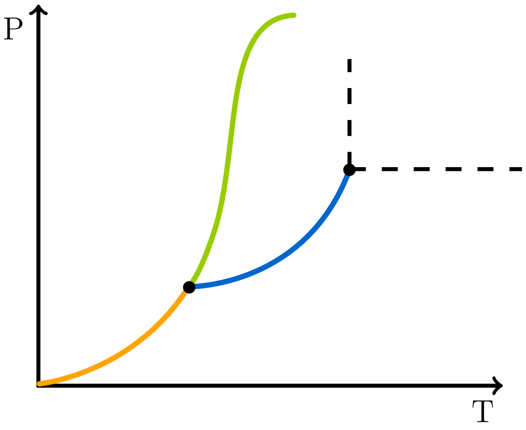
# Statistical Physics and Thermodynamics



Lecture notes

Based on the lecture held by

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# Preface

These lecture notes accompany the course *Statistical Physics and Thermodynamics* taught by Prof. Dr. Roland Netz at the Department of Physics, Freie Universität Berlin.

The document is based on a continuously developed collection of material from previous editions of the lecture. Lennart Schmidt and Till Sehmer wrote up notes in German language when Professor Netz held the lecture at Technische Universität München in 2009. At FU, Martin Borchert turned his own notes from the 2016 lecture into a document that was revised by Professor Netz, Philip Loche, Jan Daldrop, and Douwe Bonthuis in the following years. The present fully revised edition builds on this work and combines it with Professor Netz's more recent hand-written notes as well as personal notes from the 2017 and 2018 lectures.

Although these lecture notes (+ problem sets) cover the content of the course, they are not meant to substitute a monograph. Recommended literature for the lecture includes:

- R.K. Pathria, *Statistical Mechanics* (Butterworth Heinemann 1996)
- F. Schwabl, *Statistical Mechanics* (2nd ed., Springer 2006)
- F. Reif, *Fundamentals of statistical and thermal physics* (McGraw-Hill 1965)
- W. Nolting, *Grundkurs theoretische Physik 6: Statistische Physik* (Springer 2005)

If you find any errors, please help improving these notes and send an email to `rnetz@physik.fu-berlin.de`.

Please contact Professor Netz about questions regarding distribution rights of this document to people outside of the Physics Department and/or any use beyond the course.

We very much hope these lecture notes will prove helpful for your studies, your understanding of and curiosity for *Stat Mech*. Enjoy the course!

# Contents

# 1 Introduction

One mole of a substance contains $N_A \approx 6.022 \cdot 10^{23}$ particles[1]. This corresponds to 12 grams of carbon $^{12}$C or about 2 to 100 grams of a gas, depending on its type. At room temperature and atmospheric pressure, 1 mol of a gas takes up a volume of approximately 24.6 liters. Knowing that even the three-body problem does not possess a general closed-form solution, it seems hopelessly complicated to calculate properties of a system of this size. However, we will see in the course of this lecture that large systems are particularly amenable to statistical treatment. In the regime of the thermodynamic limit, where the particle number $N \to \infty$, things can in fact become easier – as long as we are only interested in statistical properties of the system as a whole. This is the central motivation behind Statistical Physics and Thermodynamics.

## 1.1 Objective of Statistical Physics and Thermodynamics

The fields of Statistical Physics and Thermodynamics are concerned with physical systems containing a large number of particles. Examples include gases, liquids, solids, and photon gases. In fact, most systems are large; isolated particles rarely occur.

The key objective of Statistical Physics (or Statistical Mechanics, SM) is to predict the behavior of a large system based on known properties of the individual particles and their interactions. In principle, we can write down the equations of motion of an $N$-particle system. Solving this problem, however, is difficult or impossible. Furthermore, the solution would not be very interesting because we could not test its details experimentally. From an experimental perspective, we are interested in *macroscopic* parameters like temperature, pressure, heat capacity, etc. Statistical Mechanics aims at deriving these macroscopic parameters from *microscopic* properties of the system.

Conversely, Thermodynamics (ThD) states relations between macroscopic quantities without considering microscopic details. These relations result from the *laws of Thermodynamics*, a set of heuristic rules that have been deduced and generalized from experimental findings. While these laws are very general, allowing various predictions of a system's behavior regardless of its particular composition, they fail to yield substance-specific properties like heat capacity, compressibility or the expansion coefficient.

## 1.2 A brief history

Historically, Thermodynamics was developed earlier than Statistical Mechanics and even before scientists understood the atomic structure of matter. The idea of the equivalence

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[1] 1 mol is defined as the amount of substance containing exactly $N_A$ elementary entities (atoms, molecules, ...), where $N_A$ is the Avogadro constant.

of heat and energy (Mayer 1842, Joule 1849) marked an important milestone. The laws of Thermodynamics were formulated by Clausius and Kelvin around 1850; Gibbs completed their work in 1878. The theory of Statistical Mechanics was developed mainly by Boltzmann and Gibbs between 1860 and 1900. With the emergence of Quantum Mechanics, many results of Statistical Mechanics were modified; yet the original framework remains valid today.

In this lecture, we will not follow the historical path but instead focus on deriving thermodynamic results from the theory of Statistical Mechanics.

## 1.3 Systems and equilibrium

We distinguish between three types of idealized systems.

- **Isolated system.** A system that is completely isolated from the surrounding environment, i.e. it exchanges neither energy nor particles with the environment. (Example: hot coffee in a closed thermos bottle.)
- **Closed system.** A system that may exchange energy but not particles with its environment. (Example: hot coffee in a closed glass jar.)
- **Open system.** A system that may exchange both energy and particles with the surrounding environment. (Example: hot coffee in an open cup.)

In reality, even the best thermos bottle exchanges some energy and some particles with the outside world. The isolated system and the closed system are idealizations that serve merely as approximations of real-world systems.

**Equilibrium.** A system is said to be in *equilibrium* when none of the macroscopic parameters of the system change in time. Systems that are not in equilibrium will change their macroscopic properties until eventually reaching an equilibrium state.

*Example 1.1.* **Tea with sugar**

Imagine you add a cube of sugar to your hot tea. When the cube dissolves, it initially forms a layer at the bottom of the tea cup, leading to an inhomogeneous sugar concentration. After a while, the sugar is completely dissolved and homogeneously distributed in the tea.

Equilibrium states are significantly easier to describe than non-equilibrium states. This lecture will mainly restrict itself to the former case. Transitions between two equilibrium states may be interpreted as a quasi-continuous concatenation of equilibrium states, as long as the transition process is sufficiently slow.

*Example 1.2.* **Quasi-static compression**

Consider the compression of a gas in a cylinder with a moveable piston. As long as the piston motion is slow enough, the density distribution of the gas inside the cylinder is homogeneous and the gas pressure corresponds to the equilibrium pressure at all times.

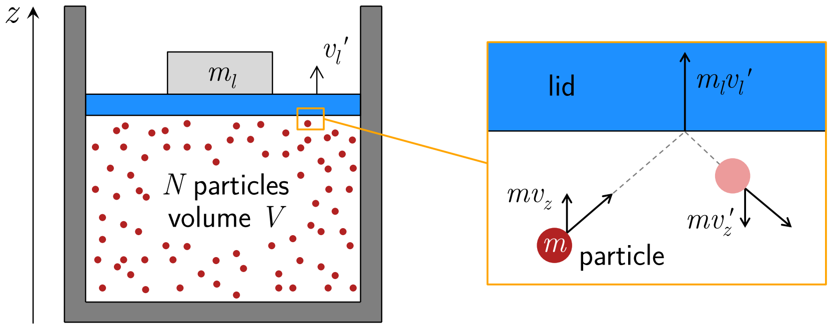


**Figure 1.1: Gas in a container with moveable lid.** Left: $N$ particles of an ideal gas are confined in a container of volume $V$ which is sealed with a moveable lid of mass $m_l$. Right: Illustration of the scattering process. A particle with mass $m$ and vertical velocity $v_z$ collides elastically with the lid ($m \ll m_l$). After the collision, the particle has a vertical velocity of $v_z{}' = -v_z$; the momentum transfer to the lid is $m_l v_l{}' = 2 m v_z$.

## 1.4 Introductory example: The Boyle-Mariotte law

Before diving into the theory, let us look at a simple example that illuminates how Statistical Mechanics works. To do this we only need Newton's laws and a bit of statistics.

Consider an ideal gas composed of $N$ non-interacting identical mass points (particles), confined in a container of volume $V$. The container is sealed by a lid of surface area $A$ that may move up and down in the $z$ direction due to an external force (see fig. 1.1). The lid, with a weight of mass $m_l$, experiences a downwards-oriented gravitational force $F$. In equilibrium, this force is compensated by the pressure $P = F/A$ the gas exerts on the lid from below. The pressure results from the elastic scattering of particles against the bottom surface of the lid.

During each elastic collision, momentum and energy must be conserved. We assume that before the collision, the lid is at rest. Let $m$ be the mass of a particle, $v$ its velocity before the collision, and $v'$ its velocity after the collision. Furthermore, we denote by $v_l{}'$ the velocity (in the $z$ direction) of the lid after the collision. Conservation of momentum and energy requires

$$\begin{aligned} m v_z &= m v_z{}' + m_l v_l{}' \\ \frac{m v_z{}^2}{2} &= \frac{m v_z{}'^2}{2} + \frac{m_l v_l{}'^2}{2} \ , \end{aligned} \tag{1.1}$$

where $v_z$ represents the $z$ component of the particle velocity (normal to the lid surface $A$; components parallel to the lid surface are not relevant). The first line of eq. (1.1) can be rewritten as

$$m v_z{}'^2 = \frac{1}{m} \left( m v_z - m_l v_l{}' \right)^2 \ .$$

Inserting this into the second line of eq. (1.1) yields

$$m_l v_l{}' = \frac{2 m v_z}{1 + \frac{m}{m_l}} \ . \tag{1.2}$$

If the lid is much heavier than the particle ($\frac{m}{m_l} \to 0$), the momentum transfer from the particle to the lid becomes

$$m_l v_l{}' = 2 m v_z \ . \tag{1.3}$$

According to Newtonian mechanics, the force acting on the lid equals the time derivative of its momentum. To compute the total force $F$ exerted by the gas, we must find out how many particles collide with the lid in a certain time interval $\Delta t$. The vertical distance a particle travels during this time is $\Delta z = v_z \Delta t$. Assuming that half of the particles move upwards ($v_z > 0$) while the other half moves downwards ($v_z < 0$), the probability that a particle in the volume $V_{\text{coll}} = A v_z \Delta t$ collides with the lid is $p = 1/2$. Particles outside $V_{\text{coll}}$ will not reach the lid during the time interval $\Delta t$. Thus, the number $N_{\text{coll}}$ of particles colliding with the lid during $\Delta t$ is

$$N_{\text{coll}} = \frac{1}{2} \rho A v_z \Delta t \ ,$$

where $\rho := N/V$ denotes the particle density. The force $F$, given by the total momentum transfer per time, reads

$$\begin{aligned} F &= \frac{N_{\text{coll}} \cdot m_l v_l{}'}{\Delta t} \\ &= \rho A m v_z^2 \ , \end{aligned} \tag{1.4}$$

where we have used eq. (1.3). This leads to a gas pressure $P = F/A$ of

$$P = \frac{N}{V} m v_z^2 \ . \tag{1.5}$$

Actually, particles in a gas follow a continuous velocity *distribution* and the pressure $P$ should depend on the average of the squared velocity $\langle v_z^2 \rangle$ (more on statistical distributions follows in chapter 2). Thermal particle motion in a gas has no preferred direction, i.e. $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$ and the average kinetic energy $\langle E_{\text{kin}} \rangle$ is given by

$$\begin{aligned} \langle E_{\text{kin}} \rangle &= \frac{m}{2} \left\langle v_x^2 + v_y^2 + v_z^2 \right\rangle \\ &= \frac{3m}{2} \left\langle v_z^2 \right\rangle \ . \end{aligned} \tag{1.6}$$

With eq. (1.6), we may write the pressure (eq. (1.5)) as

$$P = \frac{2}{3} \frac{N}{V} \langle E_{\text{kin}} \rangle \ . \tag{1.7}$$

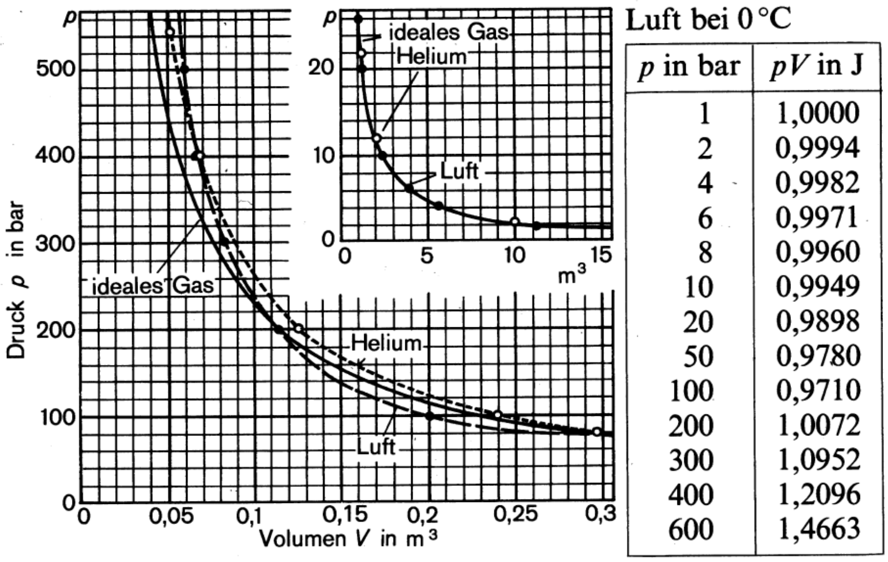
This agrees with the experimentally known result that the pressure of a gas is inversely proportional to its volume,

$$\boxed{P \propto \frac{1}{V}}, \tag{1.8}$$

which is referred to as the Boyle-Mariotte law.

