon_F} d\epsilon D(\epsilon) \epsilon + (\mu - \epsilon_F) \bar{\epsilon} D(\bar{\epsilon}) + \frac{\pi^2}{6\beta^2} \left[ \mu D'(\mu) + D(\mu) \right] \\
\approx \frac{E_0}{N} + (\mu - \epsilon_F) \epsilon_F D(\epsilon_F) + \frac{\pi^2}{6\beta^2} \left[ \epsilon_F D'(\epsilon_F) + D(\epsilon_F) \right] \\
\Rightarrow \quad E = E_0 + N\frac{\pi^2}{6} D(\epsilon_F) (k_B T)^2
$$

$$
\Rightarrow \quad \epsilon_T = \frac{\partial E}{\partial T} \bigg|_V = N\frac{\pi^2}{3} k_B^2 D(\epsilon_F) T
$$
The specific heat of an electron gas at $T \ll \frac{\epsilon_F}{k_B}$ is linear in temperature $T$. We use $D(\epsilon) = A \frac{\epsilon^\frac{3}{2}}{2}$ to write

$$1 = \int_0^{\epsilon_F} d\epsilon D(\epsilon) = A \int_0^{\epsilon_F} d\epsilon \sqrt{\epsilon}$$

$$= \frac{2}{3} A \epsilon_F^{\frac{3}{2}} = \frac{2}{3} D(\epsilon_F) \epsilon_F$$

$$\Rightarrow \quad D(\epsilon_F) = \frac{3}{2\epsilon_F}$$

$$\Rightarrow \quad c_V = \frac{N \pi^2 k_B T}{2 \epsilon_F k_B}$$

Disregarding the numerical prefactor, this result is easy to understand: a fraction $\frac{\epsilon_F}{k_B T}$ of the electrons from the Fermi sea is thermally excited, each contributing around $k_B$. Our calculation is only valid for $T \ll \frac{\epsilon_F}{k_B}$. At high temperature, we have to recover the classical limit:

$$c_V = \frac{3}{2} N k_B$$

Therefore the complete result schematically has to look like shown in Figure 5.9.

We also comment on the role of lattice vibrations. From the Debye model we know that lattice vibrations contribute a term $\propto T^3$.

$$\Rightarrow \quad c_V = a T + b T^3$$

One can measure $a$ and $b$ experimentally and thus extract the Fermi energy $\epsilon_F$ and the Debye frequency $\omega_D$. With these two values, we know the most important numbers for a given solid.
Figure 5.9: Two regime behaviour of the specific heat at constant volume: While for $T \ll T_0 = \frac{\epsilon}{k_B}$, $c_V \propto T$, $c_V$ is approximately constant for $T \gg T_0$.

Full solution

Until now we have worked in an expansion around the $T = 0$-case. We can also write the full solution for arbitrary $T$, however we will end up with integrals that cannot be solved but rather lead to definitions of new functions.

We start with the grandcanonical potential and use the same concepts as above:

$$
\Psi(T, V, \mu) = -k_B T \ln Z_G = -\frac{k_B T}{h^3} 2V(4\pi) \int_0^{\infty} p^2 dp \ln \left(1 + e^{\beta(\epsilon - \mu)}\right) = -2k_B TV \frac{f_{5/2}(z)}{\lambda^3}
$$

where we have defined a new function

$$
f_{5/2}(z) := \frac{4}{\sqrt{\pi}} \int_0^{\infty} x^2 dx \ln \left(1 + ze^{-x^2}\right) = \sum_{1}^{\infty} (-1)^{a+1} \frac{z^a}{a^{5/2}}
$$

and where we have used the dimensionless momentum $x$ defined by $x^2 = \beta p^2 / 2m$ and fugacity $z = e^{\beta \mu}$.

Particle number can be written in a similar manner:

$$
N = \frac{2V(4\pi)}{h^3} \int_0^{\infty} p^2 dp \left(\frac{1}{e^{\beta(\epsilon - \mu)} + 1}\right) = \frac{2V}{h^3} \frac{4}{\sqrt{\pi}} \int_0^{\infty} x^2 dx \left(\frac{z}{e^{x^2} + z}\right) = \frac{2V}{\lambda^3} f_{3/2}(z)
$$

with another new function

$$
f_{3/2}(z) := \frac{4}{\sqrt{\pi}} \int_0^{\infty} x^2 dx \left(\frac{z}{e^{x^2} + z}\right) = \sum_{1}^{\infty} (-1)^{a+1} \frac{z^a}{a^{3/2}}
$$

As a function of $z$, both functions increase monotonously from $0$ with a decreasing slope.
One can easily check that the two formula are consistent:

\[ N = \frac{1}{\beta} \partial_\mu \ln Z_G = \frac{1}{\beta} (\beta z) \partial_z \ln Z_G = \frac{2V}{\lambda^3} (z \partial_z) f_{5/2}(z) = \frac{2V}{\lambda^3} f_{5/2}(z) \]

One can also calculate the variance as \( \sigma_N^2 = (1/\beta) \partial N / \partial \mu \). For low temperature, we would get the same results as above.

**Fermi pressure**

We consider the definition of pressure:

\[ p = -\frac{\partial E}{\partial V}\bigg|_{T,N} = -\sum_{\vec{k},m} \frac{\partial \epsilon_{\vec{k},m}}{\partial V} n_{\vec{k},m} \]

where in the last step we have neglected any temperature-dependent change in the occupation level (second order effect, a more rigorous treatment would again start from the grandcanonical ensemble). Since \( \epsilon_{\vec{k}} = \frac{(\hbar k)^2}{2m} \) and \( k_i \propto \frac{1}{\sqrt{V}} \), we have

\[ \epsilon_{\vec{k}} \propto \frac{1}{V^{\frac{3}{2}}} \Rightarrow \frac{\partial \epsilon_{\vec{k},m}}{\partial V} = -\frac{2 \epsilon_{\vec{k},m}}{3V} \]

\[ \Rightarrow \quad p = \frac{2E}{3V} = \frac{2E_0}{3V} + \frac{\pi^2 N k_B T}{6V} \epsilon_F \]

\[ \to 0 \quad \text{for} \quad T \to 0 \quad \text{like for the ideal gas} \]

Interestingly, this contribution to the pressure is always positive, showing that the Fermi gas is effectively like a gas with repulsive interactions. There is also a temperature-independent term:

\[ \frac{E_0}{N} = \int_0^{\epsilon_F} \text{d}e \, D(e) \text{e} = \frac{3}{5} \epsilon_F \]

\[ \Rightarrow \quad p \to 0 \quad \frac{2N}{5V} \epsilon_F = \left( \frac{3\pi^2}{5} \right)^{\frac{2}{3}} \frac{\hbar^2}{m v^3} \]

The ‘Fermi pressure’ in a Fermi fluid at very low temperature accounts for the incompressibility of matter and essentially results from the Pauli principle. For example, it prevents that the earth collapses under gravitation. This is also true for white dwarfs (electrons) or neutron stars, but not for the sun. In the latter case classical ideal gas pressure at \( T = 5 \cdot 10^7 \) K (temperature in the center of the sun) balances gravitational attraction.
5.3 The ideal Bose fluid

We now turn to Bose fluids with

\[ \epsilon = \frac{\hbar^2 k^2}{2m} \]

and conserved particle number \( N \).

Example:

A fluid of \(^4\)He, which in contrast to \(^3\)He is a boson. Both types of helium have the same weak van der Waals interaction and the same chemistry, but one is a bosonic, the other a fermionic fluid. We demonstrate now that the bosonic system undergoes a ‘Bose-Einstein condensation’ at a critical temperature \( T_c \).

\( \epsilon = \frac{p^2}{2m} \) has two main consequences for Bose fluids:

1. \( D(\epsilon) \propto \epsilon^{\frac{1}{2}} \): like for Fermi fluids

2. \( \epsilon \geq 0 \Rightarrow \mu \leq 0 \): otherwise the mode with \( \epsilon = \mu \) would have an infinite occupation number

\( \mu = 0 \) is allowed as the contribution to \( n_B \) at \( \epsilon = \mu \) vanishes in a continuum framework:

\[
\frac{d\bar{p}}{p^2} n_B \propto dp \rightarrow 0
\]

We consider the particle number \( N \) for spin-0 bosons (degeneracy \( g = 1 \)):

\[
N = \frac{V}{\hbar^3} \int d\vec{p} \frac{1}{e^{\beta (\epsilon - \mu)} - 1} = \frac{V}{(2\pi)^3} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty d\epsilon \frac{e^{\frac{\beta}{2m} \epsilon^2}}{e^{\beta (\epsilon - \mu)} - 1}
\]

For fixed \( \mu \), increasing \( T \) shifts \( n_B \) to higher values. In order to keep \( N \) constant, \( \mu \) must decrease (as for the Fermi fluid).

For \( T \rightarrow \infty, \mu \rightarrow -\infty \) we recover the classical limit. Compare with the ideal gas result:

\[
\mu = k_B T \ln \rho \lambda^3 = k_B T \ln \left( \frac{p}{p_0} \right) \text{ with } p_0 = \frac{k_B T}{\lambda^3} \approx \text{GPa}, \text{ atmospheric pressure } 0.1 \text{ MPa} \rightarrow \mu < 0
\]

We now consider the integral for \( N \):

\[
N = \frac{V}{\hbar^3} \int d\vec{p} \frac{1}{e^{\beta (\epsilon - \mu)} - 1} = \frac{V}{\hbar^3} \sum_{l=1}^{\infty} e^{\beta \mu l} \int d\vec{p} \frac{e^{-\frac{\beta p^2}{2m} l}}{e^{\beta (\epsilon - \mu)} - 1} = \frac{V}{\hbar^3} \sum_{l=1}^{\infty} \frac{z^l}{l^\frac{3}{2}} = \frac{V}{\lambda^3} \sum_{l=1}^{\infty} \frac{z^l}{l^\frac{3}{2}} = g_3(z)
\]

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\[ n_B, D \]

\[ n_B(T_1) \]

\[ n_B(T_2) \]

\[ T_2 > T_1 \]

\[ D \propto \epsilon^\frac{1}{2} \]

Figure 5.10: The bosonic occupation number \( n_B \) as a function of \( \epsilon \) for different temperatures (blue and red curves) next to the density of states \( D \) (green).

\[ \Rightarrow N = \frac{V}{\lambda^3 g_\frac{3}{2}(z)} \]

Here we used the substitution \( x^2 = p^2 l \), identified the fugacity \( z \) and the thermal wavelength \( \lambda \)

\[ z = e^{\beta \mu}, \quad \lambda = \frac{h}{(2\pi mk_B T)^\frac{1}{2}} \]

and the generalized Riemann Zeta function

\[ g_\nu(z) = \sum_{l=1}^{\infty} \frac{z^l}{l^\nu} \]

\[ g_\frac{3}{2}(z) = z + \frac{z^2}{2\sqrt{2}} + \frac{z^3}{3\sqrt{3}} + ... \]

For high temperatures:

\[ \lambda \rightarrow 0, g_\frac{3}{2}(z) \rightarrow 0, z \rightarrow 0, \mu \rightarrow -\infty \]

\[ \Rightarrow N = \frac{V}{\lambda^3} e^{\beta \mu} \quad \text{classical result (with corrected counting)} \]

Upon lowering temperature, \( z \) approaches 1, where

\[ g_\frac{3}{2}(1) = \zeta \left( \frac{3}{2} \right) = 2.612 \]

with the Riemann Zeta function \( \zeta(\nu) = g_\nu(1) = \sum_{l=1}^{\infty} \frac{1}{l^\nu} \).
The maximal value $\mu = 0$ is reached when

$$\lambda^{3/2} \rho = \zeta \left( \frac{3}{2} \right) = 2.612 \quad \text{where} \quad \rho = \frac{N}{V}$$

surprisingly, this happens at a finite temperature $T_c$:

$$T_c = \frac{2\pi \hbar^2 \rho^\frac{3}{2}}{(\zeta \left( \frac{3}{2} \right))^{\frac{3}{2}} k_B m} \quad \text{Einstein 1924}$$

$T_c$ is the critical temperature for the 'phase transition'. At this point the system changes its state characteristics.

Figure 5.12: The chemical potential $\mu$ as a function of temperature. Below $T = T_c$, $\mu$ equals zero.
In the case of $^4\text{He}$ we estimate

$$v = \frac{V}{N} \approx 46 \, \text{Å}^3, \quad m = 4 \, \text{u} \Rightarrow T_c = 3.13 \, \text{K}$$

Experimentally one finds $T_c = 2.17 \, \text{K}$ for the so-called $\lambda$-transition to superfluidity. The difference comes from direct interactions which we neglected here (ideal gas of point particles).

Below $T_c$, the chemical potential $\mu$ must be identical zero and our procedure to treat momenta and energies in a continuum approach fails. We therefore revert to a finite system size and a discretized framework. However, we only treat the ground state as discrete and all excited states we treat as before as continuum.

At $T$ below $T_c$, some particles condense into the ground state for which we introduce an extra particle number:

$N_0$: number of atoms in the ground state, $N_e$: number of atoms in the excited state

$$\Rightarrow \quad N_e = \frac{V}{\lambda^3} \frac{3}{2} = \frac{\lambda^3}{\lambda^3} \frac{V}{\lambda^3} \frac{3}{2} = N \left( \frac{T}{T_c} \right)^\frac{3}{2} \quad \text{for } T < T_c$$

$$N = N_0 + N_e \Rightarrow \frac{N_0}{N} = 1 - \left( \frac{T}{T_c} \right)^\frac{3}{2}$$

This result is plotted in Figure 5.14.

![Figure 5.13: The occupation number $n_B$ as a function of $\epsilon$. In the continuum description the ground state does not contribute. Therefore we introduce it here as an additional degree of freedom (black box at $\epsilon = 0$).](image-url)
At $T = 0$, all $N$ particles have condensed into the ground state. For $0 \leq T \leq T_c$, a finite fraction is condensed. For $T > T_c$, all particles are excited.

Next we calculate the energy of the ideal Bose fluid:

$$E = N_0 \epsilon_0 + \frac{V}{h^3} \sum_{l=1}^{\infty} \frac{e^{\beta \mu l}}{l^3} \int \frac{d\mathbf{p}}{2m} \frac{p^2}{2m} e^{-\beta \varepsilon_{2l}}$$

$$= \frac{V}{\lambda^3} \sum_{l=1}^{\infty} e^{\beta \mu l} \left( \frac{1}{\lambda^3 l^2} \right)$$

$$E = \frac{3}{2} k_B T \frac{V}{\lambda^3} \delta_{\frac{3}{2}} (z) = \frac{3}{2} k_B T N_e \frac{\delta_{\frac{5}{2}} (z)}{\delta_{\frac{3}{2}} (z)}$$

This result (Figure 5.16) is valid for all temperatures.

Next we calculate the specific heat for $T \leq T_c$:

$$\Rightarrow \mu = 0, z = 1, \lambda \propto T^{-\frac{1}{2}}, E \propto T^5$$

$$\Rightarrow c_V = \frac{dE}{dT} = \frac{3}{2} k_B N \frac{d}{dT} T \left( \frac{T}{T_c} \right)^{\frac{3}{2}} \frac{\zeta (\frac{5}{2})}{\zeta (\frac{3}{2})}$$

$$\Rightarrow c_V = \frac{15}{4} k_B N \left( \frac{T}{T_c} \right)^{\frac{5}{2}} \frac{\zeta (\frac{5}{2})}{\zeta (\frac{3}{2})} \quad T \leq T_c$$

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For $T > T_c$ we get

$$\frac{dE}{dT} = \frac{15}{4} k_B \frac{V}{\lambda^3 \delta_2^2(z)} + \frac{3}{2} k_B T \frac{V}{\lambda^3 \delta_2'(z)} \frac{dz}{dT}$$

The chemical potential $\mu$ is determined by

$$N = \frac{V}{\lambda^3 \delta_2^2(z)}$$

$$\Rightarrow 0 = \frac{3}{2} \frac{V}{\lambda^3 \delta_2(z)} + \frac{V}{\lambda^3} \frac{dz}{dT} = \frac{3}{2} \frac{\delta_2(z)}{\delta_2'(z)}$$

$$\Rightarrow \frac{dz}{dT} = -\frac{3}{2} \frac{\delta_2(z)}{\delta_2'(z)}$$

Here we used

$$\frac{dg_\nu(z)}{dz} = \sum_{l=1}^{\infty} l z^{l-1} = \frac{1}{z} \sum_{l=1}^{\infty} \frac{z}{l^{\nu-1}} = \frac{1}{z} g_{\nu-1}(z)$$

in the last step.

High temperature limit: $z \to 0, g_\nu(z) \to z$

$$\Rightarrow c_V = \left( \frac{15}{4} \frac{9}{4} \right) k_B N = \frac{3}{2} k_B N \text{ classical limit}$$

$$T = T_c: \quad z \to 1, g_\frac{1}{2}(1) = \infty$$

$$\Rightarrow c_V = \frac{15}{4} k_B N \frac{\zeta \left( \frac{5}{2} \right)}{\zeta \left( \frac{3}{2} \right)} = 1.925 k_B N$$

The specific heat has a unique cup at $T = T_c$ (Figure 5.15). A similar behaviour has been experimentally observed for $^4\text{He}$. The energy $E$ and its first derivative $c_V$ are continuous; only the second derivative has a jump.
Figure 5.15: The specific heat \( c_V \) as a function of temperature has a unique cup at \( T = T_c \).