Experiments have shown that the product $PV$ is constant at constant temperature $T$ (for sufficiently low pressure, see fig. 1.2). This holds independently of the type of gas and is thus independent of the particle mass $m$; we will see later why this is the case. At the same time, the temperature relates closely to the average kinetic energy $\langle E_{\text{kin}} \rangle$. Indeed, as we will derive in chapter 3, we may define the temperature of a mono-atomic gas as

$$T := \frac{2}{3} \frac{\langle E_{\text{kin}} \rangle}{k_B} \ . \tag{1.9}$$



Luft bei 0 °C

| $p$ in bar | $pV$ in J |
|---|---|
| 1 | 1,0000 |
| 2 | 0,9994 |
| 4 | 0,9982 |
| 6 | 0,9971 |
| 8 | 0,9960 |
| 10 | 0,9949 |
| 20 | 0,9898 |
| 50 | 0,9780 |
| 100 | 0,9710 |
| 200 | 1,0072 |
| 300 | 1,0952 |
| 400 | 1,2096 |
| 600 | 1,4663 |

**Figure 1.2:** Pressure of ideal and real (air and helium) gases at constant temperature 0°C. Data in the figure are for one kmol of gas. The table is for an amount of air that at 0°C and normal pressure of 1 bar has a volume of 10 cm$^3$. Up to pressures of ca. 10 bar the ideal gas law works well. For higher pressures interactions between gas molecules give rise to corrections that can be treated by the virial expansion.

Here, $k_B$ denotes the Boltzmann constant. Its value $k_B \approx 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$ is chosen such that water freezes at $T = 273.15\,\mathrm{K}$ (0°C) and boils at $T = 373.15\,\mathrm{K}$ (100°C). The Boltzmann constant serves the purpose of aligning the thermodynamic temperature scale (in units of Kelvin) with the Celsius scale; it is *not* a natural constant.

Now, we may invoke eq. (1.9) to replace the average kinetic energy in eq. (1.7) with the temperature, leading to the ideal gas law:

$$\boxed{PV = Nk_BT} \tag{1.10}$$

Fig. 1.2 shows that even real gases with particle-particle interaction follow the ideal gas law for pressures up to 10 bar. We will return to the ideal gas in sec. 3.6.

**Velocity of gas particles.** In the derivation above, the average squared velocity $\langle v^2 \rangle = \langle v_x^2 + v_y^2 + v_z^2 \rangle$ of gas particles appeared. How fast are gas molecules actually, say, of molecular Hydrogen $H_2$ or Oxygen $O_2$? Equations (1.6) and (1.9) yield an expression for the average velocity $\bar{v}$ in terms of temperature as well as the particle mass $m$:

$$\bar{v} := \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_BT}{m}} \,. \tag{1.11}$$

At $T = 273\mathrm{K}$, we find

$$\begin{array}{llll} \text{for Hydrogen:} & m_{\mathrm{H}_2} \approx \phantom{3}2 \cdot 1.661 \times 10^{-27}\,\mathrm{kg} & \Rightarrow & \bar{v} \approx 1800\,\mathrm{m\,s^{-1}} \\ \text{for Oxygen:} & m_{\mathrm{O}_2} \approx 32 \cdot 1.661 \times 10^{-27}\,\mathrm{kg} & \Rightarrow & \bar{v} \approx 460\,\mathrm{m\,s^{-1}} \,. \end{array}$$

Hence gas molecules move quite fast! Furthermore, the relation between temperature and average kinetic energy,

$$\langle E_{\mathrm{kin}} \rangle = \frac{3}{2} k_B T \,,$$

implies the existence of *absolute zero*: a minimum value ($T = 0\,\mathrm{K}$) of the thermodynamic temperature scale where particles do not move (according to the classical description, in disagreement with quantum mechanics).

# 2 Mathematical Statistics

In this chapter, we will establish the mathematical theory necessary to formulate Statistical Physics and illuminate some central results of mathematical statistics in the limit of a large number of experiments $N$. We begin with basic statistics, introducing the mean, variance, and deviation of a probability distribution. Furthermore, we discuss the binomial distribution. We show that in the limit of large $N$ and finite probability $p$, the binomial distribution simplifies to the normal distribution. On the other hand, if $N$ is very large but $p$ very small, we will see that the binomial distribution crosses over to the Poisson distribution. Subsequently, the characteristic function is introduced as a powerful tool to calculate moments of a probability distribution. The chapter concludes with a derivation of the important central limit theorem.

## 2.1 Probability

We demonstrate the key characteristics of a statistical description with the help of an *experiment* which we conduct $N$ times. As an *outcome*, each experiment yields an integer $m$. After $N$ repetitions the *overall outcome* is the set $\{m_i\}$ with $i = 1, \ldots, N$. The *absolute frequency* of the *event* $m$, denoted my $n(m)$, states how often the event $m$ occurred. We define the *relative frequency* $h$ of the event as

$$h(m) := \frac{n(m)}{N} \ ,$$

which is a normalized quantity such that $\sum_m h(m) = 1$.

In the limit of a large number of experiments ($N \to \infty$), the relative frequency converges to the *probability* $p$ of an event,

$$p(m) := \lim_{N\to\infty} h(m) \qquad \text{where } \sum_m p(m) = 1 \ . \tag{2.1}$$

**Addition theorem.** For mutually exclusive events, the probability of observing any of these events in an experiment is given by the sum of individual probabilities:

$$p(m_1 \vee m_2 \vee m_3 \vee \cdots) = p(m_1) + p(m_2) + p(m_3) + \cdots \ . \tag{2.2}$$

Here, the symbol ∨ means “or.”

*Example 2.1.* **Rolling a one or a two**

Imagine we roll a single die. The probability of obtaining either a 1 or a 2 is the sum of individual probabilities,

$$p(1 \vee 2) = p(1) + p(2) = \frac{1}{6} + \frac{1}{6} = \frac{1}{3} \; .$$

**Multiplication theorem.** The probability of observing two independent events simultaneously is given by the product of individual probabilities:

$$p(m_1 \wedge m_2) = p(m_1) \cdot p(m_2) \; , \tag{2.3}$$

where the symbol $\wedge$ means "and."

*Example 2.2.* **Rolling two ones**

Now we roll two dice at the same time. The probability of obtaining 1 two times is the square of the probability of observing one 1 alone,

$$p(1 \wedge 1) = p(1) \cdot p(1) = \frac{1}{6} \cdot \frac{1}{6} = \frac{1}{36} \; .$$

*Example 2.3.* **Rolling a straight**

As a slightly more complicated example, consider the chance of rolling a straight (1,2,3,4) with four dice. If we roll the dice in a specific order, the probability of first rolling 1, then 2, then 3, and then 4 is

$$p(1 \wedge 2 \wedge 3 \wedge 4) = \left(\frac{1}{6}\right)^4 = \frac{1}{1296} \approx 0.0008 \; ,$$

according to the multiplication theorem. However, also (1243) or (3142) qualify as a straight if the order of the dice does not matter. In total there exist $4! = 4 \cdot 3 \cdot 2 \cdot 1 = 24$ possibilities to arrange the numbers 1, 2, 3, and 4. Therefore, according to the addition theorem, the probability of observing any of the 24 possible arrangements of a straight is

$$p\Big([1 \wedge 2 \wedge 3 \wedge 4] \vee [1 \wedge 2 \wedge 4 \wedge 3] \vee \cdots\Big) = \frac{4!}{6^4} \approx 0.019 \; .$$

In the above example, we introduced the *factorial* of a positive integer $n$,

$$n! := n(n-1)(n-2)\cdots 2 \cdot 1 \; ,$$

which states the number of permutations (possible distinct arrangements) of $n$ distinct items.

## 2.2 Expectation value, variance, and deviation

Let $x$ be an arbitrary system variable which takes the value $x(m)$ when the system is in the state $m$. In terms of the normalized probability distribution $p(m)$, we define the *expectation value* or *mean value* $\langle x \rangle$ as

$$\langle x \rangle := \sum_m x(m) p(m) \; . \tag{2.4}$$

*Example 2.4.* **Fair die**

A fair die has a uniform probability distribution $p(m) = \frac{1}{6}$ for $m = 1, 2, \ldots, 6$. Furthermore, we assume $x(m) = m$. The expectation value of $x$ is thus

$$\langle x \rangle = \sum_{m=1}^{6} \frac{m}{6} = \frac{1+2+3+4+5+6}{6} = \frac{21}{6} = 3.5 \; .$$

To quantify deviations from the expectation value, we define the *variance* $\Delta x^2$,

$$\Delta x^2 := \left\langle \Big( x - \langle x \rangle \Big)^2 \right\rangle \; , \tag{2.5}$$

which states the mean squared deviation of $x$ from the expectation value $\langle x \rangle$. Expanding the square, we can rewrite the variance as

$$\begin{aligned} \Delta x^2 &= \left\langle x^2 - 2x \langle x \rangle + \langle x \rangle^2 \right\rangle \\ &= \langle x^2 \rangle - 2 \langle x \rangle \langle x \rangle + \langle x \rangle^2 \\ &= \langle x^2 \rangle - \langle x \rangle^2 \; . \end{aligned} \tag{2.6}$$

Thus, the variance is given in terms of the expectation values of $x$ and $x^2$. The *deviation* $\Delta x$ is defined as the square root of the variance,

$$\Delta x := \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \; . \tag{2.7}$$

*Example 2.5.* **Deviation of dice roll results**

What is the deviation of the number of pips when rolling a die? In example 2.4, we calculated the expectation value of the number of pips, $\langle x \rangle = 7/2$. Moreover, we have

$$\langle x^2 \rangle = \sum_{m=1}^{6} \frac{m^2}{6} = \frac{1+4+9+16+25+36}{6} = \frac{91}{6} \; .$$

Thus, the deviation is

$$\Delta x = \sqrt{\frac{91}{6} - \left(\frac{7}{2}\right)^2} \approx 1.7 \; .$$

## 2.3 Binomial distribution

Imagine a *random walker* in one dimension who, per unit time, takes a step upwards with probability $p$ or a step downwards with probability $q = 1 - p$. Random walks are used to model the food search of animals, fluctuations in protein configuration, diffusion processes, and many other applications in science. What is the probability that the walker, after taking $N = 5$ steps, will end up one step higher than its original starting point? The *binomial distribution* provides the answer.

To arrive one step higher after five steps, three of the walker's steps must go up, while two must go down. According to the multiplication theorem (eq. (2.3)), the probability of such a path is $p^3q^2$. However, since we disregard the order in which the walker goes up or down, there exist ten distinct paths to reach the desired final position. The number of possible paths can be found by calculating

$$10 = \frac{5!}{3! \cdot 2!} \ ,$$

where $n!$ again denotes the factorial of $n$, stating the number of possible ways to arrange $n$ distinguishable objects in a line. The denominator accounts for the fact that not all five steps are distinct: the three steps upwards (as well as the two steps downwards) are indistinguishable among each other, and exchanging them will not change the path. Consequently, the probability of taking three steps up and two steps down in an arbitrary order is $P_5(3) = 10p^3(1-p)^2$.

*Example 2.6.* **Five unbiased random steps**

If $p = 1/2$, i.e. a step up is as probable as a step down, the probability of a net upwards movement of one step after $N = 5$ steps is

$$P_5(3) = 10 \cdot \left(\frac{1}{2}\right)^5 \approx 0.3 \ .$$

Generally, if a random walker takes $N$ steps of which $m$ go upwards (and $N-m$ downwards), the total number of distinct paths is given by the *binomial coefficient*,

$$\binom{N}{m} := \frac{N!}{m!(N-m)!} \ . \tag{2.8}$$

We may think of the binomial coefficient as the number of possibilities to allocate $m$ objects to $N$ places, or to choose $m$ objects from among $N$ objects. The probability of taking $m$ steps upwards among $N$ steps in total is thus given by the *binomial distribution*

$$\boxed{P_N(m) = \binom{N}{m} p^m (1-p)^{N-m} \ .} \tag{2.9}$$

Ultimately, the binomial distribution states the probability of observing precisely $m$ single events of probability $p$ in a total of $N$ experiments. It is suitable for repeated experiments with “digital” outcome (e.g. yes/no, up/down, success/failure, one/zero).

*Example 2.7.* **Boys and girls**

The probability of a newborn child being a girl is approximately $p \approx 1/2$. Therefore, the probability that a family with three children has two girls is $P_3(2) \approx 0.375$.

*Example 2.8.* **Birthdays**

The probability of being born on New Year's Eve is $p = 1/365$ (except in leap years). This implies that the probability of having precisely one student with birth date December 31 in a Stat Mech lecture of 50 students is $P_{50}(1) \approx 0.12$.