Figure 5.16: The energy \( E \) of the ideal Bose fluid as a function of temperature. For low temperatures (quantum regime), \( E \propto T^{5/2} \) while \( E \propto T \) for high temperatures (classical limit).

**Ultracold atoms**

Bosonic atoms like \( ^{87}\text{Rb} \) or \( ^{23}\text{Na} \) can be captured in magnetic traps because they have unpaired electrons that interact with magnetic fields. To first order, this is a harmonic oscillator with frequency \( \omega \).

\[
\epsilon_{n_x,n_y,n_z} = \hbar \omega \left( n_x + n_y + n_z + \frac{3}{2} \right)
\]
For \( \mu = \mu_c = \epsilon_{000} = \frac{3}{2} \hbar \omega \), \( N_0 \) atoms condensed into a BEC:

\[
N = N_0 + \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \frac{1}{e^{\beta \hbar \omega (n_x + n_y + n_z)} - 1}
\]

Here the contribution \( \epsilon_{000} - \mu = 0 \) vanishes from the exponential. Converting the three sums into integrals, using the geometrical sum and performing the integrals gives

\[
N = N_0 + \zeta(3) \left( \frac{k_B T}{\hbar \omega} \right)^3 \quad T \leq T_c
\]

The critical temperature follows from \( N_0 \to 0 \):

\[
T_c = \frac{\hbar \omega}{k_B} \left( \frac{N}{\zeta(3)} \right)^{1/3}
\]

For \( \hbar \omega \approx 10^{-8} \) \( k_B \) \( K \) and \( N = 4 \cdot 10^4 \) this gives

\[
T_c \approx 3 \cdot 10^{-7} \text{ K}
\]

In 1995 such a Bose-Einstein condensate was achieved for the first time (Nobel Prize 2001 for Ketterle, Cornell and Wieman). Usually they are demonstrated by the expansion following shutoff of an atomic trap. In 2010 a BEC was achieved for photons (Weitz group, Bonn).

### 5.4 Classical limit

As we have seen above, both for Fermi and Bose fluids the classical limit emerges as \( \mu \to -\infty \). Then the two grandcanonical distribution functions become the same classical Maxwell-Boltzmann distribution:

\[
n_{F/B} = \frac{1}{e^{\beta (\epsilon - \mu)} \pm 1} \to e^{\beta \mu} e^{-\beta \epsilon}
\]

In this limit, all occupied states are in the tail of the distributions, which is the same for both. The normalization condition now becomes, using \( \epsilon = p^2/2m \), which is valid for both cases and therefore give the same density of states:

\[
N = g V \left( \frac{2m}{\hbar^2} \right)^{3/2} e^{\beta \mu} \int d\epsilon \epsilon^{1/2} e^{-\beta \epsilon} = g \frac{V}{\lambda^3} e^{\beta \mu}
\]

where degeneracy \( g = 2 \) for electrons and \( g = 1 \) for spin-0 particles. For the average energy we get

\[
E = g \frac{V}{(2\pi)^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} e^{\beta \mu} \int d\epsilon \epsilon^{3/2} e^{-\beta \epsilon} = \frac{3}{2} k_B T g \frac{V}{\lambda^3} e^{\beta \mu} = \frac{3}{2} k_B T N
\]
which is simply the caloric equation of state of the classical ideal gas. The boundary to the quantum regime occurs at fugacity $e^{\beta\mu} = z \approx 1$, which from the first equation corresponds to $v \approx \lambda^3$. When the density is sufficiently high or the temperature is sufficiently low that the specific volume approaches the volume defined by the thermal wavelength, then quantum effects will dominate. Note that the classical limit corresponds to the calculation with corrected counting. Without this factor $N!$, we would not have achieved agreement with the full quantum calculations (and also not with the thermodynamic result).
6 Phase transitions

6.1 Ising model

As the two most important examples for classical phase transitions, we now discuss
the Ising model and the real gas. In fact the Ising model is the most important model
in statistical physics, both historically and conceptually. It is one of the few analytically
solvable models with interactions and a phase transition. In 1920 it was invented by
Wilhelm Lenz as an exercise in ferromagnetism and given to his PhD student Ernst
Ising, who solved the one-dimensional case (publication Z. Phys. 31, 253-258, 1925),
which has a phase transition only at \( T = 0 \) (some textbooks therefore state that it has
no phase transition at all, which is true as a statement on finite temperature). In 1933
Rudolf Peierls used scaling arguments to show that the 2D version must have a phase
transition at finite temperature. In 1944 Lars Onsager solved the two-dimensional Ising
model in vanishing magnetic field with algebraic methods (publication Phys. Rev. 65,
117, 1944). Generations of theoretical physicists worked on this and related models,
leading to the developments of concepts such as universality, renormalization group
theory and symmetry breaking. The two-dimensional Ising model with magnetic field
and the three-dimensional Ising model are still not solved and this is one of the greatest
challenges in theoretical physics (like solving the Navier-Stokes equation). However,
it has been extensively studied with numerical methods (again like the Navier-Stokes
equation), so that we can say that in principle, we know everything about it. Thus the
Ising model is for statistical physics what the harmonic oscillator is for mechanics, the
hydrogen atom for quantum physics and the fruit fly for biology.

The Ising model is defined on a lattice of given connectivity and dimension, thus in
principle, there are infinitely many Ising models. Figure 6.1 shows some examples in
two dimensions. Usually however one studies it on a simple cubic lattice. The Ising
model is an example for a lattice spin model. More complicated lattice models of this
kind are the n-vector model, the XY-model, the Heisenberg model and the Potts-model.
In each lattice site \( i \), we consider a spin \( S_i \) with two possible states: \( S_i = \pm 1 \) (cor-
responding to \( |\uparrow\rangle \) and \( |\downarrow\rangle \)). Nearest neighbours interact with an energy scale \( J \). In
addition there might be an external magnetic field \( B \) giving a preference for one direc-
tion. Note that although we talk about spins and the cartoon show vectors, we really
have only a scalar degree of freedom, which is binary; this makes it the simplest model
possible, like the flip of a coin in probability theory.

The Hamiltonian of the Ising model reads

\[
\mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j - B \mu \sum_i S_i
\]

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Figure 6.1: Ising lattice examples in two dimensions: cubic (\# neighbours $z = 4$, left), triangular ($z = 6$, center) and hexagonal (honeycomb) ($z = 3$, right).

Here $\langle ij \rangle$ indicates summation over nearest neighbours and $\mu$ is the magnetic moment of a spin. In non-dimensional units we have

$$\beta H = - K \sum_{\langle ij \rangle} S_i S_j - H \sum_i S_i$$

where now both the coupling constant $K = \beta J$ and the external field $H = \beta B \mu$ depend on temperature.

For $J > 0$ the symmetric configurations $\uparrow\uparrow$ and $\downarrow\downarrow$ are favorable and $\uparrow\downarrow$ and $\downarrow\uparrow$ are unfavorable. Thus the system wants to avoid grain boundaries between regions with up and down spins, at least at low temperature. At high temperature, grain boundaries will proliferate because the correspond to a lot of entropy.

For $B = 0$ the system is invariant under $S_i \Rightarrow -S_i$. If $B > 0$, $\uparrow$-spins are favored. Using the canonical formalism the partition sum for $N$ spins reads:

$$Z_N(K, H) = \sum_{S_1 = \pm 1} \sum_{S_2 = \pm 1} \cdots \sum_{S_N = \pm 1} e^{-\beta H}$$

In practice one often uses periodic boundary conditions for lattice models to avoid boundary effects, or finite size scaling to get rid of boundary effects by making the system larger and larger.

Usually the Ising model is treated in magnetic language: $J > 0$ represents a ferromagnetic interaction and $B$ is a magnetic field. However, it can be used in many other ways, e.g. in socioeconomic physics to present the spread of a opinion in a population (spin up = believer, spin down = non-believer, you start to believe if your neighbors are believers) or in biophysics to present the spread of a conformation in a molecular ensembles (a molecule goes into another conformation if the neighbors have switched, too).

In order to decide if the microscopic rules lead to a macroscopic change, one has to introduce an order parameter. For a magnetic model like the Ising model, the natural choice is the magnetisation:

$$M(K, H) = \left\langle \mu \sum_{i=1}^{N} S_i \right\rangle$$
which is a measure for the averaged spin orientation. $B > 0$ will lead to $M > 0$. If for $B = 0$ we find $M \neq 0$, then the system has spontaneously polarized itself (an example of spontaneous symmetry breaking). In the following we will discuss two important results:

1. The one-dimensional Ising model shows a phase transition only at $T = 0$ (Figure 6.2).

2. The two-dimensional Ising model shows a phase transition at finite temperature $T_c$ (Figure 6.3).

Figure 6.2: 1D Ising model: Magnetisation $M$ as a function of temperature $T$. For $T \neq 0$ $M$ vanishes and shows a jumping behaviour at $T = 0$.

Figure 6.3: 2D Ising model: Magnetisation $M$ as a function of temperature $T$. For values $T \leq T_c$ $M$ has a finite value.

If $M$ changes in a smooth way at the transition (no jumps), we talk about a phase transition of second order or continuous phase transition. The 2D Ising model is the paradigmatic case for such a transition at the critical temperature $T_c$. In the region around the critical point, the system has very unusual properties (large fluctuations, universality, critical slowing down).
6.2 The 1D Ising model

In one dimension the Ising model is an ‘Ising chain’ of spins (Figure 6.4). With periodic boundary conditions this chain becomes a ring.

![1D Ising model: 'Ising chain' of N spins.](image)

Without periodic boundary conditions and considering the external field to vanish, hence $H = 0$, $Z_N$ becomes:

$$Z_N = \sum_{S_1=\pm1} \sum_{S_2=\pm1} \ldots \sum_{S_N=\pm1} e^{K(S_1S_2 + S_2S_3 + \ldots + S_{N-1}S_N)}$$

$$= \sum_{S_1=\pm1} \ldots \sum_{S_{N-1}=\pm1} e^{K(S_1S_2 + \ldots + S_{N-1}S_{N-1})} \sum_{S_N=\pm1} e^{K_{N-1}S_N}$$

$$= Z_{N-1} 2 \cosh K$$

$$= (2 \cosh K)^{N-1} Z_1 \approx (2 \cosh K)^N = Z_N$$

Hence the free energy expression becomes, remembering $K = \beta J$:

$$F = -k_B T N \ln \left( \frac{2 \cosh \frac{J}{k_B T}}{2} \right)$$

Because this is an analytical function for finite temperature, one already expects that no phase transition takes place at finite $T$. We show this by considering spin correlations:

For each spin pair we introduce a different coupling constant $K_i$:

$$\beta H = -K \sum_{i=1}^{N-1} S_i S_{i+1} \rightarrow -\sum_{i=1}^{N-1} K_i S_i S_{i+1}$$

$$\Rightarrow \langle S_iS_{i+j} \rangle = \frac{1}{Z_N} \sum_{\{S_i\}} (S_iS_{i+j}) e^{-\beta H}$$

$$= \frac{1}{Z_N} \sum_{\{S_i\}} \underbrace{(S_iS_{i+j})}_{\text{Neq}} e^{-\sum_{i=1}^{N-1} K_i S_i S_{i+1}}$$

$$= (S_i \underbrace{S_{i+1}S_{i+1} \ldots S_{i+j-1}}_{N-1} S_{i+j})$$

$$= \partial_{K_i} \partial_{K_{i+1}} \ldots \partial_{K_{i+j-1}}$$

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\[ Z_N \text{ then can be calculated iteratively as above:} \]

\[ Z_N = 2^N \prod_{i=1}^{N-1} \cosh K_i \]

\[ \Rightarrow \quad \langle S_i S_{i+j} \rangle = \frac{\cosh K_1 \cdots \sinh K_i \cdots \sinh K_{i+j-1} \cdots \cosh K_{N-1}}{\cosh K_1 \cdots \cosh K_i \cdots \cosh K_{i+j-1} \cdots \cosh K_{N-1}} = \prod_{k=1}^{j} \tanh K_{i+k-1} \]

\[ \forall i : K_i = K \quad \Rightarrow \quad \langle S_i S_{i+j} \rangle = (\tanh K)^j \]

The resulting spin correlations are shown in Figure 6.6. Despite the short-ranged interaction - we only consider nearest neighbour interactions - a longer ranged correlation emerge from the statistical average, which decays exponentially with distance. Most importantly, for \( T = 0 \) we have \( \tanh K \) and the correlations do not decay at all.

![Graph of tanh(x) as a function of x.](image)

**Figure 6.5:** \( \tanh(x) \) as a function of \( x \). For \( x > 0 \) \( \tanh(x) > 0 \); \( \tanh(x) \xrightarrow{x \to \pm \infty} \pm 1 \).

Because the system is homogeneous:

\[ \forall i : \quad \langle S_i \rangle = \langle S \rangle \]

\[ \Rightarrow \quad M = \mu N \langle S \rangle \]

\[ \langle S_i S_{i+j} \rangle \xrightarrow{j \to \infty} \langle S_i \rangle \langle S_{i+j} \rangle = \langle S \rangle^2 \]

\[ M^2 = \mu^2 N^2 \lim_{j \to \infty} \langle S_i S_{i+j} \rangle = \begin{cases} \mu^2 N^2 & T = 0 \\ 0 & T > 0 \end{cases} \]

At finite \( T \) no spontaneous magnetisation occurs. At \( T = 0 \) we have a phase transition (compare Figure 6.2). For \( T \to 0 \) we have first made this limit and then the thermodynamic limit \( N \to \infty \).
Figure 6.6: $\langle S_i, S_{i+j} \rangle = (\tanh(x))^j$ as a function of $j$. As can be seen in Figure 6.5, tanh($x$) > 0 for $x > 0$. For the plot tanh($x$) was taken to be 0.5. For $T = 0$, this curve would not decay.

**Transfer matrix method**

Next we investigate the case $H \neq 0$ using the transfer matrix method introduced by Onsager for the 2D Ising model:

$$\beta \mathcal{H} = -K \sum_{\langle ij \rangle} S_i S_j - H \sum_i S_i$$

We now use periodic boundary conditions: $S_{N+1} = S_1$ (compare Figure 6.7). In the thermodynamic limit $N \to \infty$, boundaries become irrelevant.

Figure 6.7: With periodic boundary conditions the one-dimensional Ising chain becomes a ring.
We define a ‘transfer function’:

\[ T_{i,i+1} := e^{KS_iS_{i+1} + \frac{1}{4}H(S_i+S_{i+1})} \]

\[ \Rightarrow e^{-\beta H} = T_{1,2} T_{2,3} \ldots T_{N,1} \]

Each transfer function has four possible values which define a symmetric ‘transfer matrix’:

\[ T = \begin{pmatrix} e^{K+H} & e^{-K} \\ e^{-K} & e^{K-H} \end{pmatrix} \]

In quantum mechanical notation:

\[ |S_i = +1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad |S_i = -1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \]

\[ \Rightarrow T_{i,i+1} = \langle S_i | T | S_{i+1} \rangle \]

\[ \Rightarrow Z_N = \sum_{\{S_i\}} e^{-\beta H} \]

\[ = \sum_{\{S_i\}} \langle S_1 | T | S_2 \rangle \langle S_2 | T | S_3 \rangle \ldots \langle S_N | T | S_1 \rangle \]

\[ = \sum_{S_i=\pm 1} \langle S_1 | T^N | S_1 \rangle \]

\[ = (T^N)_{11} + (T^N)_{22} = \text{tr}(T^N) \]

\[ = \lambda_1^N + \lambda_2^N \]

We note that solving the Ising model amounts to an eigenvalue problem with \( \lambda_i \) being the eigenvalues of T. This implies:

\[ \det \begin{pmatrix} e^{K+H} - \lambda & e^{-K} \\ e^{-K} & e^{K-H} - \lambda \end{pmatrix} = 0 \]

\[ (e^{K+H} - \lambda) (e^{K-H} - \lambda) - e^{-2K} = 0 \]

\[ \lambda^2 - 2e^K \cosh H \lambda + e^{2K} - e^{-2K} = 0 \]

\[ \Rightarrow \lambda_{1,2} = e^K \cosh H \pm \sqrt{e^{2K} \cosh^2 H - 2 \sinh 2K} \]

\[ = e^K \left[ \cosh H \pm \sqrt{\cosh^2 H - 2e^{-2K} \sinh 2K} \right] \]

Thus we have arrived at an exact solution for the one dimension Ising model with external field:

\[ Z_N = \lambda_1^N + \lambda_2^N \]

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In the thermodynamic limit, only the larger eigenvalue $\lambda_1$ is relevant:

$$ Z_N = \lambda_1^N \left( 1 + \left( \frac{\lambda_2}{\lambda_1} \right)^N \right) \xrightarrow{N \to \infty} \lambda_1^N $$

For $H = 0$ we get:

$$ \lambda_1 = e^K + \sqrt{e^{2K} - (e^{2K} - e^{-2K})} = e^K + e^{-K} = 2 \cosh K $$

$$ \Rightarrow Z_N = (2 \cosh K)^N \quad \text{for } N \gg 1 $$

like before from the solution by direct summation (but different boundary conditions).

With the full solution we now can calculate any thermodynamic quantity of interest. The thermal equation of state describes the magnetisation:

$$ M(T, B) = \frac{1}{Z} \sum_{\{S_i\}} \left( \mu \sum_i S_i \right) e^{-\beta H} $$

$$ = \mu \partial_H \ln Z_N = \frac{\mu N}{\lambda_1} \partial_H \lambda_1 $$

$$ = \frac{\mu N \sinh H}{\sqrt{\cosh^2 H - 2e^{-2K} \sinh 2K}} $$

![Figure 6.8: The magnetisation M as a function of magnetic field B plotted for different temperatures.](image)

We note that $M(T \neq 0, B = 0) = 0$ and no spontaneous magnetisation at finite $T$ occurs. For strong fields, hence

$$ M(T \neq 0, B \to \pm \infty) \to \pm \mu N $$

magnetisation saturates. For $T \to 0$ $M$ turns into a step function (compare Figure 6.8).
Next we calculate the entropy for $B = 0$:

$$F = -Nk_B T \ln (2 \cosh K)$$

$$\Rightarrow S = -\frac{\partial F}{\partial T} = Nk_B \left[ \ln (2 \cosh K) - K \tanh K \right] \quad \text{(Figure 6.9)}$$

Considering the low and high temperature limits:

$$S \xrightarrow{T \to \infty, K \to 0} Nk_B \ln 2$$

$$S \xrightarrow{T \to 0, K \to \infty} Nk_B (K - K) = 0$$

where we recovered the third law of thermodynamics.

![Figure 6.9: The entropy $S$ as a function of temperature $T$. For high temperatures $S$ approaches $S_0 = Nk_B \ln 2$ asymptotically.](image)

From this we calculate the heat capacity in absence of a field:

$$c_B = T \frac{\partial S}{\partial T} \bigg|_{B=0} = k_B \frac{K^2}{\cosh^2 K} \quad \text{(Figure 6.10)}$$

Finally we consider the isothermal susceptibility (needs $H$):

$$\chi_T = \frac{1}{N} \frac{\partial M}{\partial B} \bigg|_T = \beta \mu \frac{\partial H}{\partial T} M$$

$$= \frac{\beta \mu^2}{N} \frac{\partial^2 H}{\partial T^2} \ln Z_N = \beta \mu^2 \frac{\partial^2 H}{\partial T} \ln \lambda_1$$

In the special case $B = 0$, $\chi_T$ becomes:

$$\chi_T = \frac{\beta \mu^2}{(1 - \tanh K)}$$
Figure 6.10: The heat capacity $c_B$ as a function of temperature shows a similar shape as the one for the two state model (compare Fig. ??).

$$\chi_T \xrightarrow{T \to \infty} \frac{1}{T} \quad \text{law of Curie}$$

In Figure 6.11 $\chi_T$ is plotted as a function of temperature.

Figure 6.11: The susceptibility $\chi_T$ as a function of temperature. $\chi_T$ diverges for $T \to 0$, hence for $T$ approaching the phase transition. In general this is a typical signature of a phase transition. For large temperatures: $\chi_T \propto 1/T$ (law of Curie).

We also note an interesting relation between susceptibility (a response function like viscosity) and spin correlations (describing thermally activated ‘fluctuations’):
\[ \chi_T = \left. \frac{1}{N} \frac{\partial M}{\partial B} \right|_T = \frac{\beta \mu}{N} \partial_H \left\{ \frac{1}{Z \{S_i\}} \left( \mu \sum_i S_i \right) e^{-\beta \mathcal{H}} \right\} \]

\[ = \frac{\beta \mu^2}{N} \left( \sum_i \sum_j \langle S_i S_j \rangle \right) = \chi_T \]

'fluctuation dissipation theorem' for the Ising model

For the one-dimensional Ising model and the limit \( N \to \infty \) the result becomes:

\[ \chi_T = \frac{\beta \mu^2}{N} N \sum_{j=0}^{\infty} (\tanh K)^j = \frac{\beta \mu^2}{1 - \tanh K} \]

which is the same as above.

As \(-1 \leq \langle S_i S_j \rangle \leq 1\) this implies \( \chi_T \) can only diverge when

1. \( N \to \infty \) (thermodynamical limit)

2. The range of the correlations must diverge, such that infinitively many terms give a non-finite contribution. Therefore phase transitions are related to a divergence of the 'correlation length'. This implies that microscopic details become irrelevant because the system becomes correlated on a macroscopic scale ('critical fluctuations').

6.3 The Peierls argument

Starting around 1933, Peierls published scaling arguments why a phase transition should occur in 2D as opposed to 1D. Here we report a few of these kinds of arguments to demonstrate their spirit. Note that their validity also comes from the fact that thanks to Onsager, we have an exact solution and thus can check back if they describe the core of the problem or not.

Simple argument for 1D

We consider an Ising chain with all spins up and then select a few neighboring spins and flip the whole island over. This creates two domain walls (also called grain boundaries or defects) in the chain. The change in energy is

\[ \Delta E = 2 \cdot 2J \]
because there are two defects, each with an energy penalty $2J$. The change in entropy corresponds to the number of ways to choose the positions of the two defects:

$$\Delta S = k_B \ln \frac{N(N - 1)}{2} \approx 2k_B \ln N$$

where we assume the number of lattice sites $N \gg 1$ in the thermodynamic limit. Thus the change in free energy reads

$$\Delta F = 4J - 2k_B T \ln N < 0$$

for any temperature $T$ in the thermodynamic limit. This means that it is always favorable to create grain boundaries due to entropic reasons and a phase transition to order cannot occur at finite temperature.

**More complex argument for 1D**

We now look at an arbitrary number of domain walls, not only at one island with two of them. We introduce the number of such domain walls $M$ and write the free energy in the domain wall picture:

$$F = 2JM - k_B T \ln \left( \frac{N}{M} \right)$$

In the thermodynamic limit and with the Stirling formula we get

$$\frac{F}{N} = 2Jx + k_B T (x \ln x + (1 - x) \ln (1 - x))$$

where $x = M/N$ is the domain wall density. If we minimize $F$ for $x$ we get

$$x_{eq} = \frac{1}{e^{2J/k_B T} + 1}$$

thus at finite $T$ there is always a finite domain wall density and correlations decay over a finite distance. Moreover the system will not feel the effect of the boundary conditions. Only at $T = 0$ we have $x_{eq} = 0$, because then entropy does not matter.

**Simple argument for 2D**

We now want to make the simple argument for 2D rather than for 1D. We immediately encounter the problem that now there are two processes we have to account for: where to place the domain walls, and which shape to assign to them. With some intuition, we anticipate that shape fluctuations are now more important than where the islands are located. Thus we consider one island of down spins in a sea of up spins. The change in energy is

$$\Delta E = L \cdot 2J$$
where $L$ is the contour length of the domain. A crude estimate for the number of possible shapes is $3^L$, assuming a random walk on a 2D cubic lattice and neglecting intersections and the fact that it has to close onto itself (at each lattice site, there are three possibilities to proceed). Thus for entropy we have

$$\Delta S = k_B \ln 3^L.$$ 

Together we get

$$\Delta F = L(2J - k_B T \ln 3)$$

and thus $\Delta F < 0$ only for $T > T_c = 2J / (\ln 3 k_B)$ even in the thermodynamic limit $L \to \infty$. Thus this simple argument predicts that in 2D a phase transition can take place at finite $T$, and the reason is a feature that is only present in two and higher dimensions, namely shape fluctuations of the domain walls.

**More complex argument for 2D**

Another way to identify a phase transition is to investigate the effects of boundaries. We consider a quadratic field of spins and fix all the ones at the boundary to point up. We then consider the spin in the middle and ask if it keeps the up-preference of the boundary in the TD-limit ($p_+ > 1/2$?). One can show that for sufficiently low but finite $T$, indeed this happens. This means that correlations do not decay completely and that spontaneous magnetisation can emerge, indicating a phase transition.

We consider the quantity $m = p_+ - p_- = 2p_+ - 1$, which will be finite if spontaneous magnetisation exists and vanish otherwise. We can write

$$m = \frac{1}{Z} \sum_{\Sigma_+} e^{-\beta H} - \frac{1}{Z} \sum_{\Sigma_-} e^{-\beta H} = \frac{1}{Z} \sum_{\Sigma_+} e^{-\beta H} (1 - \Sigma)$$

The first and second terms are sums over all configurations with a positive and negative central spin, respectively. The basic idea of the newly defined quantity $\Sigma$ is that each configuration with a positive central spin can be turned into one with a negative central spin by flipping all spins in the surrounding positive domain. Importantly, the difference in energy is simply $2Jl$, where $l$ is the length of the domain wall surrounding this domain. Therefore one can write

$$\Sigma = \sum_{l=4}^{\infty} e^{-2J\beta l} = \sum_{l=4}^{\infty} g(l) e^{-2J\beta l}$$

where the sum is now over all configurations which have been obtained by flipping. In the second step we have rewritten the sum in terms of the length of the boundary. Here $g(l)$ is the number of domains with length $l$. We note that the minimum $l$ is 4 (one spin flipped) and that one only will have even values ($l = 4, 6, \ldots$), because adding spins one by one to the domain increases $l$ by 2.
In order to prove the polarization, we have to show that $\Sigma$ can be smaller than 1. We do this by establishing an upper bound for $g(l)$:

$$g(l) < \left(\frac{l}{4}\right)^2 \cdot 4 \cdot 3^{l-1} \cdot \frac{1}{2^l} = \frac{l}{24}$$

The first term is the maximal area corresponding to the contour length $l$. The second term is the number of possible paths starting from each point within this area: 4 for the first step and 3 for each additional step (on a 2D simple cubic lattice). The last term corrects for the fact that a path can go in two directions and can start at any point along the contour of a boundary. We now transfer this into an upper bound for $\Sigma$:

$$\Sigma < \sum_{l=4}^{\infty} \frac{l}{24} w^l = \frac{1}{24} \sum_{n=2}^{\infty} (2n) w^{(2n)} = \frac{w^4 (2 - w^2)}{12(1 - w^2)^2}$$

where $w = 3e^{-2\beta J}$. We thus obtain $\Sigma < 1$ for $w < w_c = 0.87$. This in turn translates into a critical temperature

$$T_c = \frac{2J}{k_B \ln(3/w_c)} = 1.6J/k_B$$

The exact result for the 2D Ising model is $T_c = 2.269J/k_B$ (see below). Thus the Peierls argument does not only prove the transition, but even gives a reasonable first estimate for its value. Note that here we have established only an upper bond for $\Sigma$. This does not mean that $\Sigma$ will be different from 1 above the critical temperature, we only showed that it will certainly become smaller than this value at sufficiently low temperature. Our argument is obviously very crude because we neglect interactions between boundary loops, which will strongly bring down the number of possible paths.

### 6.4 The 2D Ising model

Several methods of solution have been reported since Onsager’s original proof based on the mapping to a quantum mechanical problem using transfer matrices (by graphical solution summing over graphs, Grassmann algebra etc.). The exact solution for the free energy is:

$$F = -k_B T N \left\{ \ln 2 + \frac{1}{8\pi^2} \int_0^{2\pi} \int_0^{2\pi} dq_1 dq_2 \ln \left[ (1 - \sinh 2K)^2 + \sinh 2K \left( 2 - \cos q_1 - \cos q_2 \right) \right] \right\}$$

This double integral cannot be reduced anymore. A phase transition occurs when the logarithm diverges:

$$\sinh 2K_c = 1$$
$$K_c = \frac{1}{2} \ln(1 + \sqrt{2}) \approx 0.4407$$
$$T_c = 2J / \ln(1 + \sqrt{2}) \approx 2.269J/k_B$$
We define the ‘reduced temperature’:

\[ \epsilon := \frac{T - T_c}{T_c} \]

and ‘critical exponents’ for the divergences (for \( B = 0 \)) around \( T_c \):

\[
c_B = \begin{cases} 
(\epsilon)^{-\alpha'} & T < T_c \\
\epsilon^{-\alpha} & T > T_c 
\end{cases}
\]

\[
M = \begin{cases} 
(\epsilon)^{\beta} & T < T_c \\
0 & T > T_c 
\end{cases}
\]

From the exact solution one finds:

1. \( c_B \) has a logarithmic divergence (Figure 6.12).
   \[ \Rightarrow \quad \alpha = \alpha' = 0 \]

2. \( M = \left(1 - \sinh^{-4} 2K\right)^{\frac{1}{8}} \) (Figure 6.13)
   \[ \Rightarrow \quad \beta = \frac{1}{8} \]
   This result was announced by Onsager in 1948 at a conference, but never published by himself.

![Figure 6.12: \( c_B \) as a function of temperature with a divergence at \( T = T_c \).](image)

From the result for the magnetisation (which is the order parameter of the phase transition) one can construct the phase diagram. Figure 6.14 (left) shows the phase diagram in the T-M-plane. Values for the magnetisation in the grey area (two-phase region) cannot be realized in one system, because a self-polarized system jumps to the upper or lower values of \( M \). However, such a magnetisation can be realized by two systems, so the system has to split into two. For example, \( M = 0 \) can be realized by two equally...
large systems with up and down magnetisation, respectively. Using the lever rule, each desired value of \( M \) can be realized. Figure 6.14 (right) shows the phase diagram in the \( T-B \)-plane. Now the two-phase region reduce to a line because any small external field will immediately bias the system to up or down. Only for \( B = 0 \) phase coexistence can occur.

**Figure 6.14:** Left: Phase diagram with excluded ‘two-phase region’ where the system splits into two parts. Right: The two-phase region becomes a line in the \( B(T) \) diagram.

In order to understand the mechanisms underlying this phase transition, we now consider the ‘mean field theory’ for the Ising model. This theory approximates a system of interacting particles by a system of non-interacting particles. It can be made rigorous by the ‘Gibbs-Bogoliubov-Feynman inequality’ and as such is a ‘perturbation theory’ (similar to the ‘Hartree-Fock approximation’ in quantum mechanics). In general, it is important to have as many exactly solvable models in Statistical Physics as possible, even if they might be physically not so realistic because they are built around some mathematical
trick to solve them. Nevertheless they can be very useful as starting points for perturbative analyses.

**Perturbation theory**

We start from a model Hamiltonian \( \mathcal{H}_0 \) for which an exact solution is known:

\[
\mathcal{H}(\lambda) = \mathcal{H}_0 + \lambda \mathcal{H}_1
\]

1. \( \mathcal{H}(\lambda = 0) = \mathcal{H}_0 \) reference case
2. \( \mathcal{H}(\lambda = 1) = \mathcal{H} \) case of interest
3. \( \mathcal{H}_1 = \mathcal{H} - \mathcal{H}_0 \)

\[
\Rightarrow -\beta F(\lambda) = \ln \sum_j e^{-\beta E_j(\lambda)} = \ln \left( \text{tr} \left\{ e^{-\beta \mathcal{H}(\lambda)} \right\} \right)
\]

where \( \sum_j \) is the sum over all eigenvalues.

\[
F(0) = F_0 \quad F(1) = F \quad \text{result of interest}
\]

\[
\Rightarrow \frac{dF}{d\lambda} = \frac{\text{tr} \left\{ \mathcal{H}_1 e^{-\beta (\mathcal{H}_0 + \lambda \mathcal{H}_1)} \right\}}{\text{tr} \left\{ e^{-\beta (\mathcal{H}_0 + \lambda \mathcal{H}_1)} \right\}} = \langle \mathcal{H}_1 \rangle (\lambda)
\]

\[
\frac{d^2 F}{d\lambda^2} = -\beta \left\{ \frac{\text{tr} \left\{ \mathcal{H}_1^2 e^{-\beta (\mathcal{H}_0 + \lambda \mathcal{H}_1)} \right\}}{\text{tr} \left\{ e^{-\beta (\mathcal{H}_0 + \lambda \mathcal{H}_1)} \right\}} - \left( \frac{\text{tr} \left\{ \mathcal{H}_1 e^{-\beta (\mathcal{H}_0 + \lambda \mathcal{H}_1)} \right\}}{\text{tr} \left\{ e^{-\beta (\mathcal{H}_0 + \lambda \mathcal{H}_1)} \right\}} \right)^2 \right\}
\]

\[
= -\beta \left( \langle \mathcal{H}_1^2 \rangle - \langle \mathcal{H}_1 \rangle^2 \right) = -\beta \left( \langle \mathcal{H}_1 \rangle - \langle \mathcal{H}_1 \rangle \right)^2 \leq 0
\]

\[
\Rightarrow F(\lambda) \leq F(0) + \lambda \left. \frac{dF}{d\lambda} \right|_{\lambda=0}
\]

\[
\lambda=1 \Rightarrow F \leq F_u = F_0 + \langle \mathcal{H}_1 \rangle_0 \quad \text{Bogoliubov inequality}
\]

A visualisation of the Bogoliubov inequality is sketched in Figure 6.15. Note that the real \( F \) is everywhere concave, not only at \( \lambda = 0 \), so we can use \( \lambda = 1 \) without problems. In order to optimize the approximation one minimizes the upper bound with respect to the free model parameters. The modern master of this type of perturbation theory was Richard Feynman.
Application to the Ising model

We consider no external field:

\[ \mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j \]

However, we note that a spontaneous magnetization looks like there was an effective magnetic field. We therefore choose as our unperturbed reference Hamiltonian

\[ \mathcal{H}_0 = -B \sum_i S_i \]

where we set \( \mu = 1 \) for convenience and have introduced an effective magnetic field \( B \).