**Expectation value.** First, let us prove that the binomial distribution is a normalized probability distribution. This is not simple when applying brute force, but invoking the $N$-th order binomial formula,

$$(p+q)^N = \sum_{m=0}^{N} \binom{N}{m} p^m q^{N-m} \ ,$$

brings us directly to the result. With $q = 1 - p$, the proof reads

$$\begin{aligned} \sum_{m=0}^{N} P_N(m) &= \sum_{m=0}^{N} \binom{N}{m} p^m (1-p)^{N-m} \\ &= (p + (1-p))^N \\ &= 1 \qquad \text{q.e.d.} \end{aligned} \tag{2.10}$$

Since the binomial distribution $P_N(m)$ is a normalized probability distribution, its expectation value (or mean) is, according to the definition in eq. (2.4),

$$\langle m \rangle = \sum_{m=0}^{N} m P_N(m) \ . \tag{2.11}$$

Now, we use the binomial formula again to obtain a simple expression for $\langle m \rangle$ in terms of $N$ and $p$:

$$\begin{aligned} \langle m \rangle &= \sum_m m P_N(m) \\ &= \sum_m m \frac{N!}{m!(N-m)!} p^m q^{N-m} \\ &\overset{*}{=} p \frac{\partial}{\partial p} \sum_m \frac{N!}{m!(N-m)!} p^m q^{N-m} \\ &\overset{**}{=} p \frac{\partial}{\partial p} (p+q)^N \\ &= pN(p+q)^{N-1} \\ &= pN \ , \end{aligned}$$

where we have used $p + q = 1$ in the final step. Note that at $*$ we rewrote the expression in terms of a partial derivative, $\langle m \rangle = p \frac{\partial}{\partial p} \sum_m P_N(m)$, to get rid of the factor $m$ in the sum. This is a trick worthy to remember, as we will use it more often in the course of this lecture. At $**$, we inserted the binomial formula. In summary, the expectation value of the binomial distribution is given by

$$\boxed{\langle m \rangle = Np \ .} \tag{2.12}$$

This result agrees with the addition theorem for independent events (sec. 2.1).

**Variance.** To find the variance, we must additionally calculate the expectation value of $m^2$. The procedure is similar to the calculation above, though with two partial derivatives this time:

$$\begin{aligned}\left\langle m^2\right\rangle &= \sum_m m^2 P_N(m)\\ &= \sum_m m^2 \frac{N!}{m!(N-m)!} p^m q^{N-m}\\ &= p\frac{\partial}{\partial p} p\frac{\partial}{\partial p}\sum_m \frac{N!}{m!(N-m)!} p^m q^{N-m}\\ &= p\frac{\partial}{\partial p} p\frac{\partial}{\partial p}(p+q)^N\\ &= p\frac{\partial}{\partial p}\left(pN(p+q)^{N-1}\right)\\ &= pN(p+q)^{N-1} + p^2N(N-1)(p+q)^{N-2}\\ &= pN + p^2N(N-1)\ ,\end{aligned}$$

where we used $p+q=1$ in the last step. Together with eq. (2.12), we have

$$\begin{aligned}\Delta m^2 &= \langle m^2\rangle - \langle m\rangle^2\\ &= pN + p^2N(N-1) - p^2N^2\\ &= pN - p^2N\ .\end{aligned}$$

Thus the variance of the binomial distribution is given by

$$\boxed{\Delta m^2 = pN(1-p)\ .} \tag{2.13}$$

**Relative Deviation.** By taking the square root of the variance (eq. (2.13)), we obtain the deviation $\Delta m$ from the mean for the binomial distribution:

$$\boxed{\Delta m = \sqrt{pN(1-p)}\ .} \tag{2.14}$$

When comparing probability distributions characterized by different expectation values, the comparison of deviations is not very meaningful unless they are put in relation to their respective mean. A standardized measure which takes this into account is the *relative deviation* $\sigma_{\text{rel}}$ defined by

$$\sigma_{\text{rel}} := \frac{\Delta m}{\langle m\rangle}\ . \tag{2.15}$$

The relative deviation quantifies the dispersion of a probability distribution relative to its mean value $\langle m\rangle$. For the binomial distribution, the relative deviation is given by

$$\boxed{\frac{\Delta m}{\langle m\rangle} = \sqrt{\frac{1-p}{pN}} \quad \sim \frac{1}{\sqrt{N}}\ .} \tag{2.16}$$

Since the relative deviation is proportional to the reciprocal of the square root of $N$, it approaches zero as $N$ gets very large:

$$\lim_{N\to\infty}\frac{\Delta m}{\langle m\rangle} = 0\ , \tag{2.17}$$

unless $p$ is very small. This important result is known as the *law of large numbers*. It justifies describing the properties of statistical systems in terms of mean values, as long as the number of experiments $N$ is sufficiently large.

*Example 2.9.* **Particle number fluctuations in a large system**

Consider $N = 10^{24}$ molecules of a gas (roughly 1 mol) in a box of volume $V$. We divide the box into two equally large sub-volumes. Then, the probability of finding $m$ out of $N$ molecules in one of the sub-volumes is given by the binomial distribution. Let us assume that a molecule is equally likely to be in either of the sub-volumes, such that $p = q = 1/2$. On average, there are $\langle m \rangle = Np = 0.5 \cdot 10^{24}$ molecules in a sub-volume. The deviation of this mean occupation number is $\Delta m = \sqrt{Npq} = \sqrt{N/4} = 0.5 \cdot 10^{12}$ (half a trillion molecules!). However, in relation to the expectation value $\langle m \rangle$, we obtain a negligible relative deviation of $\frac{\Delta m}{\langle m \rangle} = 10^{-12}$. This illustrates why Thermodynamics works: since most physical systems are very large, the probability distributions of statistical system properties have very sharp peaks (relative to the mean value).

**Rare events.** There exist situations where $N \gg 1$ is very large but the probability $p \ll 1$ is very small, such that the product $\langle m \rangle = Np$ is finite[1]. This characterizes *rare events* for which the relative deviation may in fact be large. To demonstrate this, let us consider the following example.

*Example 2.10.* **Car accidents**

The number of car trips $N$ a driver undertakes in a lifetime can arguably be very large, whereas the probability $p$ of having an accident per car ride is pretty small. For $p \ll 1$, the deviation $\Delta m$ is approximately

$$\Delta m = \sqrt{Np(1-p)} \approx \sqrt{Np} = \sqrt{\langle m \rangle} \ ,$$

where $\langle m \rangle$ gives the average number of accidents in a lifetime. Then, the relative deviation,

$$\frac{\Delta m}{\langle m \rangle} \approx \frac{1}{\sqrt{\langle m \rangle}} \ ,$$

does not become negligible for large $N$ since $\langle m \rangle$ remains finite. For example, if the mean of a rare event is $\langle m \rangle = 0.1$, the relative deviation is approximately $\frac{\Delta m}{\langle m \rangle} \approx 3$. Thus, we may expect significant deviations from the mean, which is why it is wise to insure yourself against rare events with large relative deviations!

A comparison of the binomial distribution with random walk simulations and two other important distributions is shown in figs. 2.1 and 2.2. These two distributions are the *normal distribution* and the *Poisson distribution*, which we introduce in the following sections.

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[1] Here we mean *finite* in the sense that $Np$ is not a very large number like $N$.

## 2.4 Normal distribution

We can simplify the binomial distribution (eq. (2.9)) in the limit of large $N \gg 1$, when $p$ is a finite number, such that $Np \to \infty$. Let us take the logarithm of the binomial distribution,

$$\begin{aligned}\ln P_N(m) &= \ln\left(\frac{N!}{m!(N-m)!}p^m(1-p)^{N-m}\right)\\ &= m\ln p + (N-m)\ln(1-p) + \ln(N!) - \ln(m!) - \ln((N-m)!)\ .\end{aligned} \tag{2.18}$$

This expression may be simplified using the *Stirling formula*,

$$\boxed{\ln(N!) = N\ln N - N + \mathcal{O}(\ln N)}\ . \tag{2.19}$$

To derive the formula (2.19) in a simple fashion, we first rewrite

$$\ln(N!) = \ln\left(\prod_{j=1}^{N} j\right) = \sum_{j=1}^{N}\ln j\ . \tag{2.20}$$

Since $N \gg 1$, we may approximate the sum by an integral:

$$\begin{aligned}\sum_{j=1}^{N}\ln j &\approx \int_1^N \mathrm{d}x\ln x\\ &= x\ln x - x\Big|_1^N\\ &= N\ln N - N + 1\\ \Rightarrow\quad \ln(N!) &= N\ln N - N + \mathcal{O}(\ln N)\ .\end{aligned} \tag{2.21}$$

Choosing $N$ as the upper boundary of the integral is merely an approximation, such that the formula contains an error in the order of $\ln N$. Inserting the Stirling formula (eq. (2.19)) into eq. (2.18), we obtain

$$\ln P_N(m) = m\ln p + (N-m)\ln(1-p) + N\ln N - m\ln m - (N-m)\ln(N-m)\ . \tag{2.22}$$

$P_N(m)$ has a sharp peak at $\langle m\rangle$ for large $N$, as we know from the law of large numbers. This also holds for the logarithm, $\ln P_N(m)$. We perform a Taylor expansion around the maximum $m^*$:

$$\ln P_N(m) = \ln P_N(m^*) + \frac{1}{2}(m-m^*)^2\,\frac{\mathrm{d}^2}{\mathrm{d}m^2}\ln P_N(m)\Big|_{m=m^*} + \ldots\ , \tag{2.23}$$

where $m^*$ is defined by

$$0 = \frac{\mathrm{d}}{\mathrm{d}m}\ln P_N(m)\Big|_{m=m^*}\ ,$$

such that the linear term vanishes in the expansion. At the maximum, we have

$$\begin{aligned} 0 = \frac{\mathrm{d}}{\mathrm{d}m} \ln P_N(m) &= \ln \frac{p}{1-p} + \ln \frac{N-m}{m} \\ \Rightarrow \quad \ln \frac{1-p}{p} &= \ln \frac{N-m}{m} \\ \frac{1-p}{p} &= \frac{N-m}{m} \\ \frac{1}{p} &= \frac{N}{m} \quad \Rightarrow \quad m^* = Np \ . \end{aligned} \tag{2.24}$$

Thus, the maximum $m^*$ of our approximation for $\ln P_N(m)$ coincides with the exact mean $\langle m \rangle = Np$ calculated earlier (eq. (2.12)). As we might have expected, the mean is equivalent to the most probable value in the limit of $N \to \infty$. Using this result, the second derivative reads

$$\begin{aligned} \frac{\mathrm{d}^2}{\mathrm{d}m^2} \ln P_N(m) \bigg|_{m=m^*} &= \left( -\frac{1}{m} - \frac{1}{N-m} \right) \bigg|_{m=m^*} \\ &= -\frac{1}{Np} - \frac{1}{N-Np} \\ &= -\frac{1}{Np} - \frac{1}{Nq} \\ &= -\frac{q+p}{Npq} \\ &= -\frac{1}{Npq} = -\frac{1}{\Delta m^2} \ , \end{aligned} \tag{2.25}$$

where $q = 1 - p$ and the last line follows from the result for the variance $\Delta m^2$ of the binomial distribution (eq. (2.13)). Finally, it is easily verified by inserting $m^* = Np$ into eq. (2.22) that the constant term of the Taylor expansion vanishes, $\ln P_N(m^*) = 0$. The expansion up to second order therefore reads

$$\ln P_N(m) = -\frac{(m-m^*)^2}{2\Delta m^2} + \mathcal{O}\Big(m^3\Big) \ . \tag{2.26}$$

Exponentiating both sides yields an approximation $W(m)$ of the binomial distribution,

$$W(m) \propto \exp\left( -\frac{(m - \langle m \rangle)^2}{2\Delta m^2} \right) \ , \tag{2.27}$$

where we replaced $m^*$ by $\langle m \rangle$. Note that by Taylor expanding the logarithm of the binomial distribution instead of $P_N(m)$ itself, we obtained an exponential solution for $W(m)$ that is normalizable (such that $\int_{-\infty}^{\infty} \mathrm{d}m \, W(m) = 1$), as required for a probability distribution. The normalized *normal distribution* $W(m)$ is given by

$$\boxed{W(m) = \frac{1}{\sqrt{2\pi\Delta m^2}} \exp\left( -\frac{(m - \langle m \rangle)^2}{2\Delta m^2} \right)} \ . \tag{2.28}$$

As a simplification of the binomial distribution, the normal distribution is valid in the limit of $N \to \infty$ while $p$ remains finite. It is fully determined by the mean $\langle m \rangle$ and the variance $\Delta m^2$.

## 2.5 Poisson distribution

For very large $N \gg 1$ but simultaneously $p \ll 1$, such that the product $Np$ is finite, we can simplify the binomial distribution in a different way. This case leads us to the Poisson distribution. Let us break down the binomial distribution (eq. (2.9)) into parts,

$$P_N(m) = \frac{N!}{(N-m)!}\,\frac{1}{m!}\left(\frac{p}{1-p}\right)^m (1-p)^N \; . \tag{2.29}$$

First, we approximate the factor $(1-p)^N$ by writing

$$(1-p)^N = \exp\Big[N\ln(1-p)\Big] \approx e^{-Np} \; , \tag{2.30}$$

where we have Taylor expanded the logarithm up to first order, $\ln(1+x) = x + \mathcal{O}(x^2)$. Secondly, we use $p \ll 1$ to approximate

$$\left(\frac{p}{1-p}\right)^m \approx p^m \; . \tag{2.31}$$

Lastly, we tackle the binomial coefficient:

$$\begin{aligned}
\frac{N!}{(N-m)!} &= \exp\Big[\ln(N!) - \ln((N-m)!)\Big] \\
&\overset{*}{\approx} \exp\Big[N\ln(N) - N - (N-m)\ln(N-m) + N - m\Big] \\
&= \exp\left[N\ln\left(\frac{N}{N-m}\right) + m\ln(N-m) - m\right] \\
&= \exp\left[-N\ln\left(\frac{N-m}{N}\right) + m\ln\left(\frac{N-m}{N}\right) + m\ln N - m\right] \\
&= \exp\left[-N\ln\left(1-\frac{m}{N}\right) + m\ln\left(1-\frac{m}{N}\right) + m\ln N - m\right] \\
&\overset{\dagger}{\approx} \exp\left[m + \mathcal{O}\left(\frac{m^2}{N}\right) + \mathcal{O}\left(\frac{m^2}{N}\right) + m\ln N - m\right] \\
&\approx \exp\left[m\ln N\right] = N^m \; .
\end{aligned} \tag{2.32}$$

Here we applied the Stirling formula at $*$ and used the Taylor series up to first order, $\ln(1+x) = x + \mathcal{O}(x^2)$, in the step marked by $\dagger$. Putting things together, we arrive at an approximation of the binomial distribution for finite $Np$,

$$P_N(m) \approx N^m \frac{1}{m!} p^m e^{-Np} \; . \tag{2.33}$$

For simplicity we define $\lambda := Np$. Then, the *Poisson distribution* is given by

$$\boxed{W(m) = \frac{\lambda^m}{m!}e^{-\lambda}} \; . \tag{2.34}$$

This result turns out to be normalized: using $N \to \infty$ we show

$$\sum_{m=0}^{N} W(m) \approx \sum_{m=0}^{\infty} W(m) = \sum_{m=0}^{\infty} \frac{\lambda^m}{m!}e^{-\lambda} = e^{\lambda}e^{-\lambda} = 1 \; . \tag{2.35}$$

**Expectation value.** Let us calculate the expectation value of the Poisson distribution:

$$\begin{aligned} \langle m \rangle &= \sum_{m=0}^{\infty} m W(m) \\ &= e^{-\lambda} \sum_{m=0}^{\infty} \frac{m\lambda^m}{m!} \\ &= e^{-\lambda}\, \lambda \frac{\partial}{\partial \lambda} \sum_{m=0}^{\infty} \frac{\lambda^m}{m!} \\ &= e^{-\lambda}\, \lambda \frac{\partial}{\partial \lambda} e^{\lambda} \\ &= e^{-\lambda} \lambda e^{\lambda} \\ &= \lambda \; . \end{aligned} \tag{2.36}$$

As expected, the expectation value of the Poisson distribution, $\langle m \rangle = \lambda = Np$, is identical to the expectation value of the binomial distribution.