For \( \mathcal{H} = \mathcal{H}_0 \) we know the free energy expression:

\[ F_0 = -Nk_B T \ln \left( \frac{e^{\beta B} + e^{-\beta B}}{2 \cosh \beta B} \right) \]

The Bogoliubov inequality then states

\[ F \leq F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0 \]
\[ = -Nk_B T \ln \left( 2 \cosh (\beta B) \right) - J \sum_{\langle ij \rangle} \langle S_i S_j \rangle_0 + B \sum_i \langle S_i \rangle_0 = F_u \]

Here \( z \) is the number of nearest neighbours and we have to correct with a factor of 2 so that we count each bond only once (compare Figure 6.1).

\[ \langle S \rangle_0 = \frac{e^{\beta B} - e^{-\beta B}}{e^{\beta B} + e^{-\beta B}} = \tanh \beta B \]
We now fix $B$ such that the upper bound $F_u$ becomes minimal:

$$0 = \frac{1}{N} \frac{dF_u}{dB} = -\langle S \rangle_0 - Jz \langle S \rangle_0 \frac{d\langle S \rangle_0}{dB} + \langle S \rangle_0 + B \frac{d\langle S \rangle_0}{dB}$$

$$\Rightarrow B = Jz \langle S \rangle_0 = Jz \tanh \beta B$$

Note that a factor of 2 has canceled here. We note that our central result is a self-consistent relation for the effective field $B$. We could have obtained this result directly from a mean field reasoning, but it is more rigorous to derive it from the Bogoliubov inequality.

Figure 6.16: $M(x) = \tanh(x)$ (blue) as a function of $x$. For $Kz < 1$ there is only one intersection with $g(x) = \frac{x}{Kz}$ (red) at $x = 0$. For $Kz > 1$ there is also an intersection with $g(x) = \frac{x}{Kz}$ (green) at finite $x$.

We define $x = \beta B$ and have a look at the intersection of $f(x) = \tanh(x)$ and $g(x) = \frac{x}{Kz}$ (Figure 6.16). We note:

1. $Kz < 1 \Rightarrow$ only intersection at $x = 0$

2. $Kz > 1 \Rightarrow$ also two interactions at finite $x \neq 0$

$$\Rightarrow K_c = \frac{1}{z} \Rightarrow T_c = \frac{z J}{k_B}$$

For the two-dimensional Ising model with cubic arrangement:

$$z = 4 \Rightarrow K_c = \frac{1}{4} = 0.25$$
Compare exact solution: $K_c = 0.4407$. Obviously the mean field theory is just a crude approach because it predicts a phase transition in any dimension $d$. It becomes exact for $d \to \infty$.

How does magnetisation behave below $T_c$? One can show that $\langle S \rangle = \langle S \rangle_0$ using an external field. Assuming a small magnetisation just below $T_c$, we can do a Taylor expansion:

$$\langle S \rangle = \tanh \beta B \approx \beta B - \frac{1}{3} (\beta B)^3$$

$$\beta B = zK \langle S \rangle$$

$$\Rightarrow \langle S \rangle \approx zK \langle S \rangle - \frac{1}{3} (zK \langle S \rangle)^3$$

$$\Rightarrow \langle S \rangle^2 = (-3) \frac{1 - zK}{zK} \Rightarrow \langle S \rangle = 3^{\frac{1}{2}} \left( \frac{T_c - T}{T_c} \right)^{\frac{1}{2}}$$

We see that our approximative calculation yields a critical exponent $\beta = \frac{1}{2}$ (compare exact solution $\beta = \frac{1}{8}$).

**Computer simulations of the Ising model**

Exact enumerations are not feasible for large systems. Consider that for a $50 \times 50$ 2D Ising system we would have already $2^{2500} = 10^{753}$ states. Therefore it is better to use ‘importance sampling’. Here only the relevant configurations are sampled. For the canonical ensemble this means that we want to sample according to the Boltzmann distribution

$$p_i = \frac{1}{Z} e^{-\beta E_i}$$

We now look for a procedure which effectively generates this distribution. Usually such a procedure is implemented using random numbers (‘Monte Carlo simulations’). A standard tool is the ‘Metropolis algorithm’. This algorithm generates a series of configurations (‘Markov chain’) such that:

1. Any configuration can be reached in principle.
2. Averaging over all configurations in the Markov chain amount to doing the average with exact enumeration.

For the Ising model this means flipping one spin at random. We compare two configurations $i$ and $j$ with:

$$\frac{P_i}{P_j} = e^{-\beta (E_i - E_j)}$$

We define $p_{i \to j}$ to be the ‘transition probability’ for one spin to go from state $i$ to $j$.

$$\Rightarrow \sum_j p_{i \to j} = 1$$
We now require that locally we have *detailed balance* (should follow from time reversal invariance):

\[
\frac{p_{i \rightarrow j}}{p_{j \rightarrow i}} = \frac{p_j}{p_i} = e^{-\beta(E_j - E_i)}
\]

\[\Rightarrow p_i = \left( \sum_j p_{i \rightarrow j} \right) p_i = \sum_j p_{j \rightarrow i} p_j \]

We note that \(p_i\) is an eigenvector of the transition probability matrix. Thus a rule that obeys detailed balance brings us to a steady state distribution \(\{p_i\}\). The simplest implementation of this is the *Metropolis algorithm*:

1. Pick a spin \(i\) by random.
2. Calculate the energy change \(\Delta E\) upon flipping the spin.
3. If \(\Delta E < 0\), accept the spin flip.
4. If \(\Delta E > 0\), accept the flip with probability \(e^{-\beta \Delta E}\).

By going downhill, the algorithm samples regions of high importance. By hopping over barriers (compare 6.17), it allows to escape from metastable states. One can come up with more complicated MC-moves than simply flipping spins. In MC-simulations of the Ising model, it is very common to flip whole clusters. With this, one can get very exact values, e.g. \(T_c = 0.221654\) for the critical temperature of the 3D Ising model (strangely enough, this is close to the suggestion by Rosengreen 1986, \(T_c = \tanh^{-1}(\left(\sqrt{5} - 2\right)\cos(\pi/8)) = 0.221658\)).

For more details on Monte Carlo simulations, check the book by Kurt Binder and Dieter Heermann (Springer 2010).

![Figure 6.17: Sketch visualising the Metropolis algorithm and how it recovers from local minima.](image)
Some applications of the Ising model

1. **ferromagnetism:**
   The Ising model is the scalar version of the three-dimensional ‘Heisenberg model’:
   \[
   \mathcal{H} = -J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j - \mu \vec{B} \sum_i \vec{S}_i
   \]

2. **binary alloys and lattice gases:**
   Each lattice site is occupied either by an atom A or B. Nearest neighbour interactions are \( \epsilon_{AA} \), \( \epsilon_{BB} \) and \( \epsilon_{AB} \). We identify A with \( S_i = 1 \) and B with \( S_i = -1 \). The Hamiltonian then is:
   \[
   \mathcal{H} = - \sum_{\langle i,j \rangle} J_{ij} S_i S_j
   \]
   with \( J_{ij} = \epsilon_{AB} - \frac{1}{2} (\epsilon_{AA} + \epsilon_{BB}) \). Thus the Ising model describes order-disorder transitions in regard to composition.

3. **spin glasses:**
   now each bond is assigned an individual coupling constant \( J \) and they are drawn from a random distribution. E.g., one can mix ferromagnetic and anti-ferromagnetic couplings. This is an example for a structurally disordered system, on top of which we can have a thermal order-disorder transition.

4. **conformations in biomolecules:**
   a famous example is the helix-coil transition from biophysics. \( S_i = 1 \) a hydrogen bond in a DNA-molecules is closed; \( S_i = -1 \) the bond is open. The phase transition is between a straight DNA-molecule (helix) and a coiled DNA-molecule. Other examples are the oxygen-binding sites in hemoglobin, chemotactic receptors in the receptor fields of bacteria, or the molecules building the bacterial flagellum, which undergo a conformational switch if the flagellum is rotated in the other direction (switch from run to tumble phases).

5. **neural networks representing the brain:**
   \( S_i = 1 \) a synapse is firing, \( S_i = -1 \) it is resting. The Hopfield model for neural networks is a dynamic version of the Ising model and Boltzmann machines recognise handwriting by using the Ising model.

6. **spread of opinions or diseases:**
   Spread of opinions, rumours or diseases in a society; these kinds of models are used in socioeconomic physics. If nearest neighbour coupling is sufficiently strong, the system gets ‘infected’.
6.5 Real gases

We consider the Hamiltonian of an ideal gas with \( N \) particles:

\[
H = \sum_{i=1}^{N} \frac{p_i^2}{2m}
\]

The canonical partition sum in this case reads:

\[
Z_{id} = \frac{1}{N!} \left( \frac{1}{h^3} \int \frac{d\vec{p}}{=1/\lambda^3} e^{-\beta \frac{p^2}{2m}} \right)^N \left( \int d\vec{q} \right)^N = \frac{1}{N! \lambda^{3N}} V^N
\]

with the thermal wavelength \( \lambda = \frac{\hbar}{(2\pi mk_BT)^{1/2}} \). Based on the partition sum we can calculate the free energy:

\[
\Rightarrow F_{id} = -k_B T \ln Z_{id} \\
\Rightarrow p_{id} = -\frac{\partial F_{id}}{\partial V} \bigg|_{T,N} = \frac{Nk_B T}{V} = \rho k_B T
\]

The ideal gas is an appropriate description for diluted gases (small density \( \rho \)). At higher densities, interactions become important.

We consider a pairwise additive and isotropic interaction potential \( U \) as the simplest case:

\[
H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{j<i} U\left( \frac{|\vec{r}_i - \vec{r}_j|}{r_{ij}} \right)
\]

There is no dependence on

1. momenta (only positions)
2. relative orientations

of the particles.

An example for which the second assumption does not hold are liquid crystals (Figure 6.18).

An example for an isotropic potential is the ‘Lennard-Jones potential’ introduced by John Lennard-Jones in 1924:

\[
U(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
\]

The potential consists of two elements:
Figure 6.18: Liquid crystals: For increased density orientational, but not positional order is established. This is the ‘isotropic-nematic transition’ of liquid crystals that has been calculated by Lars Onsager in 1949.

1. a universal attraction between neutral atoms and molecules (‘van der Waals interaction’) proportional to $1/r^6$

2. stability is provided by short-ranged ‘Born repulsion’ ($\propto 1/r^{12}$).

Figure 6.19: The Lennard-Jones potential $U$ as a function of inter-particle distance $r$.

For computer simulations one typically shifts and truncates the potential to achieve a finite interaction range. These simulations can be done based on ‘Monte Carlo’ or ‘Molecular Dynamics’ procedures.

Figure 6.20: A generic phase diagram typical for a simple one-component system. $T_c$ indicates the temperature of the ‘critical point’ where phase boundaries cease to exist.
Figure 6.20 shows a phase diagram which is typical for a simple one-component system (as for example described by the Lenard-Jones potential). We now return to the analytical description.

\[
Z = \frac{1}{N!} \left( \frac{1}{h^3} \int d\vec{p} \ e^{-\beta p^2/(2m)} \right)^N = Z_{id} \quad V^N \int dN \vec{q} e^{-\beta \sum_{i<j} U(r_{ij})} = Z_{int}
\]

\[\Rightarrow F = -k_B T \ln Z = F_{id} + F_{int}\]

\[p = \left. -\frac{\partial F}{\partial V} \right|_{T,N} = p_{id} + p_{int}\]

The interaction part does not factorise into single particle properties. Hence one needs approximations. Because we understand the dilute case, we now introduce the ‘virial expansion’, which is an expansion in low density around the ideal gas as a reference system. We note that corrections to the ideal case pressure have to be of order \(\rho^2\) or higher, because they arise if two particles or more collide.

\[\Rightarrow p_{int} = k_B T \sum_{i=2}^\infty B_i(T) \rho^i = k_B T B_2(T) \rho^2 + O(\rho^3)\]

Here the \(B_i(T)\) are termed ‘virial coefficients’. In lowest order of the correction we thus have

\[\Rightarrow F = N k_B T \left[ \ln \left( \rho \lambda^3 \right) - 1 + B_2 \rho \right]\]

\[p = \rho k_B T \left[ 1 + B_2 \rho \right]\]

**Calculation of \(B_2(T)\)**

In the following we use the grand canonical formalism to calculate \(B_2(T)\) from \(U(r)\):

\[Z_G(T, V, \mu) = \sum_{N=0}^\infty Z(T, V, N) \left( e^{\beta \mu} \right)_N^{Z_{N}}\]

In the high temperature limit \(z = \frac{\mu}{k_B T} \ll 1\) we expand this expression in \(z\):

\[\Rightarrow Z_G = Z_0 + Z_1 z + Z_2 z^2 + O(z^3)\]

\[Z_0 = 1, \quad Z_1 = \frac{V}{\lambda^3}\]

\[Z_2 = \frac{1}{2! \lambda^6} \int d\vec{r}_1 \int d\vec{r}_2 e^{-\beta U(|\vec{r}_1 - \vec{r}_2|)} = \frac{V^4 \pi}{2 \lambda^6} \int dr r^2 e^{-\beta U(r)}\]

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Next we use the Euler relation for the grand canonical potential:

\[ J = -k_B T \ln Z_G = -pV \]

\[ \Rightarrow \quad \frac{pV}{k_B T} = \ln Z_G \approx \ln (Z_0 + Z_1z + Z_2z^2) \]

\[ \approx Z_1z + Z_2z^2 - \frac{Z_2^2}{2}z^2 \]

Were we used the approximation \( \ln (1 + x) \approx x - \frac{x^2}{2} \) for \( x \ll 1 \).

Obviously the virial expansion is similar to the expansion in fugacity \( z \):

\[ \frac{pV}{k_B T} = V [\rho + B_2 \rho^2 + O (\rho^3)] \]

To make a comparison of coefficients we need the relation between \( z \) and \( \rho \).

\[ \rho = \frac{\langle N \rangle}{V}, \quad z = e^{\beta \mu} \Rightarrow \mu = \frac{\ln z}{\beta} \]

\[ \Rightarrow \quad \partial_\mu = \beta z \partial_z \]

\[ \langle N \rangle = \frac{1}{\beta} \partial_\mu \ln Z_G = z \partial_z \ln Z_G \]

\[ \approx Z_1z + (2Z_2 - Z_1^2)z^2 \]

We note that the first order

\[ z \approx \frac{\langle N \rangle}{Z_1} = \rho \lambda^3 \]

in our approximation reproduces our well known ideal gas result (\( \rho = \rho k_B T \)).

We need the next higher order to calculate \( B_2 \):

\[ \frac{\langle N \rangle}{Z_1} = z + \left( \frac{2Z_2 - Z_1^2}{Z_1} \right) z^2 \]

\[ \Rightarrow \quad z = \frac{-1 + \sqrt{1 + 4ac}}{2a} \approx \frac{-1 + 1 + \frac{1}{2} (4ac) - \frac{1}{8} (4ac)^2}{2a} \]

\[ = c(1 - ac) \]

\[ = \frac{\langle N \rangle}{Z_1} \left[ 1 - \frac{\langle N \rangle}{Z_1} \frac{2Z_2 - Z_1^2}{Z_1} \right] \]

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Here we used $\sqrt{1 + x} \approx 1 + \frac{1}{2} x - \frac{1}{8} x^2$ for $x \ll 1$ in the first step.

\[
\Rightarrow \quad \frac{pV}{k_B T} = \ln Z_G \\
= V [\rho + B_2 \rho^2 + O (\rho^3)] = \langle N \rangle [1 + B_2 \rho + O (\rho^2)] \\
= Z_1 z + \left( Z_2 - \frac{1}{2} Z_1^2 \right) z^2 \\
= Z_1 \frac{\langle N \rangle}{Z_1} \left[ 1 - \frac{\langle N \rangle}{Z_1} \left( \frac{2Z_2 - Z_1^2}{Z_1} \right) \right] + \left( Z_2 - \frac{Z_1^2}{2} \right) \frac{\langle N \rangle^2}{Z_1^2} + O (\rho^3) \\
= \langle N \rangle \left[ 1 + \frac{\langle N \rangle}{Z_1^2} \left( -2Z_2 - Z_1^2 + Z_2 - \frac{1}{2} Z_1^2 \right) \right] + O (\rho^3) \\
= \langle N \rangle \left[ 1 - \left( Z_2 - \frac{Z_1^2}{2} \right) \frac{\langle N \rangle}{Z_1^2} \right]
\]

\[
\Rightarrow \quad B_2(T) = -V \left( \frac{Z_2}{Z_1^2} - \frac{1}{2} \right) \\
= -\frac{1}{2} \int d\vec{r} \left( e^{-\beta U(\vec{r})} - 1 \right) \\
B_2(T) = -2\pi \int r^2 \, dr \left( e^{-\beta U(r)} - 1 \right)
\]

Higher virial coefficients follow in a systematic manner from the (graphical) cluster expansion.

**Examples**

1. **hard spheres**
   
   Spheres of radius $d/2$ which cannot penetrate each other. This yields an excluded region of radius $d$ (Figure 6.21).

   \[
   \Rightarrow \quad B_2(T) = -2\pi \int_0^d r^2 (-1) \, dr = \frac{2\pi}{3} d^3 = \frac{1}{2} V_{\text{excl}} = 4V_{\text{sphere}} > 0
   \]

   Due to $B_2$ being positive, a finite, excluded volume increases the pressure. $B_2$ does not depend on temperature, because there is no finite interaction energy.

2. **square well**

   We consider a potential well of depth $\epsilon$ between $d$ and $d + \delta$ (Figure 6.22).

   \[
   \Rightarrow \quad B_2(T) = -2\pi \int_d^{d+\delta} r^2 \, dr \left( e^{\beta \epsilon} - 1 \right) \approx -2\pi d^2 \delta \beta \epsilon < 0 \quad \text{for} \; \epsilon \ll k_B T
   \]

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$B_2(T)$ vanishes at high temperature. The attraction of the particles decreases the pressure. This effect increases with increasing interaction energy $\epsilon$ and range $\delta$.

Hard core repulsion and attraction

As a course approximation to particle interactions with repulsive core and attractive well, we combine a hard hard sphere with an attractive well (Figure 6.23):

$$B_2(T) = \frac{2\pi}{3} d^3 - 2\pi d^2 \delta \beta \epsilon = b - \frac{a}{k_B T}$$

with constants $a, b > 0$.

$$\Rightarrow pV = Nk_B T \left(1 + B_2(T) \frac{N}{V}\right)$$
$$= Nk_B T \left(1 + b \frac{N}{V}\right) - \frac{N^2}{V} a \approx \frac{Nk_B T}{1 - b \frac{N}{V}} - \frac{N^2}{V} a$$
Figure 6.23: Combination of the potentials for the hard spheres and the square well. The resulting form is similar to the Lennard-Jones potential.

Figure 6.24: \( B_2 \) as a function of temperature. It vanishes at the 'Boyle temperature'.

Introducing the specific volume \( v = \frac{V}{N} = \frac{1}{\rho} \) this yields

\[
p = \frac{k_B T}{v - b} - \frac{a}{v^2}
\]

van der Waals equation of state

The excluded volume (b) reduces the accessible volume for the particles while an attractive interaction (a/v^2) reduces pressure.

For \( T < T_c = \frac{8a}{\pi^2 k_B} \), \( p(v) \) will have a minimum and maximum (see Figure 6.25).

In the region between the minimum and maximum we have \( \frac{dp}{dv} > 0 \). This implies a local fluctuation to higher density (smaller v) to cause an increase in pressure which then itself leads to a further increase in density. Due to this instability a part of the system collapses and becomes a liquid. Hence we obtain a phase transition.

The details of the phase transition follow from the 'Maxwell construction'. We consider
the Gibbs free energy as we control temperature T and pressure p:

\[ G = E - TS + pV = \mu N \]

\[ \Rightarrow \quad \mu = \frac{F}{N} + p \cdot \frac{V}{N} \]

For two coexisting phases L and G in equilibrium the intensive parameters T, p and \( \mu \) have to be the same:

\[ \mu_L(T, p) = \mu_G(T, p) \]

\[ \Rightarrow \quad f_G - f_L = p_t (v_L - v_G) \]

Here \( p_t \) is the transition pressure.

The left hand side can be calculated by integration along the isotherm:

\[ f_G - f_L = \int_{v_L}^{v_G} dv \left( \frac{\partial f(T, v)}{\partial v} \right) = -\int_{v_L}^{v_G} dv \ p(T, v) \]
\[ p_T (v_L - v_G) = \int_{v_G}^{v_L} dv \; p(T, V) \]

Geometrically this means that in Figure 6.26 the dotted area has to equal the one below the solid line. Hence \( p_t \) can be determined based on the equality of areas 1 and 2.

We therefore have arrived at the following picture:

If several phases can exist at constant \((T,p)\), the one with the lowest chemical potential \( \mu \) is stable (lowest \( G/N \)). At the transition point, the chemical potentials are equal. However, their slopes can have jumps (compare Figure 6.27).

![Figure 6.27: Left: The chemical potential \( \mu \) as a function of pressure for phases G and L. At the transition point \( \mu_G = \mu_L \), but the slopes have jumps. Right: The specific volume \( v = \left. \frac{\partial \mu}{\partial p} \right|_T \) as a function of pressure has a jump at the transition pressure \( p_t \).](image)

In order to bring the fluid from liquid to gas, we need the ‘heat of evaporation’ or ‘latent heat’ \( Q \):

\[ Q = \int_{T_{t-}}^{T_{t+}} T \; dS = \int_{V_{t-}}^{V_{t+}} dH = H_G - H_L \]

where we used \( dH = TdS + Vdp \) and \( p = p_t = \text{const.} \)

\[ \Rightarrow \quad H = \frac{H}{N} = \frac{E + pV}{N} = \underbrace{\varepsilon(T)}_{\text{kinetic energy contr.}} - \frac{a}{v} + pv \]

\[ q = \frac{Q}{N} = h_G - h_L = \frac{a}{v_L} - \frac{a}{v_G} + p \; (v_G - v_L) \approx \frac{a}{v_L} + pv_G \quad (v_G \gg v_L) \]

\( \frac{a}{v_L} \) is the energy required to overcome attraction while \( pv_G \) is the energy required for expansion.

\[ G = \mu N, \quad dG = -SdT + Vdp + \mu dN \]

\[ \Rightarrow \quad \left. \frac{\partial \mu}{\partial T} \right|_{p,N} = \left. \frac{1}{N} \frac{\partial G}{\partial T} \right|_{p,N} = -\frac{1}{N} S \]
We conclude that both \( v = \frac{\partial \mu}{\partial \rho} \bigg|_T \) and \( s = -\frac{\partial \mu}{\partial T} \bigg|_\rho \) jump at the transition (compare Figures 6.27 and 6.28 respectively). Therefore this phase transition is called to be of ‘first order’ or ‘discontinuous’. Both jumps disappear at the critical point, where the isotherm becomes horizontal at the transition. From

\[
\frac{\partial p}{\partial v} \bigg|_T = \frac{\partial^2 p}{\partial v^2} \bigg|_T = 0
\]

one calculates the critical values:

\[
v_c = 3b, \quad T_c = \frac{8a}{27bk_B}, \quad p_c = \frac{a}{27b^2}
\]

for water: \( p_c = 217 \text{ atm}, \quad T_c = 647 \text{ K} \)

\[
\Rightarrow \quad \frac{p_cv_c}{k_BT_c} = \frac{3}{8} = 0.375 \text{ independent of } a \text{ and } b
\]

Experimental values are similar, but slightly smaller (around 0.3).

If \( p, v \) and \( T \) are expressed in terms of their critical values:

\[
\tilde{p} = \frac{p}{p_c}, \quad \tilde{v} = \frac{v}{v_c}, \quad \tilde{T} = \frac{T}{T_c}
\]

the van der Waals equation becomes

\[
\left( \tilde{p} + \frac{3}{\tilde{v}^2} \right) (3\tilde{v} - 1) = 8\tilde{T}
\]

Figure 6.29 shows van der Waals isotherms for different temperatures with respect to \( T_c \).
This reduced equation leads to the ‘law of corresponding states’: Two fluids with the same \( (\tilde{p}, \tilde{v}, \tilde{T}) \) are in equivalent states. Indeed experimental curves show surprisingly good data collapse. Even more surprisingly, their behaviour becomes almost identical at the critical point - large fluctuations render microscopic details irrelevant.

The ‘van der Waals’ equation of states predicts the fluid-fluid phase transition caused by attractive interactions. The fluid-solid phase transition can be predicted by a simple entropic argument. Recall the van der Waals theory for a hard sphere fluid:

\[
F = N k_B T \left\{ \ln \left( \frac{N \lambda^3}{V - Nb} \right) - 1 \right\}
\]

\[
\Rightarrow \quad p = -\frac{\partial F}{\partial V}_{T,N} = \frac{N k_B T}{V - Nb}
\]

\[
b = 4V_s \quad \Rightarrow \quad V - Nb = V(1 - \rho_b) = \alpha V
\]

with \( \alpha = 1 - \rho / \rho_0 \) and \( \rho_0 = 1/b \). \( \alpha V \) is the free volume in the fluid.

Based on Figure 6.30 and \( L = V^{1/3} \) we define the free volume of a solid as:

\[
\alpha V \approx \left( V^{1/3} - d \right)^3 = \left[ 1 - \left( \frac{p}{\rho_0} \right)^{1/3} \right]^3 V
\]

The free volume vanishes at close packing.
Figure 6.30: Unit cell with hard spheres of diameter $d$. The grey shaded region indicates the free volume.

\[ F_1 - F_2 = N k_B T \ln \frac{a_2}{a_1} \]

Hence the phase with larger $\alpha$ is favored. For that reason the fluid $F$ and the solid $S$ are stable at low and high densities, respectively. Figure 6.31 shows how the Maxwell construction looks like in this case.

Figure 6.31: Free energy for liquid ($F$) and solid phase ($S$) as a function of density $\rho$. The tangent represents the Maxwell construction.

We now can understand the complete phase diagram of a simple one-component fluid:

**Distribution functions**

In contrast to thermodynamics, statistical physics not only predict phase behaviour, but also structure. The central quantity in both theory and experiments is the 'radial distribution function'.
Figure 6.32: Combining the two transitions in (a), one gets the complete phase diagram in (b). In (c) we swap $T$ and $\rho$ axes. By replacing $\rho$ by $p$, we get the final phase diagram in (d). Two-phase coexistence regions become lines in this representation.

We first define the distribution function for absolute position:

$$p(\vec{r}_1, ..., \vec{r}_N) = \frac{e^{-\beta \sum_{i<j} U(r_{ij})}}{\int d\vec{r}_1 ... d\vec{r}_N e^{-\beta \sum_{i<j} U(r_{ij})}}$$

By defining $W := \sum_{i<j} U(r_{ij})$, the probability that any particle is at position $\vec{r}$ can be written as:

$$n_1(\vec{x}) = \sum_{k=1}^{N} \langle \delta (\vec{x} - \vec{r}_k) \rangle$$

$$= \frac{\int d\vec{r}_1 ... d\vec{r}_N \left( \sum_{k=1}^{N} \delta (\vec{x} - \vec{r}_k) \right) e^{-\beta W}}{\int d\vec{r}_1 ... d\vec{r}_N e^{-\beta W}}$$

$$= N \frac{d\vec{r}_2 ... d\vec{r}_N e^{-\beta W(\vec{x}, \vec{r}_2, ..., \vec{r}_N)}}{\int d\vec{r}_1 ... d\vec{r}_N e^{-\beta W}}$$
\[ n_1 (\vec{x}) \text{ ideal gas } \overline{N} = \rho \]

The probability that some particle is at \( \vec{x}_1 \) and another at \( \vec{x}_2 \) is:

\[ n_2 (\vec{x}_1, \vec{x}_2) = \sum_{i \neq j} \langle \delta (\vec{x}_1 - \vec{r}_i) \delta (\vec{x}_2 - \vec{r}_j) \rangle \]

\[ = N(N - 1) \int \frac{d\vec{r}_3 \ldots d\vec{r}_N e^{-\beta W(\vec{x}_1, \vec{x}_2, \ldots, \vec{r}_N)}}{d\vec{r}_1 \ldots d\vec{r}_N e^{-\beta W}} \]

\[ n_2 (\vec{x}_1, \vec{x}_2) = \overline{n_2 (\vec{x}_1, \vec{x}_2)} \text{ ideal gas } \overline{N} = \rho^2 \]

For the pairwise additive potential everything follows from \( n_1 \) and \( n_2 \). Eg the averaged interaction energy:

\[ \langle W \rangle = \sum_{i < j} \langle U(r_{ij}) \rangle \]

\[ = \frac{1}{2} \sum_{i \neq j} \int d\vec{x}_1 d\vec{x}_2 \langle U (\vec{x}_1 - \vec{x}_2) \delta (\vec{x}_1 - \vec{r}_i) \delta (\vec{x}_2 - \vec{r}_j) \rangle \]

\[ = \frac{1}{2} \int d\vec{x}_1 d\vec{x}_2 U (\vec{x}_1 - \vec{x}_2) n_2 (\vec{x}_1, \vec{x}_2) \]

In a homogeneous system:

\[ n_2 (\vec{x}_1, \vec{x}_2) = n_2 (|\vec{x}_1 - \vec{x}_2|) \]

We define the ‘radial distribution function’ \( g \) by:

\[ n_2 (|\vec{x}_1 - \vec{x}_2|) = \rho^2 g (|\vec{x}_1 - \vec{x}_2|) \]

\[ \Rightarrow \overline{\langle W \rangle} = \frac{N^2}{2V} \int d\vec{r} U(r) g(r) \]

\( \rho g(r) 4\pi r^2 dr \) is the average number of particles in a spherical shell of width \( dr \) at a distance \( r \) from any particle.

While for the ideal gas \( g = 1 \), \( g(r) \) has damped oscillations for a real gas (compare Figure 6.33).

The pair correlation function \( g(r) \) can be measured in scattering experiments (x-rays, neutrons, electrons, light):

Interaction between probe at \( \vec{r} \) and particles at \( \{ \vec{r}_i \} \):

\[ \sum_{i=1}^{N} U (\vec{r} - \vec{r}_i) \]

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Figure 6.33: The correlation function $g$ for a real gas as a function of distance $r$. The oscillations damp away with distance.

Figure 6.34: Schematic sketch of a scattering experiment. If $\vec{k}$ denotes the wave vector of the incoming wave and $\vec{k}'$ for the outgoing wave, the wave-fluid interaction results in a momentum transfer $q = \vec{k}' - \vec{k}$ with $|\vec{k}'| = |\vec{k}|$.

Fermi’s golden rule for the transition rate $I$ states:

$$I(\vec{q}) \propto |\langle \vec{k}' | \sum_{i=1}^{N} U(\vec{r} - \vec{r}_i) | \vec{k} \rangle|^2$$

$$\propto f(\vec{q}) \cdot S(\vec{q})$$

The ‘form factor’ describes the interaction between probe and particles and depends on the experiment.

$$f(\vec{q}) = |U(\vec{q})|^2$$

$$U(\vec{q}) = \int d\vec{r} U(\vec{r}) e^{-i\vec{q} \cdot \vec{r}}$$

The ‘structure factor’ represents the internal structure and is independent of the type of probe.

$$S(\vec{q}) = \frac{1}{N} \left\langle \sum_{i \neq j} e^{i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)} \right\rangle = 1 + \rho \int d\vec{r} \left( g(r) - 1 \right) e^{i\vec{q} \cdot \vec{r}}$$

We note that $S(\vec{q})$ is essentially the Fourier transform of $g(r)$ (qualitative shape similar to $g(r)$ - compare Figure 6.33).
7 Thermodynamics

7.1 Axiomatic structure

Thermodynamics has evolved in the 19th century as the science of heat transfer. It gives the same results as statistical physics in the limit of large system size. In contrast to statistical physics, it is a phenomenological theory and does not have a microscopic basis. One can consider this either as strength or weakness, depending on the viewpoint. Traditionally, it is explained starting from the four laws of thermodynamics. Here we choose the axiomatic viewpoint following the presentation by Callen.

The following four axioms together completely determine the formal structure of classical thermodynamics:

1. Simple isolated systems in equilibrium are characterised by the state variables \((E, V, N)\).

2. For each equilibrium state an entropy function \(S(E, V, N)\) exists. After removal of an internal constraint, the system obtains the state of maximal entropy.

3. Entropy is additive over subsystems and increases monotonously with \(E\).

4. Entropy vanishes at \(\frac{\partial E}{\partial S} = 0\) (Nernst postulate for \(T = 0\)).

Thus a thermodynamic system is located on the ‘entropy manifold’ in a four dimensional state space \((E, V, N, S)\). This is similar to a classical system being located on a ‘energy manifold’ in \(6N\) dimensional phase space \((\vec{p}, \vec{q})\). Quasi-static processes only involve equilibrium states. They can proceed only up or sidewards on the entropy manifold.

The total differential of the entropy function is:

\[
\begin{align*}
\frac{dS}{dE} &= \left. \frac{\partial S}{\partial E} \right|_{V,N} dE + \left. \frac{\partial S}{\partial V} \right|_{E,N} dV + \left. \frac{\partial S}{\partial N} \right|_{V,E} dN \\
&= \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN
\end{align*}
\]

Because \(S\) is an increasing function of \(E\), one can always solve for \(E = E(S, V, N)\):

\[
\begin{align*}
dE &= T \frac{dS}{\text{heat}} - p \frac{dV}{\text{mechanical work}} - \mu \frac{dN}{\text{chemical energy}}
\end{align*}
\]

The three terms represent different ways to transfer energy.
Both $S(E, V, N)$ and $E(S, V, N)$ are fundamental equations which contain the complete thermodynamical information. Their partial derivatives can be interpreted as ‘thermodynamical forces’ in analogy to the mechanical forces $F = -\nabla V$:

$$T = \left. \frac{\partial E(S, V, N)}{\partial S} \right|_{V, N}$$  temperature as driving force for entropy (heat) exchange

$$p = \left. -\frac{\partial E(S, V, N)}{\partial V} \right|_{S, N}$$  pressure as driving force for volume exchange

$$\mu = \left. \frac{\partial E(S, V, N)}{\partial N} \right|_{S, V}$$  chemical potential as driving force for particle exchange

Each of these three equations of state contains only incomplete thermodynamical information. Knowledge of all three means that we know the tangential plane at every point and so can reconstruct the fundamental equation $E = E(S, V, N)$.

### 7.2 Variational principles

We next consider a composite system with two subsystems. The thermodynamical state space is now spanned by $(E_1, V_1, N_1, E_2, V_2, N_2, S)$. In Figure 7.2 we schematically sketch the subsystem represented by $S, E = E_1 + E_2$ and one extensive variable of one of the two subsystems, eg $X = V_1$. 
Due to the maximal entropy principle, the equilibrium state is in fact at $A$.