*Example 2.11.* **Random walks on a computer**

As we discussed, the theoretical position distribution of a random walker (after a certain number of total steps) is given by the binomial distribution. Let us see how computer simulations of random walks compare to the binomial, normal, and Poisson distributions.

Figure 2.1 illustrates the simulated (dots) and theoretical (red line) probability distribution of the number of upward steps in an unbiased random walk of 20 steps. Based on a sample of 100 random walks, the results on the left reveal substantial numerical deviations from the binomial distribution due to the small sample size. Increasing the sample size to $10^4$ (right side) leads to a clearer agreement between theory and experiment. Note that for $N = 20$ steps with probability $p = 0.5$, the normal distribution (orange) is already very close to the binomial distribution. The Poisson distribution (blue), on the other hand, does not describe the data.

In fig. 2.2, we vary the number of steps $N$ and probability $p$ to demonstrate how this changes the distributions. As we move from $N = 20$ (left) to $N = 100$ steps (center) at fixed probability $p = 0.5$, the distribution becomes more sharply peaked. This agrees with our finding that the mean deviation scales as $N^{1/2}$, while the relative mean deviation scales as $N^{-1/2}$. If we keep $N$ fixed at 100 steps and reduce the probability of an upward step from $p = 0.5$ (center) to $p = 0.03$ (right), the simulation data shift from normally distributed to Poisson-distributed. In other words, the binomial distribution now resembles the Poisson distribution, whereas the normal distribution is inadequate for describing the data.

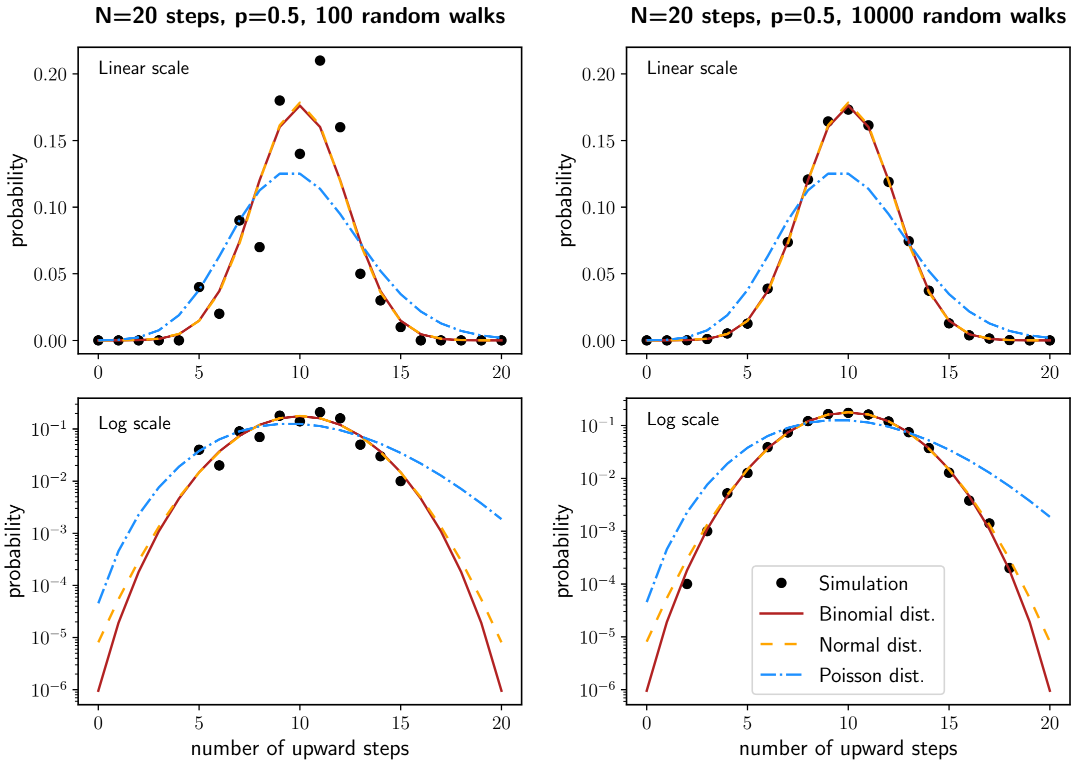

**Figure 2.1: Random walk computer simulations vs. theoretical distributions** for $N = 20$ steps and probability $p = 0.5$. The black dots in the left panels show the simulated distribution based on a sample of 100 random walks; on the right panels the sample size is $10^4$. The red, orange, and blue lines depict the binomial, normal, and Poisson distribution, respectively. *Top panels*: Linear probability scale. *Bottom*: Same information as in the top panels but on a logarithmic probability scale.

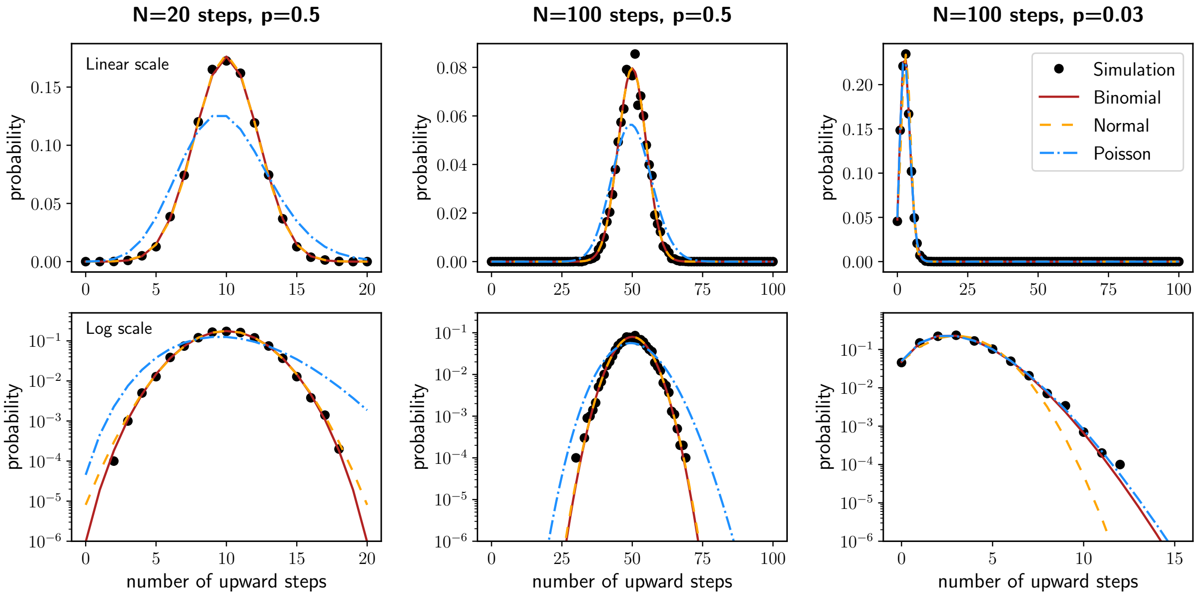

**Figure 2.2: Binomial, normal, and Poisson distributions vs. simulations** for varying number of total steps $N$ and probability $p$. *Top panels*: Linear probability scale. *Bottom*: Same information but on a logarithmic scale.

## 2.6 Continuous density distributions

Previously, we have seen two different ways of normalizing a probability distribution. The normalization of the normal distribution was carried out via integration from $-\infty$ to $\infty$, whereas we demonstrated the normalization of the Poisson distribution by means of a discrete sum over all $m$. In other words, we interpreted the normal distribution as a continuous distribution but the Poisson distribution as a discrete distribution. In this section, let us briefly address how discrete and continuous probability distributions relate.

In the continuous case, we have a continuous random variable $x$ controlled by a density distribution $p(x)$ (e.g. the normal distribution). The normalization requirement reads

$$\int_{-\infty}^{\infty} \mathrm{d}x\, p(x) = 1 \ .$$

The *moments*[2] of this density distribution are then calculated via

$$\langle x^n \rangle := \int_{-\infty}^{\infty} \mathrm{d}x\, x^n p(x) \ .$$

More generally, the expectation value of any function $f(x)$ is given by

$$\langle f \rangle := \int_{-\infty}^{\infty} \mathrm{d}x\, f(x) p(x) \ . \tag{2.37}$$

A discrete probability distribution $p_m$ may be written as a continuous density distribution $p(x)$ by summing over $\delta$-distributions representing the outcomes $x_m$, such that

$$p(x) = \sum_m p_m \delta(x - x_m) \ . \tag{2.38}$$

The $\delta$-distribution, as a reminder, is defined by its projection property,

$$\int_{-\infty}^{\infty} \mathrm{d}x\, f(x)\delta(x-y) = f(y) \ .$$

We may switch between the continuous and the discrete description of the expectation value $\langle f \rangle$ by inserting eq. (2.38) into eq. (2.37), which yields

$$\begin{aligned} \langle f \rangle &= \int_{-\infty}^{\infty} \mathrm{d}x\, f(x)p(x) \\ &= \int_{-\infty}^{\infty} \mathrm{d}x\, f(x) \sum_m p_m \delta(x - x_m) \\ &= \sum_m p_m \int_{-\infty}^{\infty} \mathrm{d}x\, f(x)\delta(x - x_m) \\ &= \sum_m p_m f(x_m) \ . \end{aligned} \tag{2.39}$$

## 2.7 Characteristic function

Let us introduce the *characteristic function* $G$,

$$G(k) := \left\langle e^{-ikx} \right\rangle = \int \mathrm{d}x\, p(x)\, e^{-ikx} \ . \tag{2.40}$$

---

[2] The $n$-th moment of the distribution $p(x)$ is defined as the expectation value $\langle x^n \rangle$. For more about moments, see section 2.7.

This is nothing but the Fourier transform of $p(x)$. As we will see, the characteristic function serves as a tool to quickly calculate moments and cumulants of a distribution.

**Moments.** The $n$-th derivative of $G(k)$ is

$$\frac{\mathrm{d}^n G(k)}{\mathrm{d}k^n} = \int \mathrm{d}x\, p(x)\, (-ix)^n\, e^{-ikx} \ .$$

Note that $n$-fold differentiation leads to a factor $(-ix)^n$ within the integral. Evaluating the derivative at $k=0$, we find

$$\left.\frac{\mathrm{d}^n G(k)}{\mathrm{d}k^n}\right|_{k=0} = \langle(-ix)^n\rangle = -i^n \langle x^n\rangle \ .$$

Thus, the $n$-th derivative of $G(k)$ is directly linked to the $n$-th moment of the distribution $p(x)$. The characteristic function allows us to easily calculate all moments:

$$\boxed{\langle x^n\rangle = i^n \left.\frac{\mathrm{d}^n G(k)}{\mathrm{d}k^n}\right|_{k=0}} \ . \tag{2.41}$$

In turn, moments of $p(x)$ correspond to coefficients of the Taylor series of $G(k)$,

$$G(k) = \sum_{n=0}^{\infty} \frac{k^n}{n!} \left.\frac{\mathrm{d}^n G(k)}{\mathrm{d}k^n}\right|_{k=0} = \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} \langle x^n\rangle \ . \tag{2.42}$$

In fact, it turns out that the logarithm of the characteristic function is much better for characterizing probability distributions. Taking the logarithm has already proven to be useful when we derived the normal distribution (see section 2.4). In many cases, the logarithm is easier to work with. For example, the normal distribution is exponential, $p(x) \propto \exp[-(x-x^*)^2]$. Its logarithm, however, is simply a second-order polynomial: $\ln p(x) \propto (x-x^*)^2$.