$\Rightarrow$ The equilibrium value of any unconstrained internal parameter $X_j$ is such as to maximize the entropy $S$ for a given value of the total energy $E$.

Note that the final state might be reached by a non-equilibrium process, but to identify the equilibrium state, one minimizes over the manifold of possible equilibrium states.

We next note that the equilibrium state $A$ can also be identified from a minimal energy principle:

$\Rightarrow$ The equilibrium value of any unconstrained internal parameter $X_j$ is such as to minimize the energy $E$ for a given value of the entropy $S$.

This is sketched in Figure 7.3.

**Proof:**

If the energy was not minimal, we could withdraw some energy as work $-pdV$ and return it as heat $TdS$. Then the system would be restored to its initial energy but with increased entropy. This is a contradiction to the maximal entropy principle.

**Example:**

We consider the heat flow between two systems of fixed volumes and particle numbers.
1 maximal entropy principle:

\[ dS = \frac{1}{T_1} \, dE_1 + \frac{1}{T_2} \, dE_2 = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \, dE_1 = 0 \Rightarrow T_1 = T_2 \]

Before the equilibrium is reached: \( dS > 0 \) \( \Rightarrow \) maximum of \( S \).

2 minimal energy principle:

\[ dE = T_1 \, dS_1 + T_2 \, dS_2 = (T_1 - T_2) \, dS_1 = 0 \Rightarrow T_1 = T_2 \]

Before the equilibrium is reached: \( dE < 0 \) \( \Rightarrow \) minimum of \( E \).

We again consider the two subsystems with an internal constraint \( X_j \). We now connect them to a heat reservoir with temperature \( T_r \).

The minimal energy principle implies:

\[ d \left( E + E_r \right) = d \left( E_1 + E_2 + E_r \right) = 0 \]

Terms related to heat exchange with the reservoir:

\[ T_1 dS_1 + T_2 dS_2 + T_r dS_r = (T_1 - T_r) \, dS_1 + (T_2 - T_r) \, dS_2 = 0 \]

\[ \Rightarrow \quad T_1 = T_2 = T_r = T \quad \text{equilibrium condition independent of internal constraint} \]
\[ 0 = d(E_r + E) = T \, dS_r + dE = -TdS + dE = d(E - TS) = dF \]

Hence the free energy \( F \) has an extremum at equilibrium. Since \( T \) is a constant and since \( S_r \) does not have a second derivative,

\[
d^2 (E_r + E) > 0
\]

implies \( d^2 F > 0 \) and thus \( F \) is minimal. The equilibrium value of any unconstrained internal parameter \( X_i \) in contact with a heat reservoir minimizes the free energy \( F \) over all states with \( T = T_r \).

### 7.3 Euler and Gibbs-Duhem relations

Energy is extensive and therefore has to be a homogeneous function of order one:

\[
E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N)
\]

\[
\Rightarrow \frac{\partial E}{\partial (\lambda S)} \frac{\partial (\lambda S)}{\partial \lambda} + \frac{\partial E}{\partial (\lambda V)} \frac{\partial (\lambda V)}{\partial \lambda} + \frac{\partial E}{\partial (\lambda N)} \frac{\partial (\lambda N)}{\partial \lambda} = E(S, V, N)
\]

\[ \lambda = 1 \Rightarrow \boxed{E = TS - pV + \mu N} \] Euler relation

\[
\Rightarrow dE = TdS + SdT - pdV - Vdp + \mu dN + Nd\mu
\]

\[
\Rightarrow SdT - Vdp + Nd\mu = 0
\]

\[
\Rightarrow \boxed{d\mu = -sdT + vd\mu} \] Gibbs-Duhem relation

The three intensive variables \((T, p, \mu)\) are not independent. There are only two thermodynamic degrees of freedom. If one knows the equations of state \( s = s(T, p) \) and \( v = v(T, p) \), one can integrate the Gibbs-Duhem relation to get \( \mu = \mu(T, p) \).

If one knows the fundamental equation, the Gibbs-Duhem relation can be directly calculated in the integrated form:

\[
E = E(S, V, N)
\]

\[
\Rightarrow p_i = \frac{\partial E}{\partial X_i} = p_i(S, V, N) = p_i(\frac{S}{N}, \frac{V}{N}, 1) = p_i(s, v)
\]

Elimination of \((s, v)\) from these three equations of state gives the Gibbs-Duhem relation between \((T, p, \mu)\).

The same arguments can be made in the entropy representation. The Euler-relation becomes

\[
S = \frac{1}{T}E + \frac{p}{T}V - \frac{\mu}{T}N
\]

and the Gibbs-Duhem relation then reads:

\[
0 = d(\frac{1}{T})E + d(\frac{p}{T})V - d(\frac{\mu}{T})N
\]
**Example: fundamental equation for ideal gas**

We now use these results to discuss the ideal gas. In thermodynamics one starts with the phenomenological observations, so we take the two well-documented gas laws

\[ pV = nRT = Nk_B T, \quad E = \frac{3}{2} nRT = \frac{3}{2} Nk_B T \]

Because \( E \) appears here, we choose the entropy representation and rewrite these equations as

\[ \frac{p}{T} = \frac{k_B}{v}, \quad \frac{1}{T} = \frac{3k_B}{2e} \]

We next integrate the Gibbs-Duhem relation

\[ d\left(\frac{\mu}{T}\right) = e\left(\frac{\mu}{T}\right) + v d\left(\frac{p}{T}\right) = e\left(\frac{-3k_B}{2e^2}\right) de + v\left(\frac{-k_B}{v^2}\right) dv = -\frac{3k_B de}{2e} - \frac{k_B dv}{v} \]

to give

\[ \frac{\mu}{T} = \left(\frac{\mu}{T}\right)_0 - \frac{3k_B}{2} \ln \frac{e}{e_0} - k_B \ln \frac{v}{v_0} \]

Inserting this result into the Euler relation gives

\[ S = S_0 + k_B N \ln \left[ \left( \frac{E}{E_0} \right)^{3/2} \left( \frac{V}{V_0} \right) \left( \frac{N_0}{N} \right)^{5/2} \right] \]

with

\[ S_0 = \frac{5k_B N}{2} - \left(\frac{\mu}{T}\right)_0 N \]

Note that we get the same result as from the microcanonical or canonical ensemble, except that we have a constant of integration that we cannot determine in thermodynamics. Here we see the essential difference to statistical physics: we cannot give a microscopic expression, but nevertheless we can get full thermodynamic information from a few experimental observations because the formal structure gives very strong constraints on the fundamental equation. We also note that in this specific and very fortunate case, we are able to integrate term-by-term, which usually is not the case. We finally note that we could have obtained the same result much easier by simply integrating the differential \( ds = (1/T) de + (p/T) dv \), but here we wanted to demonstrate the use of the Gibbs-Duhem equation.

Similar procedures can be used to obtain the fundamental equations for e.g. the van der Waals gas, the photon gas, the rubber band, etc.
7.4 Thermodynamic potentials and Legendre transformations

We reconsider the situation that the temperature $T$ is fixed by a reservoir. Now the relevant quantity is free energy $F$.

\[
S(E) = S_1(E_1) + S_2(E - E_1) \\
= S_1(E_1) + S_2(E) - \frac{\partial S_2}{\partial E_2} \bigg|_{E_1} E_1 \\
= \text{const} + \left( S_1(E_1) - \frac{1}{T_1} E_1 \right)
\]

As $S$ is maximal at equilibrium, free energy $F = E_1 - TS_1(E_1)$ is minimal. Equilibrium is a compromise between order ($E$) and disorder ($S$). The larger $T$, the more disorder takes over. Free energy $F$ is the relevant ‘thermodynamic potential’ for the choice $(T,V,N)$ as state variables.

In general one expects $2^3 = 8$ thermodynamic potentials, one for each choice of state variables:

<table>
<thead>
<tr>
<th>state variables</th>
<th>thermodynamic potential</th>
<th>description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S, V, N$</td>
<td>$E$</td>
<td>internal energy</td>
</tr>
<tr>
<td>$T, V, N$</td>
<td>$F = E - TS$</td>
<td>Helmholtz free energy</td>
</tr>
<tr>
<td>$T, p, N$</td>
<td>$G = F + pV$</td>
<td>Gibbs free energy</td>
</tr>
<tr>
<td>$S, p, N$</td>
<td>$H = E + pV$</td>
<td>enthalpy</td>
</tr>
<tr>
<td>$T, V, \mu$</td>
<td>$\Psi = F - \mu N$</td>
<td>grand canonical potential</td>
</tr>
<tr>
<td>$S, V, \mu$</td>
<td>$A_1$</td>
<td></td>
</tr>
<tr>
<td>$S, p, \mu$</td>
<td>$A_2$</td>
<td></td>
</tr>
<tr>
<td>$T, p, \mu$</td>
<td>$A_3$</td>
<td></td>
</tr>
</tbody>
</table>

$E, F, G, H$ and $\Psi$ are physically relevant. Each is minimal for the given variables (derivation as before). Obviously this range of potentials gives raise to many Maxwell relations. Note that $S$ is not a thermodynamic potential. Although it also comes with a fundamental equation, it does not obey a minimization principle (rather it obeys a maximization principle).

Different thermodynamic potentials are related to each other by Legendre transformations. We now discuss this concept for the one-dimensional case. Consider a monotonous
function \( y = f(x) \) with a unique inverse \( x = f^{-1}(y) \). We want to rewrite \( y(x) \) as a function of its derivative \( p = f'(x) = g(x) \).

\[
\Rightarrow x = g^{-1}(p) = x(p) \\
\Rightarrow y(p) = y(x(p)) = f(g^{-1}(p)) = (f \circ g^{-1})(p)
\]

However this procedure is not unique:
Curves shifted in x-direction have the same result \( y(p) \).

The underlying reason is that we work with an ODE of first order:

\[
y(x) = (f \circ g^{-1})(y'(x)),
\]

which leaves a constant of integration undetermined.
To solve this problem, we describe the curve $y(x)$ as enveloped by the family of its tangents.

![Figure 7.6: $y(x)$ can be described as enveloped by the family of its tangents.](image)

Each tangent is characterised by the slope $p = f'(x)$ and the intercept:

$$p(x) = \frac{y(x) - \Psi(x)}{x} \Rightarrow \Psi(x) = y(x) - p(x) x$$

The resulting Legendre transform

$$\Psi(p) = y(x(p)) - p x(p)$$

is a unique function of $y(x)$.

Back transform:

$$dy = p \, dx \quad \Rightarrow \quad d\Psi = dy - p \, dx - x \, dp = -x \, dp$$

$$\Rightarrow \quad \frac{d\Psi}{dp} = -x \quad \Rightarrow \quad y(x) = \Psi(p(x)) + p(x) x$$

We note that applying the Legendre transformation twice brings us back to the original function.

**Example:**

$$y = (x - x_0)^2 \quad \Rightarrow \quad p = 2(x - x_0) \quad \Rightarrow \quad x = \frac{p}{2} + x_0$$
\[ y = \left( \frac{p}{2} \right)^2 \text{ does not depend on } x_0 \]

\[ \Rightarrow \quad \Psi = y - px = \left( \frac{p}{2} \right)^2 - p \left( \frac{p}{2} + x_0 \right) = -\frac{p^2}{4} - px_0 \text{ depends on } x_0 \]

\[ -x = \frac{d\Psi}{dp} = -\frac{p}{2} - x_0 \quad \Rightarrow \quad p = 2(x - x_0) \]

\[ \Rightarrow \quad y = \Psi + px = \frac{(2(x - x_0))^2}{4} - 2(x - x_0)x_0 + 2(x - x_0) x = -(x - x_0)^2 + 2(x - x_0)^2 = (x - x_0)^2 \]

The Legendre transform of \( y(x) \) in regard to \( p \) is denoted by \( y \left[ p \right] \).

We now see that the free energy \( F \) is actually the Legendre transform \( E \left[ T \right] \) of energy \( E \) from entropy \( S \) to temperature \( T \) (alternatively it can be derived from \( \beta F = S \left[ \beta \right] \)).

\[ E = E \left( S, V, N \right) \]

\[ T(S, V, N) = \frac{\partial E}{\partial S} \quad \Rightarrow \quad S = S(T, V, N) \]

\[ F(T, V, N) = E \left[ T \right] = E(S(T, V, N), V, N) - T \, S(T, V, N) \]

\[ \Rightarrow \quad \frac{\partial F}{\partial T} = \frac{\partial E}{\partial S} \frac{\partial S}{\partial T} - S - T \frac{\partial S}{\partial T} = -S \]

\[ \frac{\partial F}{\partial V} = \frac{\partial E}{\partial S} \frac{\partial S}{\partial V} + \frac{\partial E}{\partial V} - T \frac{\partial S}{\partial V} = \frac{\partial E}{\partial V} = -p \]

\[ \frac{\partial F}{\partial N} = \frac{\partial E}{\partial S} \frac{\partial S}{\partial N} + \frac{\partial E}{\partial N} - T \frac{\partial S}{\partial N} = \frac{\partial E}{\partial N} = \mu \]

\[ \Rightarrow \quad dF = -S \, dT - p \, dV + \mu \, dN \]

### 7.5 Maxwell relations

In the last section we introduced 8 thermodynamic potentials. Each generates \( 3 \cdot 2/2 = 3 \) separate pairs of mixed second derivatives, giving rise to 24 Maxwell relations like this one:

\[ \frac{\partial^2 E}{\partial S \partial V} = -\frac{\partial p}{\partial S} \bigg|_{V,N} = \frac{\partial^2 E}{\partial V \partial S} = \frac{\partial T}{\partial V} \bigg|_{S,N} \]

It is a unique strength of thermodynamics to generate such surprising relations between seemingly unrelated physical quantities. In order to memorize these relations, the ‘thermodynamical square’ or ‘König-Born diagram’ (compare Figure 7.7) has been introduced. We keep \( N \) fixed and consider the four most important potentials.
From two neighboring corners a Maxwell relation can be read off (derived from the edge in between, ie H):

\[
\begin{align*}
\frac{\partial V}{\partial S} \bigg|_p &= \frac{\partial T}{\partial p} \bigg|_S \\
\frac{\partial^2 H}{\partial S \partial p} &= \frac{\partial^2 H}{\partial p \partial S}
\end{align*}
\]

Three other Maxwell relations follow by rotation of the scheme.
Response functions

Derivatives like $\left. \frac{\partial T}{\partial p} \right|_S$ can be measured in experiments and are called ‘response functions’.

Theorem:

There exist only three independent response functions. All others can be expressed through them.

Proof:

We reduce the derivatives using the thermodynamical square, the mathematical relations between partial derivatives (see last section of this chapter) and the Gibbs-Duhem relation for the chemical potential.

Standard choice:

For constant particle number, we define the following quantities:

\[
\alpha := \left. \frac{1}{V} \frac{\partial V}{\partial T} \right|_p \quad \text{coefficient of thermal expansion}
\]

\[
\kappa_T := -\left. \frac{1}{V} \frac{\partial V}{\partial p} \right|_T \quad \text{isothermal compressibility}
\]

\[
c_p := \left. \frac{dQ}{dT} \right|_p = T \left. \frac{\partial S}{\partial T} \right|_p \quad \text{specific heat at constant pressure}
\]

This essentially corresponds to a transformation to the Gibbs representation ($g = \frac{G}{N}$):

\[
\frac{\partial^2 g}{\partial T^2} = -\frac{c_p}{T}
\]

\[
\frac{\partial^2 g}{\partial T \partial p} = -\nu \alpha
\]

\[
\frac{\partial^2 g}{\partial p^2} = -\nu \kappa_T
\]

Example

Relation between $c_p$ and $c_V$ ($N = \text{const}$)

\[
\text{heat capacity at constant pressure: } c_p = \left. \frac{dQ}{dT} \right|_p = T \left. \frac{\partial S}{\partial T} \right|_p
\]

\[
\text{heat capacity at constant volume: } c_V = \left. \frac{dQ}{dT} \right|_V = T \left. \frac{\partial S}{\partial T} \right|_V
\]
\[
dS = \frac{\partial S}{\partial T} \mid_{V,N} \, dT + \frac{\partial S}{\partial V} \mid_{T,N} \, dV
\]

\[
= c_V \frac{dT}{T} + \frac{\partial p}{\partial T} \mid_V \left[ \frac{\partial V}{\partial T} \mid_p \, dT + \frac{\partial V}{\partial p} \mid_T \, dp \right]
\]

\[\Rightarrow \quad T \frac{\partial S}{\partial T} \mid_p = c_p = c_V + T \frac{\partial p}{\partial T} \mid_V \frac{\partial V}{\partial p} \mid_T = \alpha \kappa_T \]

\[\Rightarrow \quad \frac{\partial p}{\partial T} \mid_V = -\frac{\frac{\partial V}{\partial p} \mid_T}{\frac{\partial V}{\partial T} \mid_p} = \frac{\alpha}{\kappa_T} \]

\[\Rightarrow \quad c_p = c_V + TV \frac{\alpha^2}{\kappa_T} > c_V \quad \text{as} \quad \kappa_T > 0, \quad \frac{\alpha^2}{\kappa_T} > 0
\]

For an ideal gas this yields:

\[c_V = \frac{dE}{dT} \mid_V = \frac{3}{2} Nk_B \]

\[\alpha = \frac{1}{V} \frac{\partial V}{\partial T} \mid_p = \frac{1}{T} \]

\[\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial p} \mid_T = \frac{1}{p} \]

\[\Rightarrow \quad c_p = c_V + TV \frac{p}{T^2} = c_V + Nk_B = \frac{5}{2} Nk_B
\]

**7.6 Process-dependance of work and heat**

Recall the total differential for energy:

\[dE = T \, dS - p \, dV + \mu \, dN\]

It is instructive to compare with mechanics:

\[dE = \vec{v} \cdot d\vec{p} - \vec{F} \cdot d\vec{r} = \frac{\vec{p}}{m} \cdot d\vec{p} + \nabla V \cdot d\vec{r} = d \left( \frac{p^2}{2m} \right) + dV\]
We see that each term by itself is a total differential. This is not true in thermodynamics because $T = (S, V, N) \neq T(S)$.

Note that in both cases $E(B)$ is a state function whose value is independent of how one gets from $A$ to $B$. In this sense the system is conservative. However, the way in which energy is divided between heat and mechanical work is not universal and in this sense the system is not conservative.

Despite the path-dependent weights of the different energy forms, the partial derivatives are not arbitrary because they must belong to a fundamental equation. Therefore we must have eg:

$$\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial T}{\partial V}_{S,N}, \quad \frac{\partial E}{\partial S \partial V} = -\frac{\partial p}{\partial S}_{V,N}$$

This expression relates quantities which at first seem unrelated. We will later meet the whole set of these ‘Maxwell relations’. It is the particular strength of thermodynamics to provide these surprising relations which all have been experimentally verified.

If we neglect changes in particle number, we have

$$\text{d}E = T \text{d}S - p \text{d}V$$

We have seen before that the two quantities depend on the path taken from state $A$ to $B$. We therefore write:

$$\text{d}E = \text{d}Q + \text{d}W$$

first law of thermodynamics (energy conservation)

Here $\text{d}$ indicates ‘incomplete differentials’.

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sign convention: \( \text{d}W > 0 \) If the work increases the energy of the system.
\( \text{d}Q > 0 \) Heat flows into the system and increases its energy.

Very often one discusses expansion of gases. Then the mechanical work is \( \text{d}W = -p\text{d}V < 0 \), i.e. the system does work and looses energy, because \( p \) is positive and \( \text{d}V < 0 \).

James Joule was the first to realize that one can always measure \( \text{d}Q \) and \( \text{d}W \) for given states A and B:

1. First make an adiabatic (isentropic) experiment (thermally isolating walls). This implies:
   \[ \text{d}Q = 0 \Rightarrow \text{d}E = \text{d}W \]
   If \( A \to B \) does not work because \( \Delta S < 0 \), use \( B \to A \) with \( \Delta S > 0 \).
   Because \( \text{d}W \) can be measured by mechanical means, one gets \( \Delta E_{AB} \) in this way. Joule invented many devices to do exactly this.

2. Now make an experiment of interest with heat exchange (diathermal walls) connecting the same two states and measuring \( W_{AB} \) (now with another result).
   \[ \Rightarrow Q_{AB} = \Delta E_{AB} - W_{AB} \]
   As \( \Delta E_{AB} \) is known due to our first step, we now can calculate \( Q_{AB} \).

The essential point here is that \( E \) is a state function, while \( Q \) and \( W \) are not.

**Pond analogy**

Consider a farmer who wants to know how much water is in his pond. There are two ways its amount can change:
in- and outflow through a stream, and increase/ decrease by rain/ evaporation.
How can he control the relative importance of these two channels?
The solution is simple: First he covers the pond by a tarpaulin. He then can calibrate the water height by using flow meters in the stream. Finally removing the tarpaulin, he now can calculate back how much water results from rain/ evaporation.

**Expansion of an ideal gas**

We now discuss the expansion of an ideal gas as an example for the process-dependance of thermodynamic processes. We go from state A to B as shown in Figure 7.11.
Fundamental equation:
\[
S = S_0 + k_B N \ln \left( \frac{V E^2}{N^2} \right)
\]
Figure 7.10: The amount of water in the pond depends on rain, evaporation and in- and outflow due to a stream.

Figure 7.11: Three different paths from A to B. In each case the system cools.

For an adiabatic process (S=const) at N=const we therefore have

\[ V E^\frac{3}{2} = \text{const} \]

\[ E = \frac{3}{2} N k_B T = \frac{3}{2} p V \quad \Rightarrow \quad V^5 p^3 = \text{const} \]

\[ \Rightarrow \Delta E_{AB} = \int dW = - \int_{V_A}^{V_B} p \, dV = - p_A \int_{V_A}^{V_B} \left( \frac{V_A}{V} \right)^{\frac{5}{3}} \, dV \]

\[ = \frac{3}{2} p_A V_A^\frac{5}{3} \left( V_B^{-\frac{2}{3}} - V_A^{-\frac{2}{3}} \right) < 0 \]
The gas is doing work and loses energy.

We now calculate work and heat for the paths through D and C.

\[ W_{ADB} = - \int p \, dV = -p_A (V_B - V_A) < \Delta E_{AB} < 0 \]

The system is doing even more work.

\[ Q_{ADB} = \Delta E_{AB} - W_{ADB} > 0 \]

Heat flows into the system to compensate for this extra work.

\[ W_{ACB} = - \int p \, dV = -p_B (V_B - V_A) > \Delta E_{AB} < 0 \]

The system is doing work, but less compared with the two other paths.

\[ Q_{ACB} = \Delta E_{AB} - W_{ACB} < 0 \]

Heat flows from the system, lowering its energy.

![Diagram showing adiabatic and isothermal processes](image)

Figure 7.12: The adiabatic curve is steeper than the isothermal one. A combination can be used to get from A to D in Figure 7.11.

Note that we did not need to calculate \( \Delta E_{AD} \) or \( \Delta E_{AC} \). Indeed this is more complicated and requires the construction shown in Figure 7.11 by combining an adiabatic with an isothermal process, one can go from A to D.

### 7.7 Reversible and irreversible processes

Both statistical physics and classical thermodynamics state

\[ \Delta S \geq 0 \quad \text{second law of thermodynamics} \]

\[ \Delta S = 0 \quad \text{reversible process: can go both ways} \]

\[ \Delta S > 0 \quad \text{irreversible process: other way cannot occur spontaneously} \]
Examples

1. adiabatic expansion of an ideal gas

Figure 7.13: The ideal gas expands while the piston is moved out.

The piston is moved out with different velocities and the complete system is thermally isolated. Therefore there is no heat flux, \( dQ = 0 \). We consider the extreme cases concerning the piston’s velocity:

1. very fast: expansion into vacuum
2. very slow: quasi-static, pressure is always equilibrium pressure \( p = Nk_B T / V \)

Fundamental equation:

\[
S = S_0 + k_B N \ln \left( \frac{V E^2}{N^2} \right)
\]

expansion into vacuum (case 1):

\[
\begin{align*}
\text{d}E &= \text{d}W = 0 \\
\text{d}S &= \frac{\partial S}{\partial V} \text{d}V = k_B N \frac{1}{V} \text{d}V > 0
\end{align*}
\]

We see that no work is being done and that the process is irreversible. The entropy has to go up because now many more microstates become available.

quasi-static (case 2):

\[
\begin{align*}
\text{d}E &= \text{d}W = -p \text{d}V \\
&= -\frac{Nk_B T}{V} \text{d}V = -\frac{2}{3} \frac{E}{V} \text{d}V \\
\text{d}S &= \frac{\partial S}{\partial V} \text{d}V + \frac{\partial S}{\partial E} \text{d}E = Nk_B \frac{1}{V} \text{d}V + \frac{3}{2} Nk_B \frac{1}{E} \text{d}E = 0
\end{align*}
\]
The gas loses energy because it does work (and hence also becomes colder). The process is reversible, because the entropy increase due to the volume increase is exactly balanced by the loss of entropy due to the decrease in energy.

This situation is easy to analyze because we consider an isolated system for which we know everything. The situation is more complex if we couple it to the environment. Consider for example isothermal quasi-static expansion, so we couple the piston to a heat bath. Then it does the same work as above. However, because now \( T \) is constant, \( E \) is also constant and heat has to flow in such that \( \bar{d}Q = -\bar{d}W \).

The entropy of the piston goes up, but the reservoir loses exactly the same amount of entropy due to the heat flow and the overall entropy is constant. Therefore isothermal quasi-static expansion is also reversible.

2. warm bottle \( B \) in cold lake \( L \)
   We assume that the heat capacities of bottle \( (c_B) \) and lake \( (c_L) \) are constant.
   Fundamental equation:
   \[
   S = S(E, V, N) = S_0 + c \ln \frac{E}{E_0}
   \]
   \[
   \frac{1}{T} = \frac{\partial S}{\partial E} = c \frac{1}{E} \quad \Rightarrow \quad E = c \, T
   \]
   \[
   \Rightarrow c = \frac{dE}{dT}
   \]

   We now bring the two systems in thermal contact. The bottle will be cooled from \( T_a \) to \( T_b \). It will give away heat
   \[
   Q_B = \Delta E_B = c_B (T_b - T_a) \leq 0
   \]
   while no work is done due to the volume being constant.
   \[
   \Delta E = \Delta E_B + \Delta E_L = Q_B + Q_L = 0
   \]
   \[
   \Rightarrow \Delta T_L = \frac{|Q_L|}{c_L} = \frac{|Q_B|}{c_L} = \frac{c_B}{c_L} \Delta T_B \approx 0
   \]
   As \( c_B \ll c_L \) the temperature change of the lake can be neglected.

   Changes in entropy:
   \[
   \Delta S_L = \int_a^b \frac{dQ_L}{T} = \frac{Q_L}{T_b} = -\frac{Q_B}{T_b} = \frac{c_B}{T_b} \frac{T_a - T_b}{T_b} \geq 0 \quad \text{lake gains entropy}
   \]
   \[
   \Delta S_B = \int_a^b \frac{dQ_B}{T} = \int_{T_a}^{T_b} c_B \frac{dT}{T} = c_B \ln \left( \frac{T_b}{T_a} \right) \leq 0 \quad \text{bottle looses entropy}
   \]
The overall change in entropy thus is (defining $z := T_a/T_b \geq 1$):

$$\Delta S = \Delta S_L + \Delta S_B = c_B \left(z - 1 - \ln z\right)$$

Our result is in agreement with the second law of thermodynamics:

$$\ln z \leq z - 1 \quad \Rightarrow \quad z - 1 - \ln z \geq 0 \quad \Rightarrow \quad \Delta S \geq 0$$

The equal sign is valid for $z = 1$ ($T_a = T_b$). Otherwise $\Delta S > 0$ and the process is irreversible as heat flows from the warmer to the cooler system. Note that the same conclusion holds if we place a cold bottle in a warm lake ($z < 0$).

### 7.8 Thermodynamic engines

We again consider heat flow from a warm to a cold body. We assume constant heat capacities. The change in energy of the complete system then can be expressed as:

$$\Delta E = \int_{T_{10}}^{T_f} c_1 \, dT_1 + \int_{T_{20}}^{T_f} c_2 \, dT_2 \overset{!}{=} 0$$

$$\Rightarrow \quad T_f = \frac{c_1 T_{10} + c_2 T_{20}}{c_1 + c_2}$$

The change in entropy is:

$$\Delta S = \int_{T_{10}}^{T_f} \frac{c_1 dT_1}{T_1} + \int_{T_{20}}^{T_f} \frac{c_2 dT_2}{T_2}$$

$$= c_1 \ln \frac{T_f}{T_{10}} + c_2 \ln \frac{T_f}{T_{20}}$$

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Assuming equal heat capacities: $c_1 = c_2 = c$

$$T_f = \frac{T_{10} + T_{20}}{2}$$

$$\Delta S = 2c \ln \left( \frac{T_f}{\sqrt{T_{10} T_{20}}} \right) = 2c \ln \left( \frac{T_{10} + T_{20}}{2 \sqrt{T_{10} T_{20}}} \right) \geq 0$$

The change in entropy is always positive as the arithmetic mean is always larger than or equal to the geometrical mean.

$$\frac{T_{10} + T_{20}}{2} \geq \sqrt{T_{10} T_{20}}$$

We can see this as follows:

$$(a - b)^2 \geq 0 \Rightarrow a^2 + 2ab + b^2 \geq 4ab \Rightarrow \frac{(a + b)^2}{4} \geq ab$$

The process would be reversible for

$$T_f = \sqrt{T_{10} T_{20}}$$

However, this would lead to an energy

$$E = 2c \sqrt{T_{10} T_{20}} < 2c \frac{T_{10} + T_{20}}{2}$$

The energy difference

$$E = 2c \left[ \frac{T_{10} + T_{20}}{2} - \sqrt{T_{10} T_{20}} \right]$$

had to be spent as work. This can be accomplished by a thermodynamic engine (Wärmekraftmaschine).

How much work can one get out of the system?

We consider a final temperature $T_f$:

$$\sqrt{T_{10} T_{20}} \leq T_f \leq \frac{T_{10} + T_{20}}{2}$$

This range for the final temperature is bounded by the reversible case from below (a smaller value would correspond to negative entropy change) and the completely spontaneous process without any work being done from above (a larger value would correspond to influx of work into the system, corresponding to a heat pump but not to a heat engine).
Figure 7.15: Scheme of a power plant: 1) furnace (coal, oil ...), 2.) environment (cooling tower), M) turbine, W) power line

\[ Q_1 = c \left( T_{10} - T_f \right) \quad \text{heat taken up by M} \]
\[ Q_2 = c \left( T_f - T_{20} \right) \quad \text{heat given away by M} \]
\[ W = Q_1 - Q_2 \quad \text{work done by the system} \]

The lower \( T_f \) the more work we can get out of our machine. Work is produced by ‘slowing down’ the heat exchange.

We consider the two extreme cases:

1. \( T_f = \frac{1}{2} \left( T_{10} + T_{20} \right) \)
   no work, maximal entropy production (compare gas expansion to vacuum)

2. \( T_f = \sqrt{T_{10} T_{20}} \)
   maximal work, reversible process (compare gas expansion under quasi-static pressure changes)

We note that producing entropy is a waste of work.

We define a thermodynamic efficiency (‘Wirkungsgrad’):

\[ \eta := \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1} \]

For case 1 we get:

\[ \eta = 1 - \frac{Q_2}{Q_1} = 0 \]

\( Q_2 = 0 \) would describe a perpetuum mobile of the second kind which cannot exist. This is due to a negative entropy change for the furnace system which violates the second law of thermodynamics:
\[ \Delta S = -\frac{Q_1}{T_1} \]

As it always takes two to tango: Heat flow away from system 1 requires heat uptake by a second system to ensure \( dS \geq 0 \).

\[ \Rightarrow \quad dS = -\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} \geq 0 \]

\[ \Rightarrow \quad dQ_2 \geq dQ_1 \frac{T_2}{T_1} \quad \text{lower bound for } Q_2 \]

\[ \Rightarrow \quad \eta = 1 - \frac{Q_2}{Q_1} \leq 1 - \frac{T_2}{T_1} = \eta_{\text{ideal}} \]

No thermodynamic engine can be more efficient than \( \eta_{\text{ideal}} \).

**Maxwell demon**

The following thought experiment has been suggested for a perpetuum mobile of the second kind and goes back to Maxwell (1867). A device (‘Maxwell demon’) (see 7.16) opens a little trapdoor each time a gas molecule comes from the right (‘ratchet mechanism’). Then pressure raises on the left, which can be used to extract work. This also cools the system, which is compensated by heat flux from the environment. In this way, the device can produce work out of heat, seemingly violating the second law.

This and many other similar setups have been analyzed by many researchers. Feynman argued that it cannot work because the device itself will fluctuate (‘trembling demon’). Landauer built his argumentation on the need for storing information, thereby raising entropy.

When analyzing the thermodynamic engine, we assumed that M does not store heat or work. This is certainly true for a machine working in a cyclic manner. How can one construct such a thermodynamic engine in practice?

**Carnot cycle**

The Carnot cycle[7.17] uses an ideal gas and four steps.

1. The gas is in contact with a hot reservoir and isothermally expanded. Entropy increases while energy is constant. Heat is taken up and work is delivered.

2. The gas is adiabatically expanded. Entropy is constant, more work is delivered.
The gas is contacted with a cold reservoir and isothermally contracted. Work is consumed by the system, entropy decreases and heat is given to the reservoir.

The gas is adiabatically contracted. Entropy is constant, more work is consumed.

The grey area in the S-T-diagram is the heat delivered to the outside. The grey area in the V-p-diagram is the work delivered. The thermodynamic efficiency can be shown to be:

\[
\eta = \frac{W}{Q_{AB}} = 1 - \frac{T_2}{T_1} = \eta_{ideal}
\]

Because the Carnot cycle is reversible, it can also be used in the other direction. Then we use work to transfer heat from the cold to the hot reservoir (‘heat pump’ or ‘refrigeration’).
For a power plant we typically have:

\[ T_1 = 540 \, ^\circ C = 813 \, K \]
\[ T_2 = 40 \, ^\circ C = 313 \, K \]

\[ \Rightarrow \eta_{\text{ideal}} = 62\% \]

In practice one can reach around 45\% which corresponds to 5 kWh output energy from 1 l of oil.