**Cumulants.** In analogy to eq. (2.41), we define the $n$-th *cumulant* $\langle x^n\rangle_c$ as

$$\boxed{\langle x^n\rangle_c := i^n \left.\frac{\mathrm{d}^n \ln G(k)}{\mathrm{d}k^n}\right|_{k=0}} \ , \tag{2.43}$$

which implies that

$$\ln G(k) = \sum_{n=1}^{\infty} \frac{(-ik)^n}{n!} \langle x^n\rangle_c \ . \tag{2.44}$$

How do moments and cumulants relate? We show this with the following derivation sketch. First, we explicitly write the Taylor series in eq. (2.42),

$$G(k) = 1 \underbrace{- ik\langle x\rangle - \frac{k^2}{2}\left\langle x^2\right\rangle + \frac{ik^3}{6}\left\langle x^3\right\rangle + \dots}_{=:z} \ , \tag{2.45}$$

where we label the underbraced term $z$ and use the Taylor expansion of $\ln(1+z) = z - \frac{1}{2}z^2 + \frac{1}{3}z^3 - \frac{1}{4}z^4 + \dots$ to find

$$\ln G(k) = -ik\langle x\rangle - \frac{k^2}{2}\left\langle x^2\right\rangle + \frac{k^2}{2}\langle x\rangle^2 + \dots \ . \tag{2.46}$$

If we compare this with eq. (2.44), that is, we look at $\ln G(k) = -ik \langle x \rangle_c - \frac{k^2}{2} \langle x^2 \rangle_c + \ldots$ and compare coefficients of equal powers of $k$, we obtain the cumulants in terms of moments:

$$\begin{aligned} \langle x \rangle_c &= \langle x \rangle \\ \langle x^2 \rangle_c &= \langle x^2 \rangle - \langle x \rangle^2 \\ \langle x^3 \rangle_c &= \langle x^3 \rangle - 3\langle x^2 \rangle \langle x \rangle + 2 \langle x \rangle^3 \\ &\ldots \end{aligned} \tag{2.47}$$

Note that the first cumulant corresponds to the mean, while the second cumulant corresponds to the variance $\Delta x^2$. Generally, cumulants are very useful for characterizing probability distributions!

*Example 2.12.* **Cumulants of the normal distribution**

The normal distribution is given by eq. (2.28). According to eq. (2.40), the associated characteristic function is

$$G(k) = \int_{-\infty}^{\infty} \mathrm{d}x \, W(x) e^{-ikx} = \int_{-\infty}^{\infty} \frac{\mathrm{d}x}{\sqrt{2\pi\Delta^2}} \exp\left[-ikx - \frac{(x - x^*)^2}{2\Delta^2}\right] ,$$

where $x^*$ denotes the mean and $\Delta^2$ represents the variance. We solve the integral by applying the technique called *completing the square*. In the first step, we shift the integration variable by the mean, $x = \tilde{x} + x^*$. (The infinite integration limits remain unchanged; $x^*$ is finite.) This yields

$$G(k) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\tilde{x}}{\sqrt{2\pi\Delta^2}} \exp\left[-ikx^* - ik\tilde{x} - \frac{\tilde{x}^2}{2\Delta^2}\right] .$$

Now we complete the square in the square brackets by rewriting

$$-ik\tilde{x} - \frac{\tilde{x}^2}{2\Delta^2} = -\frac{1}{2\Delta^2}\left(\tilde{x} + ik\Delta^2\right)^2 - \frac{k^2\Delta^2}{2} .$$

We transform variables again, such that $\hat{x} = \tilde{x} + ik\Delta^2$. This results in

$$\begin{aligned} G(k) &= \int_{-\infty}^{\infty} \frac{\mathrm{d}\hat{x}}{\sqrt{2\pi\Delta^2}} \exp\left[-ikx^* - \frac{1}{2\Delta^2}\hat{x}^2 - \frac{k^2\Delta^2}{2}\right] \\ &= e^{-ikx^* - \frac{k^2\Delta^2}{2}} \int_{-\infty}^{\infty} \frac{\mathrm{d}\hat{x}}{\sqrt{2\pi\Delta^2}} e^{-\frac{\hat{x}^2}{2\Delta^2}} \\ &= \exp\left[-ikx^* - \frac{k^2\Delta^2}{2}\right] . \end{aligned} \tag{2.48}$$

Based on eq. (2.43), the cumulants of the normal distribution are found by calculating derivatives of $\ln G(k) = -ikx^* - \frac{k^2\Delta^2}{2}$, evaluated at $k = 0$. Specifically, the first and second cumulants are

$$\begin{aligned} \frac{\mathrm{d}\ln G(k)}{\mathrm{d}k} &= -ix^* - k\Delta^2 \quad \Rightarrow \quad \langle x \rangle_c = \langle x \rangle = i \cdot (-ix^*) = x^* \\ \frac{\mathrm{d}^2 \ln G(k)}{\mathrm{d}k^2} &= -\Delta^2 \quad \Rightarrow \quad \langle x^2 \rangle_c = \langle x^2 \rangle - \langle x \rangle^2 = -1 \cdot (-\Delta^2) = \Delta^2 , \end{aligned} \tag{2.49}$$

> as expected. Since $\ln G(k)$ is a quadratic function for the normal distribution (note that the logarithm is easy to work with), we immediately know that all higher derivatives vanish. Thus, all higher-order cumulants ($n > 2$) are zero; the normal distribution is characterized entirely by the first two cumulants. This implies that non-zero higher-order cumulants indicate deviations from the normal distribution.

## 2.8 Multi-dimensional probability distributions

A joint distribution of several random variables $x_1, x_2, \dots, x_n$ is determined by the multi-dimensional probability density $p(x_1, x_2, \dots, x_n)$. Normalization requires that

$$\int \mathrm{d}x_1 \int \mathrm{d}x_2 \cdots \int \mathrm{d}x_n \; p(x_1, x_2, \dots, x_n) = 1 \; . \tag{2.50}$$

To obtain the probability density for one of the variables, we must integrate over all other random variables:

$$p(x_1) = \int \mathrm{d}x_2 \cdots \int \mathrm{d}x_n \; p(x_1, x_2, \dots, x_n) \; . \tag{2.51}$$

Some refer to this projection process as the *marginalization* of the variables $x_2, \dots, x_n$: we are interested in the probability of $x_1$ regardless of the values of the other variables. Furthermore, moments are generally of the form $\langle x_1^{m_1} \dots x_n^{m_n} \rangle$. In this context, the *covariance*,

$$\mathrm{cov}(x_j, x_k) := \langle x_j x_k \rangle - \langle x_j \rangle \langle x_k \rangle \tag{2.52}$$

plays an important role as a measure of the correlation of the two random variables $x_j$ and $x_k$. In the case that their joint distribution factorizes, i.e. $p(x_j, x_k) = p(x_j)p(x_k)$, the variables are independent of one another and the covariance vanishes:

$$\begin{aligned}
\langle x_j x_k \rangle &= \int \mathrm{d}x_j \mathrm{d}x_k \, x_j x_k p(x_j) p(x_k) \\
&= \int \mathrm{d}x_j \, x_j p(x_j) \int \mathrm{d}x_k \, x_k p(x_k) \\
&= \langle x_j \rangle \langle x_k \rangle \qquad \Rightarrow \quad \mathrm{cov}(x_j, x_k) = 0 \; .
\end{aligned}$$

## 2.9 Central limit theorem

Consider a sum of random variables $x_1, x_2, \dots, x_m$,

$$y = \sum_{i=1}^{m} \frac{x_i}{m} \; , \tag{2.53}$$

where each random number $x_i$ follows the same probability distribution $p(x_i)$. What is the distribution of $y$? The central limit theorem provides the answer. To gain an intuition of what we are talking about, envision the following practical example. We will not make any additional assumptions, so our results will be transferrable to other situations where we ask about the sum of random variables.

*Example 2.13.* **Flight passenger weights**

Let $p(x)$ be the weight distribution of a single person. Then, what is the weight distribution of 100 people? This question is important, for instance, when estimating before a flight how much fuel the airplane must carry.

The average weight $y$ of 100 individuals obeys the distribution $W(y)$, given by

$$W(y) = \int \mathrm{d}x_1 \ldots \mathrm{d}x_m \, p(x_1) \cdots p(x_m) \, \delta\left(y - \sum_{i=1}^{m} \frac{x_i}{m}\right) . \tag{2.54}$$

Here $\delta$ denotes the delta distribution. Note that we assume individual weights to be uncorrelated, such that the multiplication theorem (eq. (2.3)) holds. For the $n$-th moment we find

$$\begin{aligned}\langle y^n \rangle &= \int \mathrm{d}y \, y^n W(y) \\ &= \int \mathrm{d}y \, y^n \int \mathrm{d}x_1 \ldots \mathrm{d}x_m \, p(x_1) \cdots p(x_m) \, \delta\left(y - \sum_{i=1}^{m} \frac{x_i}{m}\right) \\ &= \int \mathrm{d}x_1 \ldots \mathrm{d}x_m \, p(x_1) \ldots p(x_m) \int \mathrm{d}y \, y^n \delta\left(y - \sum_{i=1}^{m} \frac{x_i}{m}\right) \\ &= \int \mathrm{d}x_1 \ldots \mathrm{d}x_m \, p(x_1) \ldots p(x_m) \left(\sum_{i=1}^{m} \frac{x_i}{m}\right)^n \\ &= \left\langle \left(\sum_{i=1}^{m} \frac{x_i}{m}\right)^n \right\rangle .\end{aligned} \tag{2.55}$$

The characteristic function of $W(y)$ reads

$$\begin{aligned}G(k) &= \int \mathrm{d}y \, e^{-iky} W(y) \\ &= \int \mathrm{d}x_1 \ldots \mathrm{d}x_m \, p(x_1) \ldots p(x_m) \int \mathrm{d}y \, e^{-iky} \delta\left(y - \sum_{i=1}^{m} \frac{x_i}{m}\right) \\ &= \int \mathrm{d}x_1 \ldots \mathrm{d}x_m \, p(x_1) \ldots p(x_m) \, \exp\left[-ik \sum_i \frac{x_i}{m}\right] \\ &= \int \mathrm{d}x_1 \, p(x_1) e^{-ikx_1/m} \cdot \int \mathrm{d}x_2 \, p(x_2) e^{-ikx_2/m} \cdots \int \mathrm{d}x_m \, p(x_m) e^{-ikx_m/m} \\ &= \left[g\left(\frac{k}{m}\right)\right]^m ,\end{aligned} \tag{2.56}$$

where $g(k) = \int \mathrm{d}x \, p(x) e^{-ikx}$ represents the characteristic function of $p(x)$. This implies that

$$\ln G(k) = m \ln \left[g\left(\frac{k}{m}\right)\right] . \tag{2.57}$$

Consequently, the cumulants are given by

$$\begin{aligned}\langle y^n \rangle_c &= i^n \left. \frac{\mathrm{d}^n \ln G(k)}{\mathrm{d}k^n} \right|_{k=0} \\ &= i^n m \left. \frac{\mathrm{d}^n \ln g(k/m)}{\mathrm{d}k^n} \right|_{k=0} \\ &= i^n m^{1-n} \left. \frac{\mathrm{d}^n \ln g(q)}{\mathrm{d}q^n} \right|_{q=0} \end{aligned} \tag{2.58}$$

where we have substituted $q = \frac{k}{m}$ in the final step. Now, since

$$\langle x^n \rangle_c = i^n \left. \frac{\mathrm{d}^n \ln g(q)}{\mathrm{d}q^n} \right|_{q=0}$$

by definition, we obtain

$$\boxed{\langle y^n \rangle_c = m^{1-n} \langle x^n \rangle_c} \,. \tag{2.59}$$

This is the *central limit theorem.* The only assumption made here is that the $n$-th moments must exist. Importantly, the central limit theorem has the following implications.

- $n = 1 \quad \Rightarrow \quad \langle y^n \rangle_c = \langle x^n \rangle_c$ ,
  In terms of our example, the mean of the average weight of 100 people equals the mean of the weight of an individual.
- $n = 2 \quad \Rightarrow \quad \langle y^n \rangle_c = \frac{1}{m} \langle x^n \rangle_c$ .
  This underpins the law of large numbers: for the distribution $W(y)$ of the sum, the mean deviation becomes much smaller than for the individual distribution $p(x)$, if $m$ is large. Regarding fuel planning on airplanes (example 2.13), this presents a relieving result. While individual body weights might vary quite significantly among airplane passengers, the total weight of all $m = 100$ passengers will not deviate much from its mean, making safe estimates of needed fuel possible.
- $n = 3 \quad \Rightarrow \quad \langle y^n \rangle_c = \frac{1}{m^2} \langle x^n \rangle_c$ ,
  Since deviations from the normal distribution are characterized by cumulants of order $n \geq 3$ (as shown in example 2.12), this yields the key result of the central limit theorem:

  > For large $m$, the distribution of $y$ deviates very little from the normal distribution.

  Regardless of the distribution $p(x_i)$ of the individual random variables $x_i$, the sum of a large number of these random variables will be approximately normally distributed. Example 2.14 illustrates this result.

The central limit theorem offers an explanation why uncertainties may often be assumed to be normally distributed, or Gaussian. Since uncertainties in real life often arise from a combination of factors, their summed effect is often approximately Gaussian even if the individual distributions of the contributing errors are not.

### *Example 2.14.* Central limit theorem in simulation

To see the central limit theorem in action, let us explore what happens when we sum randomly generated numbers on a computer.

Consider a random variable $x$ with a uniform probability distribution in the interval $[0, 1)$, that is,

$$p(x) = \begin{cases} 1 & \text{for } 0 \le x < 1 \\ 0 & \text{else.} \end{cases}$$

This distribution has a mean $\langle x \rangle = \int_0^1 \mathrm{d}x\, x = \frac{x^2}{2}\Big|_0^1 = \frac{1}{2}$ and a second moment $\langle x^2 \rangle = \int_0^1 \mathrm{d}x\, x^2 = \frac{x^3}{3}\Big|_0^1 = \frac{1}{3}$, leading to the variance $\Delta x^2 = \langle x^2 \rangle - \langle x \rangle^2 = \frac{1}{12}$.

First, we numerically draw $N$ random numbers from the uniform distribution $p(x)$. Fig. 2.3 shows the experimental distributions for $100$ draws, $10^4$ draws, and $10^6$ draws, respectively. The data is binned in 100 equidistant bins. At $N = 100$ draws, we see substantial fluctuations due to the small sample size. As we increase the number of draws, the experimental distribution becomes more uniform. The normal distribution (orange line), which we include for reference, clearly does not describe the distribution of $x$.

What does the distribution of a sum $y = \frac{1}{2}(x_1 + x_2)$ of two random numbers $x_1$ and $x_2$, each drawn from the uniform distribution $p(x)$, look like? This case $(m = 2)$ is demonstrated in the center panel of fig. 2.4 based on $10^4$ realizations. We see that the distribution takes a triangular shape (why?). The right panel of fig. 2.4 shows the case $m = 3$ (i.e. $y = \frac{1}{3}(x_1 + x_2 + x_3)$). Here, the distribution already looks remarkably like a normal distribution with mean $\langle y \rangle = \frac{1}{2}$ and variance $\langle y^2 \rangle_c = \frac{1}{m} \cdot \frac{1}{12} = \frac{1}{36}$, as predicted by the central limit theorem.

Finally, fig. 2.5 displays simulation results for sums of $m = 100$, $1000$, and $10^4$ random variables. The simulation data are well approximated by a normal distribution. In accordance with the central limit theorem, the distribution becomes more sharply peaked around the mean $\langle y \rangle = \frac{1}{2}$ as $m$ increases, reflecting that the variance of $y$ is proportional to $\frac{1}{m}$.

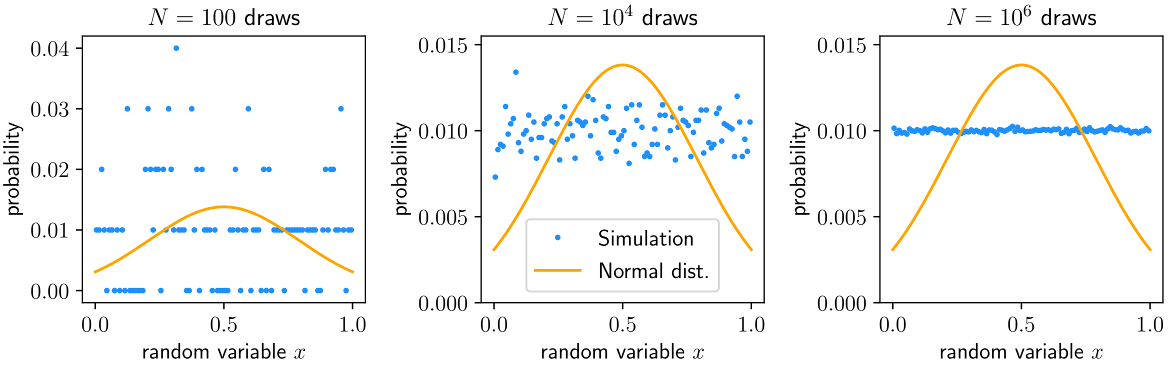

**Figure 2.3: Drawing random numbers from a uniform distribution** on a computer. The plots show the probability distribution of the random variable $x$ based on $N = 100$ (left), $10^4$ (center), and $10^6$ (right) draws, where the blue dots represent simulation data binned in 100 equidistant bins. The orange line represents the normal distribution for reference.

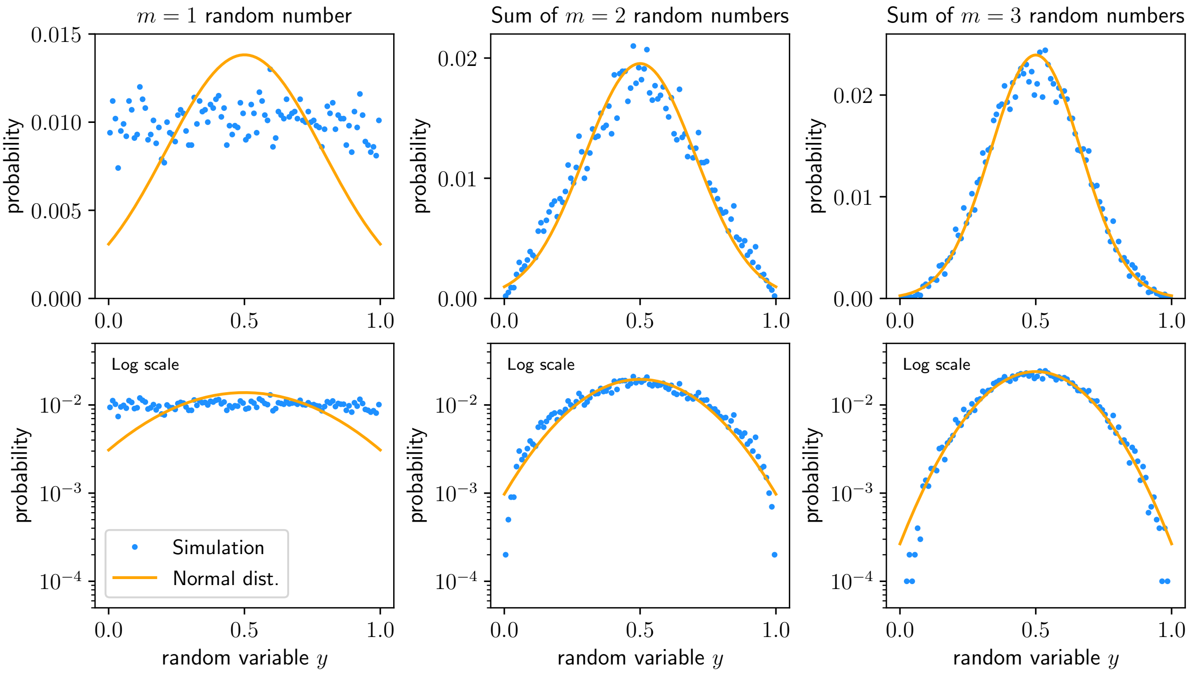

**Figure 2.4: Probability distributions of sums of $m$ random numbers.** *Left:* Same as center panel of fig. 2.3 ($m = 1$). *Center:* Sum of $m = 2$ random numbers $x_i$, $y = \frac{1}{2}(x_1 + x_2)$. *Right:* Sum of $m = 3$ random numbers $x_i$. Blue dots represent numerical simulation data (based on $10^4$ realizations and binned into 100 bins), while the orange curve shows the analytical normal distribution. The bottom panels display the same information as the respective top panels but on a logarithmic probability scale.

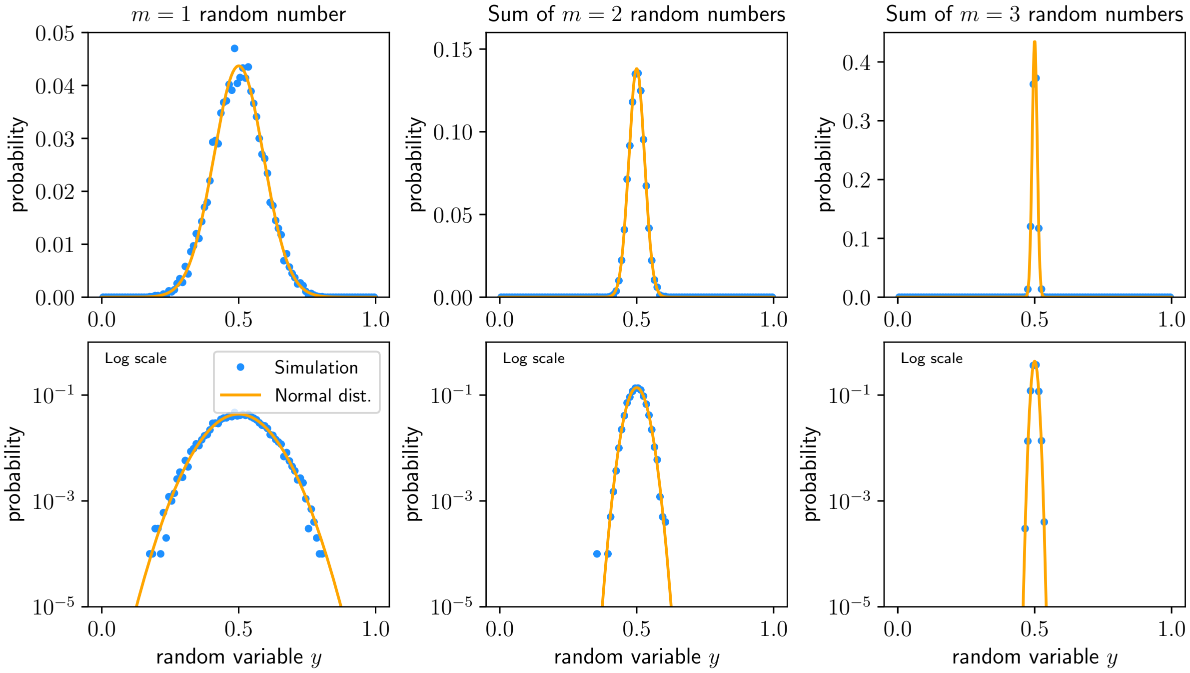

**Figure 2.5: Probability distributions for** $m = 100, 10^3, 10^4$**.** Similar to fig. 2.4, but this time summing $m = 100$ (left), $10^3$ (center), and $10^4$ (right) uniformly distributed random numbers.

# 3 Statistical Mechanics

Having established the necessary mathematical basics, this chapter brings us to the core of the lecture. Starting with a summary of classical mechanics, we introduce a statistical description of physical systems with a large number of components. This leads from microscopic properties to a macroscopic formulation where the Boltzmann distribution determines the probability of energy states. As fundamental concepts of Statistical Mechanics, we derive three statistical ensembles – the microcanonical ensemble, the canonical ensemble, and the grand canonical ensemble. Throughout the chapter, the ideal gas serves as a paradigmatic model to calculate and illustrate the relations we obtain.

## 3.1 Recap: Classical mechanics

Before introducing key concepts of Statistical Mechanics, let us recapitulate some fundamentals of classical mechanics. Newton's equation of motion in one dimension is

$$m\ddot{x}(t) = F(x,t) \ , \tag{3.1}$$

where the conservative force $F$ can be extracted from a – generally time-dependent – potential $V$ according to

$$F(x,t) = -\frac{\partial V(x,t)}{\partial x} \ . \tag{3.2}$$

In terms of the momentum $p = m\dot{x}$, eqs. (3.1) and (3.2) yield $\dot{p} + \frac{\partial V}{\partial x} = 0$ as well as

$$\begin{aligned} \dot{p} &= \frac{\mathrm{d}}{\mathrm{d}t}\Big(m\dot{x}(t)\Big) \\ &= \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial}{\partial \dot{x}}\left(\frac{m\dot{x}^2}{2}\right) \\ &= \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial T}{\partial \dot{x}} \ , \end{aligned}$$

where $T = m\dot{x}^2/2$ represents the kinetic energy. Thus, we may rewrite the equation of motion (3.1) as

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial T}{\partial \dot{x}} + \frac{\partial V}{\partial x} = 0 \ . \tag{3.3}$$

We define the Lagrange function $L$,

$$L(x, \dot{x}, t) := T(\dot{x}) - V(x,t) \ , \tag{3.4}$$

and rewrite the equation of motion in terms of $L$ to obtain the *Euler-Lagrange equation*,

$$\boxed{\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L(x,\dot{x},t)}{\partial \dot{x}} - \frac{\partial L(x,\dot{x},t)}{\partial x} = 0} \, . \tag{3.5}$$

Moreover, let us define the action $S$,

$$S := \int_{t_0}^{t_1} \mathrm{d}t \, L(x(t),\dot{x}(t)) \ , \tag{3.6}$$

where, for the moment, we have skipped the explicit time dependence of $L$. The action is a functional, i.e. a function of a function. For a functional $F[x(t)]$, its functional derivative is defined as

$$\frac{\delta F[x(\cdot)]}{\delta x(\tilde{t})} := \left. \frac{F[x(\cdot)+\varepsilon\delta(\cdot-\tilde{t})] - F[x(\cdot)]}{\varepsilon} \right|_{\varepsilon\to 0} \ . \tag{3.7}$$

Thus the functional derivative of the action reads

$$\begin{aligned} \frac{\delta S[x(\cdot),\dot{x}(\cdot)]}{\delta x(\tilde{t})} &= \int_{t_0}^{t_1} \mathrm{d}t \left[ \frac{\partial L}{\partial x}\delta(t-\tilde{t}) + \frac{\partial L}{\partial \dot{x}}\frac{\mathrm{d}}{\mathrm{d}t}\delta(t-\tilde{t}) \right] \\ &\overset{*}{=} \int_{t_0}^{t_1} \mathrm{d}t \left[ \frac{\partial L}{\partial x} - \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{x}} \right] \delta(t-\tilde{t}) \\ &= \frac{\partial L}{\partial x(\tilde{t})} - \frac{\mathrm{d}}{\mathrm{d}\tilde{t}}\frac{\partial L}{\partial \dot{x}(\tilde{t})} \overset{!}{=} 0 \ . \end{aligned} \tag{3.8}$$

Here the step marked by $*$ results from partial integration, where we used that $t_0 < \tilde{t} < t$; hence the boundary terms disappear. In the last line, we inserted the Euler-Lagrange equation. The result is Hamilton's principle which states that a solution of the Euler-Lagrange equation extremizes the action.