Heat production is unavoidable but can be used for heating (‘Wärmekraftkopplung’).

### 7.9 Chemical reactions

Chemical reactions are the basis of (bio)chemistry and the law of mass action is at the heart of any chemical reaction. Here we show how this important law emerges from thermodynamics. As a specific example, we consider the decomposition of water:

\[ H_2O \leftrightarrow H_2 + \frac{1}{2}O_2 \]

Often such reactions occur in the gas phase at constant temperature \( T \) and constant pressure \( p \). Therefore the relevant TD-potential is the Gibbs free energy \( G(T, p, N_i) = E - TS + pV \). The index \( 1 \leq i \leq r \) is used to number the \( r \) different components of the reaction mixture. The internal energy \( E = TS - pV + \sum \mu_i N_i \). After the Legendre transform we therefore have the fundamental equation

\[ dG = -SdT + Vdp + \sum \mu_i dN_i \]

At equilibrium, \( dG = 0 = \sum \mu_i dN_i \) at constant \( T \) and \( p \). From our example reaction above we see that the mole numbers change only in fixed proportions, namely -1 : +1 : +1/2 for water, hydrogen and oxygen in this special case. In general we write

\[ 0 = \sum v_i A_i \]

where the \( v_i \) are the stoichiometric coefficients and the \( A_i \) are the symbols for the chemical components. In the example, \( v_i = (-1, +1, +1/2) \). We now note that

\[ \frac{dN_i}{v_i} = \text{const} = dN \]

and therefore the requirement \( dG = 0 \) becomes

\[ \sum \mu_i v_i = 0 \]

The essential aspect here is that we have effectively only one reaction coordinate over which we can minimize \( G \). Our result is completely general and allows to determine the
mole numbers at equilibrium given the initial mole numbers, the relations \( \mu_i(T, p, N_i) \), \( T \) and \( p \).

We now apply this result to a mixture of ideal gases. Before we do this, however, we make some general comments on these systems. Because the different species do not interact, for each of them we have for the internal energy

\[
E_i = \frac{3}{2} N_i k_B T \Rightarrow E = \sum E_i = \frac{3}{2} (\sum N_i) k_B T = \frac{3}{2} N k_B T
\]

where for simplicity we have used the factor \( 3/2 \) for a monoatomic ideal gas. We conclude that the internal energy is the same as the one for an ideal gas of \( N \) molecules.

We next turn to entropy which for one species can be written as

\[
S_i = N_i s_i 0 + N_i k_B \ln \left( \frac{T}{T_0} \right)^{3/2} \frac{V}{V_0} \frac{N_i}{N} \\
\Rightarrow S = \sum S_i = \sum N_i s_i 0 + \left( \sum N_i \right) \frac{3}{2} k_B \ln \left( \frac{T}{T_0} \right) + \sum N_i k_B \ln \left( \frac{V}{V_0} \frac{N_0}{N_i} \right) \\
= \sum N_i s_i 0 + \frac{3}{2} N k_B \ln \left( \frac{T}{T_0} \right) + N k_B \ln \left( \frac{V}{V_0} \frac{N_0}{N} \right) - N k_B \sum x_i \ln x_i
\]

where \( x_i = N_i / N \) is the mole fraction of species \( i \). The last term is the entropy of mixing. If a collection of separate gases each at the same temperature \( T \) and the same density \( \rho = N/V \) (or, equivalently, at the same pressure \( P \)) is allowed to mix, then it will gain entropy because the mole fractions obey \( 0 \leq x_i \leq 1 \) and therefore the entropy gain will be positive.

We are now ready to discuss the chemical reactions again. From the discussion of mixtures, we understand that the chemical potentials are simply the ones of the separate gases:

\[
\mu_i = k_B T \ln \left( \frac{N_i \lambda^3}{V} \right)
\]

where the thermal wavelength \( \lambda \sim T^{-1/2} \). We rewrite this equation as

\[
\mu_i = k_B T \ln \left( \frac{N_i \lambda^3 N}{V \ N} \right) = k_B T [\phi_i(T) + \ln p + \ln x_i]
\]

using the ideal gas law. Here \( \phi_i(T) \) is a function of \( T \) only. We insert these relations into the general result \( \sum \mu_i \nu_i = 0 \):

\[
\sum \nu_i \ln x_i = - (\sum \nu_i) \ln p - \sum \nu_i \phi_i(T)
\]

We define the last term as \( \ln K(T) \) where \( K(T) \) is called the equilibrium constant. After exponentiation we then have

\[
\prod x_i^{\nu_i} = p^{-\sum \nu_i \phi_i(T)} = K(p, T)
\]

This is the famous law of mass action. One the right we have a product of mole fractions and on the right we have a constant that depends on \( T \) and \( p \). If one wants to suppress the pressure-dependance, one can write \( K(T, p) \) for the complete right hand side.
Example

We now discuss the dissociation of water from above as an instructive example for the kind of calculations done with the law of mass action. As initial conditions we take 2 moles of water. We take $p = 1MPa$ and $T = 2000K$. Then the equilibrium constant $K(T) = 0.088Pa^{1/2}$. The law of mass action now reads

$$\frac{x_{H_2}x_{O_2}^{1/2}}{x_{H_2}O} = p^{-1/2}K(T)$$

To solve this scalar equation, we have to introduce a reaction coordinate $\Delta N$. Then

$$N_{H_2O} = 2 - \Delta N, \ N_{H_2} = \Delta N, \ N_{O_2} = \Delta N/2$$

and thus

$$x_{H_2O} = \frac{2 - \Delta N}{2 + \Delta N/2}, \ x_{H_2} = \frac{\Delta N}{2 + \Delta N/2}, \ x_{O_2} = \frac{\Delta N/2}{2 + \Delta N/2}$$

If we insert this into the law of mass action, we get a polynomial equation that we cannot solve easily:

$$\frac{(\Delta N)^{3/2}}{\sqrt{2}(2 - \Delta N)(2 + \Delta N/2)^{1/2}} = p^{-1/2}K(T)$$

A numerical solution however is easy to get:

$$x_{H_2O} = 0.996, \ x_{H_2} = 0.003, \ x_{O_2} = 0.001$$

Thus the reaction is very much on the side of the water. Decreasing pressure pushes it slightly away from there, but not much. In fact this reaction has $\Delta G_0 = +237kJ/mol$ and therefore does not occur spontaneously.

Mass action kinetics

In (bio)chemistry, one often wants to understand also the time-dependance of the chemical reaction. If the reaction is determined mainly by collisions, then this is easy. Consider the bimolecular reaction

$$A + B \rightleftharpoons C$$

with a forward rate constant $k_+$ (also called on-rate or association rate) and a backward rate constant $k_-$ (also called off-rate or dissociation rate). Assuming a homogeneous mixture (no spatial effects), we write the ordinary differential equation

$$\frac{dA}{dt} = k_-C - k_+AB$$

The gain term results from a simple "radioactive" decay and the loss term results from a collision between one A- and one B-molecule. At equilibrium, $dA/dt = 0$ and therefore

$$\frac{C_{eq}}{A_{eq}B_{eq}} = \frac{k_+}{k_-} = K_A = \frac{1}{K_D}$$
where we have defined the association constant $K_A$ and its inverse, the dissociation constant $K_D$. Obviously we have recovered the law of mass action and $K_A = K(T, p)$ (except for the different dimensions, here we use concentrations and above we used mole fractions for the left hand side). Note that the dimensions of $k_-$ and $k_+$ are $1/s$ and $1/(\text{smol})$, respectively, such that the dimension of $K_D$ is $\text{mol}$.

We next note that $A + C = \text{const} = A_0$ and therefore we have

$$K_D = \frac{(A_0 - C_{eq})B_{eq}}{C_{eq}} \Rightarrow C_{eq} = A_0 \frac{B_{eq}}{K_D + B_{eq}}$$

Interestingly, this law has the same form as the Langmuir isotherm discussed with the grandcanonical ensemble (number of adsorbed particles as a function of pressure). We conclude that we reach half binding ($C_{eq} = A_0/2$) if $B_{eq} = K_D$. Therefore $K_D$ is a measure for how strong the two partners react: the smaller $K_D$, the weaker dissociation compared to association and the less $B_{eq}$ is required to achieve the same amount of binding (high affinity).

It is important to note that thermodynamics (the law of mass action) only makes a equilibrium statement and that mass action kinetics is only valid if the reaction is determined mainly be collisions. In fact this argument might not work at all if the reaction in addition has to cross some transition state barrier which slows down the time for reaction. The law of mass action connecting the initial and final states would still be valid, but the time for this process to occur might be very large. In such cases, one typically looks for catalysts to speed up the reaction (e.g. iron in the case of the famous Haber-Bosch-synthesis of ammonia, which in addition uses very high pressure; living systems have evolved enzymes for this purpose).

A small value of $K_D$ also means that there is a large gain in Gibbs free energy $G$ during the course of the reaction. For one mole of ideal gas, we have

$$G_i = G_{i0}(T, p) + RT \ln x_i \Rightarrow \Delta G = \sum \nu_i G_i = \Delta G_0 + RT \ln (\prod x_i^{\nu_i}) = \Delta G_0 + RT \ln K$$

At equilibrium, $\Delta G = 0$ and therefore

$$\Delta G_0 = RT \ln K_D , K_D = e^{\Delta G_0/RT}$$

The more negative $\Delta G_0$, the smaller $K_D$ and the stronger the reaction is driven to the right.

Living systems have singled out a few central biochemical reactions that have a very high gain in Gibbs free energy and therefore those are used to drive other reactions. The two most important examples are:

1. oxidation of food (glucose): $C_6H_{12}O_6 + 6O_2 \rightleftharpoons 6CO_2 + 6H_2O$ has $\Delta G_0 = -2890$ kJ/mol.

   This is the gradient which essentially drives our metabolism. If you use divide by Avogadro’s number and the usual value for $k_B T$, you see that this free energy gain is around 1000 $k_B T$ per molecule, which is huge and only possible because glucose is a complicated molecule with many bonds. In fact metabolism uses many
enzymes to completely digest glucose (part of this is the famous Krebs cycle) and
to get as much free energy out of it as possible.

ATP-hydrolysis: \( ATP \rightleftharpoons ADP + P_i \) has \( \Delta G_0 = -35 \text{kJ/mol} \). Per molecule, this is around \( 10 \, k_B T \), which is a large amount for such a small molecule in which basically only one bond is cleaved. As this was not enough, nature makes sure that this reaction is very favorable by additionally keeping the relevant concentrations out of equilibrium: with \( ATP = P_i = mM \) and \( ADP = 10 \mu M \), we have

\[
\Delta G = \Delta G_0 + RT \ln \frac{ADP \, P_i}{ATP \, 1M} = -60 \text{kJ/mol}
\]

thus the reaction becomes even more favorable (here \( 1M \) is used as reference concentration). ATP-hydrolysis drives many processes in our cells, including the movement of our muscle.
8 Dynamics

We consider the simplest case: a spherical particle in aqueous solution (compare Fig. 8.1). Collisions with the water molecules keep it in continuous motion. Obviously this is an effect of finite temperature. How can we describe this ‘Brownian motion’?

Figure 8.1: A spherical particle of radius \( R \) in a fluid with viscosity \( \eta \) and temperature \( T \) is performing a ‘Brownian random walk’.

For simplicity we work in one dimension. Newton’s second law yields a differential equation:

\[
\begin{align*}
\frac{m \ddot{x}}{\text{inertial force}} &= m \dot{v} = -\xi v \\
\frac{\text{friction force}}{} &= -\xi v
\end{align*}
\]

where \( \xi \) is the friction coefficient. The solution to the equation describes an exponential decay:

\[
v(t) = v_0 e^{-t/t_0} \quad \text{with} \quad t_0 = \frac{m}{\xi}
\]

and hence over time the particle comes to rest, which is not what we observe.

By adding a random force continuously kicking the particle we arrive at the ‘Langevin equation’:

\[
m \dot{v} = -\xi v + \sigma \eta(t)
\]

\( \sigma \) is the amplitude of the thermal noise and \( \eta \) describes Gaussian white noise which obeys:

1. \( \langle \eta(t) \rangle = 0 \)
2. \( \langle \eta(t) \eta(t') \rangle = 2\delta(t-t') \)
The formal solution is given by:

\[ v(t) = e^{-t/t_0} \left( v_0 + \int_0^t ds \, e^{s/t_0} \frac{\sigma}{m} \eta(s) \right) \]

⇒ \[ \langle v(t) \rangle = v_0 e^{-t/t_0} \]

\[ \langle v(t)v(t') \rangle = v_0^2 e^{-|t-t'|/t_0} + \left( \frac{\sigma}{m} \right)^2 \int_0^t ds \int_0^{t'} ds' e^{-|s-s'|/t_0} 2\delta(s-s') \]

= \[ e^{-t/t_0} \left( v_0^2 - \frac{\sigma^2}{m\xi} \right) + \frac{\sigma^2}{m\xi} e^{(t'-t)/t_0} \]

⇒ \[ \langle v(t)^2 \rangle = \frac{\sigma^2}{m\xi} \]

The random kicks from the environment keep the particle in motion.

Equipartition theorem:

\[ \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} k_B T \]

⇒ \[ \sigma^2 = \xi k_B T \]

fluctuation-dissipation theorem

The noise amplitude \( \sigma \) (fluctuations) is related to the friction coefficient (dissipation) through temperature. The higher \( T \), the stronger the noise.

For \( t \gg t_0 \), we can neglect inertia:

⇒ \[ \xi \dot{v} = \sigma \eta(t) = \xi \dot{x} \]

⇒ \[ x(t) = x_0 + \frac{1}{\xi} \int_0^t dt' \sigma \eta(t') \]

⇒ \[ \langle x(t) \rangle = x_0 \]

\[ \langle (x(t) - x_0)^2 \rangle = \frac{1}{\xi^2} \int_0^t dt' \int_0^t dt'' 2\sigma^2 \delta(t' - t'') \]

= \[ \frac{1}{\xi^2} 2\sigma^2 t = 2Dt \]

Here we identified the diffusion constant \( D \) from the one dimensional random walk.

⇒ \[ D = \frac{\sigma^2}{\xi^2} = \frac{k_B T}{\xi} \]

Einstein relation
If we use for the friction coefficient Stoke’s law from hydrodynamics, \( \zeta = 6\pi \eta R \) with viscosity \( \eta \) we get:

\[
D = \frac{k_B T}{6\pi \eta R}
\]

Stokes-Einstein relation

The Langevin equation is a ‘stochastic differential equation’ and requires ‘stochastic calculus’. Alternatively one can derive an equation for the probability \( p(x,t) \) to be at position \( x \) at time \( t \) starting from the Langevin equation:

\[
\xi \dot{x} = F(x) + \sigma \eta(t)
\]

\[
\Rightarrow \dot{p}(x,t) = -\frac{1}{\xi} \partial_x (F(x)p(x,t)) + D \partial^2_x p(x,t)
\]

This is the Fokker-Planck or Smoluchowski equation. It can be written as a continuity equation

\[
\dot{p} + \partial_x J = 0
\]

with probability current

\[
J = \frac{1}{\xi} Fp - D \partial_x p
\]

In the case of detailed balance:

\[
J = 0
\]

\[
\Rightarrow \frac{1}{\xi} Fp = D \partial_x p
\]

\[
\Rightarrow \frac{\partial_x p}{p} = \partial_x \ln p = \frac{F}{\xi D}
\]

\[
\Rightarrow p = p_0 e^{\int \frac{dx}{\xi D}} = p_0 e^{-\frac{V}{\xi D}}
\]

\[
= p_0 e^{-\beta V}
\]

Here we used the definition \( F = -V' \) of the potential in the second and the Einstein relation in the last step.

We note that the Boltzmann distribution arises as stationary solution of the Fokker-Planck equation.
9 Appendix

9.1 Useful relations between partial derivatives

The following relations are the basis for many more useful thermodynamical results. Consider the implicit relation

\[ f = f(x, y) = \text{const} \]

\[ \Rightarrow \quad df = \frac{\partial f}{\partial x} \bigg|_y \, dx + \frac{\partial f}{\partial y} \bigg|_x \, dy = 0 \]

\[ \Rightarrow \quad \frac{\partial y}{\partial x} \bigg|_f = -\frac{\frac{\partial f}{\partial x}}{\frac{\partial f}{\partial y}} \bigg|_x \]
\[ \frac{\partial x}{\partial y} \bigg|_f = -\frac{\frac{\partial f}{\partial y}}{\frac{\partial f}{\partial x}} \bigg|_x \]

\[ \Rightarrow \quad \frac{\partial x}{\partial y} \bigg|_f = \frac{1}{\frac{\partial y}{\partial x}} \bigg|_f \]

Now consider \( x \) and \( y \) to be a function of a variable \( u \):

\[ \frac{df}{du} = \frac{\partial f}{\partial x} \bigg|_y \, \frac{dx}{du} + \frac{\partial f}{\partial y} \bigg|_x \, \frac{dy}{du} \]

\[ \Rightarrow \quad 0 = \frac{\partial f}{\partial x} \bigg|_y \, \frac{dx}{du} \bigg|_f + \frac{\partial f}{\partial y} \bigg|_x \, \frac{dy}{du} \bigg|_f \]

\[ \Rightarrow \quad \frac{\partial y}{\partial x} \bigg|_u \bigg|_f = \frac{\partial f}{\partial x} \bigg|_y = \frac{dy}{dx} \bigg|_f \]