The Lagrangian formalism has proven to be very useful for problems with constraints. In Statistical Mechanics, however, the Hamiltonian formalism turns out more suitable. To switch from Lagrange to Hamilton, we perform a *Legendre transform* which replaces $\dot{x}$ in $L$ by the momentum $p$,

$$p(t) = m\dot{x}(t) = \frac{\partial T(\dot{x})}{\partial \dot{x}} = \frac{\partial L(x,\dot{x},t)}{\partial \dot{x}} \ . \tag{3.9}$$

The Legendre transform yields the Hamilton function $\mathcal{H}$,

$$\boxed{\mathcal{H}(x,p,t) = \dot{x}p - L(x,\dot{x},t)} \, . \tag{3.10}$$

Note that $\mathcal{H}$ does not depend on $\dot{x}$. To see this explicitly, let us write down the total differential[1] of the Hamilton function,

$$\begin{aligned} \mathrm{d}\mathcal{H}(x,\dot{x},p,t) &= \left.\frac{\partial \mathcal{H}}{\partial x}\right|_{\dot{x},p,t} \mathrm{d}x + \left.\frac{\partial \mathcal{H}}{\partial \dot{x}}\right|_{x,p,t} \mathrm{d}\dot{x} + \left.\frac{\partial \mathcal{H}}{\partial p}\right|_{x,\dot{x},t} \mathrm{d}p + \left.\frac{\partial \mathcal{H}}{\partial t}\right|_{x,\dot{x},p} \mathrm{d}t \\ &= -\left.\frac{\partial L}{\partial x}\right|_{\dot{x},p,t} \mathrm{d}x + \underbrace{p\,\mathrm{d}\dot{x} - \left.\frac{\partial L}{\partial \dot{x}}\right|_{x,p,t} \mathrm{d}\dot{x}}_{=0} + \dot{x}\,\mathrm{d}p - \left.\frac{\partial L}{\partial t}\right|_{x,\dot{x},p} \mathrm{d}t \\ &= \mathrm{d}\mathcal{H}(x,p,t) \ . \end{aligned} \tag{3.11}$$

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[1] The total differential of a function $f(x,y)$ is defined as $\mathrm{d}f(x,y) = \left.\frac{\partial f}{\partial x}\right|_y \mathrm{d}x + \left.\frac{\partial f}{\partial y}\right|_x \mathrm{d}y$.

Due to the Legendre transform, the $\dot{x}$-dependence cancels[2] (the underbraced term vanishes according to eq. (3.9)) and the three remaining variables are $(x, p, t)$. In general, Legendre transforms can be used to change independent variables of functions. Eq. (3.11) now leads to

$$\mathrm{d}\mathcal{H}(x,p,t) = -\dot{p}\,\mathrm{d}x + \dot{x}\,\mathrm{d}p - \frac{\partial L}{\partial t}\,\mathrm{d}t \ , \tag{3.12}$$

where $\dot{p} = \partial L/\partial x$ follows from the Euler-Lagrange equation (3.5). A comparison with the general form for the total differential,

$$\mathrm{d}\mathcal{H}(x,p,t) = \left.\frac{\partial H}{\partial x}\right|_{p,t}\mathrm{d}x + \left.\frac{\partial H}{\partial p}\right|_{x,t}\mathrm{d}p + \left.\frac{\partial H}{\partial t}\right|_{x,p}\mathrm{d}t \ , \tag{3.13}$$

yields the Hamilton equations,

$$\boxed{\frac{\partial \mathcal{H}}{\partial p} = \dot{x} \ , \qquad \frac{\partial \mathcal{H}}{\partial x} = -\dot{p} \ , \qquad \frac{\partial \mathcal{H}}{\partial t} = -\frac{\partial L}{\partial t}} \ . \tag{3.14}$$

These equations completely specify the dynamics of a system. By calculating the total time derivative of the Hamilton function using the chain rule,

$$\begin{aligned}
\frac{\mathrm{d}\mathcal{H}(x(t),p(t),t)}{\mathrm{d}t} &= \frac{\partial \mathcal{H}}{\partial x}\frac{\mathrm{d}x}{\mathrm{d}t} + \frac{\partial \mathcal{H}}{\partial p}\frac{\mathrm{d}p}{\mathrm{d}t} + \frac{\partial \mathcal{H}}{\partial t} \\
&= -\dot{p}\dot{x} + \dot{x}\dot{p} + \frac{\partial \mathcal{H}}{\partial t} \\
\Rightarrow \qquad \frac{\mathrm{d}\mathcal{H}}{\mathrm{d}t} &= \frac{\partial \mathcal{H}}{\partial t} \ ,
\end{aligned} \tag{3.15}$$

we see that if the potential is constant in time such that the Hamiltonian $\mathcal{H}$ is not explicitly time-dependent, i.e. $\frac{\partial \mathcal{H}}{\partial t} = 0$, then $\mathcal{H}$ is a conserved quantity. But what is $\mathcal{H}$ physically? Returning to the Legendre transform, we find

$$\begin{aligned}
\mathcal{H} &= p\dot{x} - L \\
&= m\dot{x}^2 - (T - V) \\
&= 2T - T + V \\
&= T + V \ .
\end{aligned} \tag{3.16}$$

Thus, the Hamiltonian represents the total energy! In a time-independent potential, i.e. for $\frac{\partial \mathcal{H}}{\partial t} = 0$, the total energy is conserved.

After this brief summary, let us get started with Statistical Mechanics.

## 3.2 Liouville's theorem

A gas of $N$ atoms is completely specified by $3N$ position coordinates $q_1, \ldots, q_{3N}$ and $3N$ momentum coordinates $p_1, \ldots, p_{3N}$. These variables constitute a $6N$-dimensional

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[2] Even though $\dot{x}$ still appears in the total differential (3.11) in the term $\dot{x}\,\mathrm{d}p$, it is *not* an independent variable of $\mathcal{H}$ anymore.

coordinate space termed *phase space*, or $\Gamma$-space. A point in phase space defines a *microstate*. It moves according to the canonical Hamilton equations,

$$\dot{q}_i(t) = \frac{\partial \mathcal{H}(q^{3N}, p^{3N})}{\partial p_i} \tag{3.17}$$

$$\dot{p}_i(t) = -\frac{\partial \mathcal{H}(q^{3N}, p^{3N})}{\partial q_i} \ , \tag{3.18}$$

where $i = 1, \dots, 3N$ (giving rise to $6N$ equations) and $q^{3N}$ abbreviates $q_1, q_2, \dots, q_{3N}$. Typically, we assume that $\mathcal{H}$ depends only on $q^{3N}$ and $p^{3N}$, not on time $t$, $\dot{p}$, etc. Then,

$$\frac{\mathrm{d}\mathcal{H}}{\mathrm{d}t} = \frac{\partial \mathcal{H}}{\partial t} = 0 \ .$$

As shown in the previous section, this implies conservation of total energy $\mathcal{H}$. Therefore, with given initial conditions, eqs. (3.17) and (3.18) uniquely determine $q^{3N}(t)$ and $p^{3N}(t)$ for all times $t$. This also means that $\dot{q}^{3N}(t)$ and $\dot{p}^{3N}(t)$ are unique functions, which brings about the consequence that trajectories in phase space never cross. Indeed, if a trajectory would cross itself in a certain point, there would exist two different ways to move on from that point – in contradiction with the uniqueness of solutions. Closed curves, however, are possible and describe periodic motion.

In Statistical Mechanics, where we deal with large systems, following $6N$ coordinates around is neither feasible nor worthwhile; it is simply too much information. But we do not need all details because not all microstates have distinct physical characteristics. Imagine, for example, a gas composed of $N$ identical particles. Then all $N!$ possible permutations describe identical systems but represent different points in phase space! Many microstates are equivalent and lead to the same macroscopic properties such as temperature, pressure, total energy, etc. In other words, one *macrostate* characterized by these "coarse-grained" quantities can be realized by a vast number of microstates. This motivates a probabilistic description of the problem. We assign each microstate a probability $\rho(q^{3N}, p^{3N}, t)$. The probability density can be normalized such that

$$\int \mathrm{d}^{3N}q \, \mathrm{d}^{3N}p \ \rho(q^{3N}, p^{3N}, t) = 1 \ , \tag{3.19}$$

where, in short notation, $\mathrm{d}^{3N}q = \mathrm{d}q_1 \cdots \mathrm{d}q_{3N}$. Thus, we may calculate the expectation value of any observable $A$, e.g. pressure or internal energy, according to

$$\langle A(t) \rangle = \int \mathrm{d}^{3N}q \, \mathrm{d}^{3N}p \ A(q^{3N}, p^{3N}) \, \rho(q^{3N}, p^{3N}, t) \ . \tag{3.20}$$

A probability distribution $\rho$ in phase space is also called an *ensemble*, and the expectation value in eq. (3.20) is sometimes termed *ensemble average*. We may think of an ensemble as a collection of "mental copies" of the given system, each of which represents a possible microstate the system could be in under the constraints of a given macrostate. This powerful interpretation, introduced by Gibbs, sets the conceptual foundation for much of what will follow in this lecture. We will discuss different types of ensembles soon.

What are the properties of the density distribution $\rho$, and how does it evolve in time? A microstate ($q^{3N}$, $p^{3N}$), with probability $\rho(q^{3N}, p^{3N}, t)$ at time $t$, moves along a completely determined trajectory according to the Hamilton equations (3.17), (3.18). Since probability is conserved over time when integrating over the entire phase space (there are no sources or sinks of microstates), $\rho$ must obey a so-called conservation or balance equation. Consider a fixed volume $\Omega$ in phase space: the change in probability $\rho$ integrated over $\Omega$ must be balanced by a probability flux through the surface $S(\Omega)$ of the volume $\Omega$. In mathematical terms, we write this as

$$-\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \mathrm{d}^{3N}q\,\mathrm{d}^{3N}p\;\rho(q^{3N},p^{3N},t) = \int_{S(\Omega)} \mathrm{d}s\;\vec{n}(s)\cdot\vec{v}(s)\rho(s,t)\;, \tag{3.21}$$

where $\vec{v}(s) = (\dot{q}_1,\dots,\dot{q}_{3N},\dot{p}_1,\dots,\dot{p}_{3N})$ denotes the $6N$-dimensional velocity in phase space, $s$ is the surface element, and $\vec{n}(s)$ denotes the surface normal on $S$ (pointing outwards). Using Gauss's theorem, sometimes referred to as the divergence theorem, we rewrite eq. (3.21) as

$$-\int_\Omega \mathrm{d}^{3N}q\,\mathrm{d}^{3N}p\;\frac{\partial}{\partial t}\rho(q^{3N},p^{3N},t) = \int_\Omega \mathrm{d}^{3N}q\,\mathrm{d}^{3N}p\;\vec{\nabla}\cdot\Big(\vec{v}(q^{3N},p^{3N})\,\rho(q^{3N},p^{3N},t)\Big)\;. \tag{3.22}$$

Here $\vec{\nabla}$ represents the $6N$-dimensional gradient operator,

$$\vec{\nabla} = \left(\frac{\partial}{\partial q_1},\dots,\frac{\partial}{\partial q_{3N}},\frac{\partial}{\partial p_1},\dots,\frac{\partial}{\partial p_{3N}}\right)\;.$$

Note that we could pull the time derivative inside the volume integral since we assume that $\Omega$ remains fixed in time. Rearranging eq. (3.22), we get

$$\int_\Omega \mathrm{d}^{3N}q\,\mathrm{d}^{3N}p\;\left(\frac{\partial}{\partial t}\rho(q^{3N},p^{3N},t) + \vec{\nabla}\cdot\Big(\vec{v}(q^{3N},p^{3N})\,\rho(q^{3N},p^{3N},t)\Big)\right) = 0\;. \tag{3.23}$$

We may choose the time-independent volume $\Omega$ arbitrarily, which implies that eq. (3.23) can only hold true for any test volume $\Omega$ if the integrand vanishes. This requirement results in an equation of continuity for $\rho$,

$$\begin{aligned}
-\frac{\partial\rho}{\partial t} &= \vec{\nabla}\cdot(\vec{v}\rho)\\
&= \sum_{i=1}^{3N}\left[\frac{\partial}{\partial q_i}(\dot{q}_i\rho) + \frac{\partial}{\partial p_i}(\dot{p}_i\rho)\right]\\
&= \sum_{i=1}^{3N}\left[\dot{q}_i\frac{\partial\rho}{\partial q_i} + \dot{p}_i\frac{\partial\rho}{\partial p_i} + \rho\underbrace{\left(\frac{\partial\dot{q}_i}{\partial q_i} + \frac{\partial\dot{p}_i}{\partial p_i}\right)}_{=0}\right]\;,
\end{aligned} \tag{3.24}$$

where we know from the Hamilton equations (3.17), (3.18) that the underbraced term must vanish:

$$\frac{\partial\dot{q}_i}{\partial q_i} + \frac{\partial\dot{p}_i}{\partial p_i} = \frac{\partial}{\partial q_i}\frac{\partial\mathcal{H}}{\partial p_i} - \frac{\partial}{\partial p_i}\frac{\partial\mathcal{H}}{\partial q_i} = 0\;,$$

according to Schwarz's theorem about the symmetry of partial derivatives. This leads to the *Liouville equation*,

$$-\frac{\partial\rho(q^{3N},p^{3N},t)}{\partial t} = \sum_{i=1}^{3N}\left[\dot{q}_i\frac{\partial}{\partial q_i} + \dot{p}_i\frac{\partial}{\partial p_i}\right]\rho(q^{3N},p^{3N},t)\;. \tag{3.25}$$

Defining the Liouville operator $\hat{L} := \sum_{i=1}^{3N}\left[\dot{q}_i\frac{\partial}{\partial q_i} + \dot{p}_i\frac{\partial}{\partial p_i}\right]$, we may write this compactly as[3]

$$\boxed{-\frac{\partial \rho}{\partial t} = \hat{L}\rho}\ . \tag{3.26}$$

The Liouville equation describes how $\rho$ changes in time at a fixed position in phase space $(q_1, \ldots, q_{3N}, p_1, \ldots, p_{3N})$ (Eulerian description). We might ask ourselves: how does $\rho$ evolve in time when we "go with the flow" by moving along with the trajectory as it moves through phase space (Lagrangian description)? Using the chain rule, we find that

$$\begin{aligned} \frac{\mathrm{d}\rho(q^{3N}(t), p^{3N}(t), t)}{\mathrm{d}t} &= \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left(\frac{\partial \rho}{\partial q_i}\frac{\mathrm{d}q_i}{\mathrm{d}t} + \frac{\partial \rho}{\partial p_i}\frac{\mathrm{d}p_i}{\mathrm{d}t}\right) \\ &= \frac{\partial \rho}{\partial t} + \hat{L}\rho \\ &\Rightarrow \quad \boxed{\frac{\mathrm{d}\rho}{\mathrm{d}t} = 0}\ . \end{aligned} \tag{3.27}$$

This is *Liouville's theorem.* It states that the density $\rho$ is (locally) constant when moving along with a trajectory through phase space. Essentially, $\rho$ propagates through phase space like an incompressible fluid.

## 3.3 Postulate of equal *a priori* probability

If we imagine that a trajectory visits every point in phase space compatible with energy conservation ($\mathcal{H} = \text{const.}$), then the simplest distribution compatible with Liouville's theorem (eq. (3.27)) is

$$\rho(\vec{q}, \vec{p}, t) = \begin{cases} \text{const.} & U \leq \mathcal{H}(\vec{q}, \vec{p}) \leq U + \Delta \\ 0 & \text{otherwise.} \end{cases} \tag{3.28}$$

Here we allow the total energy $\mathcal{H}$ to lie in a small interval $[U, U + \Delta]$. According to this argument – which only assumes that a trajectory may, in principle, visit every point in phase space without crossing itself –, every possible microstate which results in total energy $U$ would be equally probable. This motivates the *postulate of equal a priori probability*, which states that a system with total energy $U$ is equally likely to be in any of the compatible microstates. The distribution in eq. (3.28) defines the *microcanonical ensemble*, which we will discuss in further detail soon. Since the total energy is fixed, the microcanonical ensemble describes an isolated system.

**Remark.** If we more generally consider an ensemble where different energies are populated with different probabilities, that is,

$$\rho(\vec{q}, \vec{p}, t) = \rho(\mathcal{H}(\vec{q}, \vec{p}), t)\ , \tag{3.29}$$

---

[3] As a side remark, we mention that the Liouville operator may be used to formally solve the Liouville equation (3.25). Given an initial distribution $\rho(\vec{q}, \vec{p}, 0)$, the solution is $\rho(\vec{q}, \vec{p}, t) = \exp\left[-\hat{L}t\right]\rho(\vec{q}, \vec{p}, 0)$. This is an extremely powerful method, since it provides an exact solution of the many-body problem!

then the Liouville equation tells us that

$$\begin{aligned}
-\frac{\partial\rho(\vec{q},\vec{p},t)}{\partial t} &= \sum_{i=1}^{3N}\left[\dot{q}_i\frac{\partial\rho}{\partial q_i}+\dot{p}_i\frac{\partial\rho}{\partial p_i}\right] \\
&= \sum_{i=1}^{3N}\left[\frac{\partial\mathcal{H}}{\partial p_i}\frac{\partial\rho}{\partial\mathcal{H}}\frac{\partial\mathcal{H}}{\partial q_i}-\frac{\partial\mathcal{H}}{\partial q_i}\frac{\partial\rho}{\partial\mathcal{H}}\frac{\partial\mathcal{H}}{\partial p_i}\right] \\
&= 0\ ,
\end{aligned} \tag{3.30}$$

where we have used the Hamilton equations and the chain rule. This implies that $\rho$ cannot be explicitly time-dependent:

$$\rho(\mathcal{H}(\vec{q},\vec{p}),t)=\rho(\mathcal{H}(\vec{q},\vec{p}))\ . \tag{3.31}$$

Consequently, a distribution that depends on the Hamiltonian only and not on phase space variables directly is stationary. The statement is true for arbitrary systems and for a general Hamiltonians $\mathcal{H}(\vec{q},\vec{p})$. This general result holds also for the special case of the microcanonical ensemble (eq. (3.28)), for which $\rho(\mathcal{H}(\vec{q},\vec{p}))$ is a $\delta$ function: $\rho(\mathcal{H}(\vec{q},\vec{p}))\approx\delta(\mathcal{H}(\vec{q},\vec{p})-U)$.

## 3.4 Concepts of entropy and temperature

The "number" of microstates within the energy range $U<\mathcal{H}(\vec{q},\vec{p})<U+\Delta$ is given by the volume integral

$$\Gamma(U,V,N)=\int_{U<\mathcal{H}<U+\Delta}\mathrm{d}^{3N}q\,\mathrm{d}^{3N}p\ 1\ , \tag{3.32}$$

which quantifies the allowed volume in phase space of a system with that energy. This relates to the *density of states*: the total number of states with energy $\mathcal{H}$ below $U$ is

$$\Sigma(U)=\int_{\mathcal{H}<U}\mathrm{d}^{3N}q\,\mathrm{d}^{3N}p\ 1\ . \tag{3.33}$$

Thus, we may write the number of allowed microstates $\Gamma$ as

$$\begin{aligned}
\Gamma(U) &= \Sigma(U+\Delta)-\Sigma(U) \\
&\approx \Sigma(U)+\Delta\Sigma'(U)-\Sigma(U) \\
&= \Delta\Sigma'(U)\ ,
\end{aligned} \tag{3.34}$$

where we used the Taylor approximation up to first order, assuming that $\Delta\ll U$. Based on this, we define the density of states $\omega(U)$ for a certain energy $U$ as

$$\omega(U):=\lim_{\Delta\to 0}\frac{\Gamma(U)}{\Delta}=\Sigma'(U)\ , \tag{3.35}$$

$$\Sigma(U)=\int_{-\infty}^{U}\mathrm{d}U'\,\omega(U')\ . \tag{3.36}$$

As we will see later, it often does not make a difference whether we use $\omega(U)$ or $\Gamma(U)/\Delta$; the energy uncertainty $\Delta$ is negligible for all practical purposes.

**Two Coupled Systems.** Consider now an isolated system, characterized by fixed total

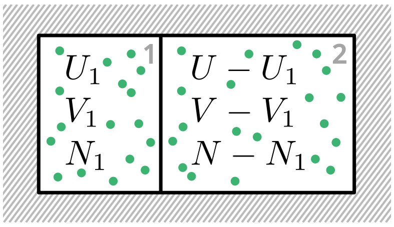

**Figure 3.1:** Two coupled subsystems (1 and 2) isolated from the environment. The subsystems may exchange energy, volume, and particles between each other.

energy $U$, particle number $N$, and volume $V$. Imagine that we insert a dividing plane which divides the system into two subsystems. The dividing plane lets energy pass from one side to the other; however, neither particles nor volume may pass through. Thus, subsystems 1 and 2 have fixed particle numbers $N_1$, $N - N_1$ as well as fixed volumes $V_1$, $V - V_1$ but fluctuating energies $U_1, U - U_1$ under the constraint $U_1 \leq U$ (see fig. 3.1). The total number of microstates $\Gamma$ for the compound system at energy $U$ is calculated as

$$\Gamma(U, V, N) = \int_0^U \mathrm{d}U_1 \, \Gamma_1(U_1) \cdot \Gamma_2(U - U_1) \; . \tag{3.37}$$

Note that for a fixed energy $U_1$, the number of microstates $\Gamma$ of the total system equals the product $\Gamma_1 \cdot \Gamma_2$ of the number of microstates of the subsystems. This is founded upon the multiplication theorem (see eq. (2.3)). Since the subsystems may exchange energy, we must furthermore integrate over all possible energies $U_1$ (from 0 to $U$).

Let us now introduce a new function which we denote as $S(U)$. The reason why we do this will become clear later; it will turn out that $S$ represents the *entropy* in Thermodynamics. We define

$$\boxed{\frac{S(U)}{k_B} := \ln(\Gamma(U))} \; . \tag{3.38}$$

Let us use this function to explore our example of a compound system further. Inserting eq. (3.37) for $\Gamma(U)$, we obtain

$$\frac{S(U)}{k_B} = \ln\left(\int_0^U \mathrm{d}U_1 \, e^{[S_1(U_1) + S_2(U - U_1)]/k_B}\right) \; . \tag{3.39}$$

Assuming that the integrand has a maximum at energy $U_1^*$, the sum $S_1 + S_2$ is also maximal at $U_1^*$ because the exponential is a monotonic equation. Therefore, we may Taylor expand the sum around its maximum,

$$\begin{aligned} S_1(U_1) + S_2(U - U_1) \approx{}& S_1(U_1^*) + S_2(U - U_1^*) \\ &+ (U_1 - U_1^*) \underbrace{\left[S_1'(U_1^*) - S_2'(U - U_1^*)\right]}_{=0} \\ &+ \frac{(U_1 - U_1^*)^2}{2} \left[S_1''(U_1^*) + S_2''(U - U_1^*)\right] + \ldots \; , \end{aligned} \tag{3.40}$$

where the first derivative vanishes at the maximum. Re-inserting the Taylor series up to second order into eq. (3.39) yields

$$\frac{S(U)}{k_B} = \ln\left(e^{[(S_1(U_1^*) + S_2(U - U_1^*)]/k_B} \int_{-\infty}^{\infty} \mathrm{d}U_1 \, e^{(U_1 - U_1^*)^2 [S_1''(U - U_1^*) + S_2''(U - U_1^*)]/(2k_B)}\right) \; .$$

Here we have pulled the $U_1$-independent part in front of the integral. Note that we have extended the integration boundaries to range from $-\infty$ to $\infty$, which is permissible if the maximum is sharp, as we will show further below. The integral is thus a Gaussian integral for which the solution is known: $\int_{-\infty}^{\infty} \mathrm{d}x\, e^{-a(x+b)^2} = \sqrt{\pi/a}$. Performing the integral, we find

$$S(U) = S_1(U_1^*) + S_2(U - U_1^*) + k_B \ln \sqrt{-\frac{2\pi k_B}{S_1''(U_1^*) + S_2''(U - U_1^*)}} \ , \tag{3.41}$$

where we assume that $S_1''(U_1*) + S_2''(U - U_1^*) < 0$ (which will be shown to hold true). From this result we may draw several fundamental conclusions:

- **The function $S(U)$ is extensive.** The entropy of the total system equals the sum of the individual entropies of the two subsystems. In other words, $S(U)$ is proportional to the system size $N$. This statement is true because in fact the square root term in eq. (3.41) becomes negligible for large $N$. To see this, imagine that each particle in a system contributes an equal share of entropy to the entropy $S$ of the whole system, such that $S = Ns$, where the lower-case $s$ denotes the entropy per particle. We can similarly define an energy per particle $u$ such that $U = Nu$ ($s$ and $u$ are independent of $N$). This implies

  $$\frac{\mathrm{d}^2 S(U)}{\mathrm{d}U^2} = \frac{\mathrm{d}^2 N s(u)}{\mathrm{d}(Nu)^2} = \frac{1}{N}\frac{\mathrm{d}^2 s(u)}{\mathrm{d}u^2} \quad \Rightarrow \quad S''(U) \sim \frac{1}{N} \ .$$

  Thus, the second derivative of $S(U)$ scales like $1/N$, and the square root term consequently scales according to

  $$k_B \ln \sqrt{-\frac{2\pi k_B}{S_1''(U_1^*) + S_2''(U - U_1^*)}} \sim \ln \sqrt{N} \ .$$

  For large $N$, we have $N \gg \ln \sqrt{N}$, such that the square root term can be neglected compared to the leading term and $S(U)$ is an extensive function, i.e.,

  $$S(U) \approx S_1(U_1^*) + S_2(U - U_1^*) \ . \tag{3.42}$$

  Eq. (3.42) is exact in the thermodynamic limit ($N \to \infty$).

  In Thermodynamics, we generally distinguish between *extensive* quantities which scale with the system size $N$ and *intensive* quantities which are independent of $N$. Other examples of extensive variables include the total system the volume $V$, energy $U$, and obviously $N$. Contrarily, the temperature $T$ or pressure $P$ belong to the intensive variables.

- **In equilibrium, $S(U)$ is maximal.** As follows from eq. (3.40), the function $S(U) \approx S_1(U_1^*) + S_2(U - U_1^*)$ is maximized with respect to the free variable $U_1$. Since $S$ relates to the phase space volume via (3.38), maximizing $S$ also maximizes $\Gamma$. Therefore, the composite system automatically goes to the state where $U_1 = U_1^*$ because this is the most probable one in equilibrium. This corresponds to the *Second Law of Thermodynamics*: in equilibrium, the entropy $S$ is maximal with respect to all "free" variables (under all constraints imposed by the macrostate).

- **Systems in contact exchange energy until they reach thermal equilibrium.** In equilibrium, where the energy of subsystem 1 has reached $U_1 = U_1^*$, we find based on eq. (3.40) that $S'(U)$ is the same for both subsystems:
$$\frac{\mathrm{d}S_1(U_1^*)}{\mathrm{d}U_1^*} = \frac{\mathrm{d}S_2(U_2^*)}{\mathrm{d}U_2^*} \ ,$$
where $U_2^* = U - U_1*$. This suggests that in equilibrium the derivative $S'$ takes a constant value, which we define as
$$\boxed{\frac{1}{T} := \frac{\mathrm{d}S(U)}{\mathrm{d}U}} \ . \tag{3.43}$$
You may have heard of $T$; in Thermodynamics it is called *temperature*. We deduce that systems in thermal contact must have the same temperature (after sufficient time, when equilibrium is reached). Otherwise, if two systems in thermal contact do not have the same temperature, they exchange energy until the two derivatives $\mathrm{d}S_1/\mathrm{d}U_1^*$ and $\mathrm{d}S_2/\mathrm{d}U_2^*$ are the same. This corresponds to the *Zeroth Law of Thermodynamics* (see chapter 4).

## 3.5 Canonical ensemble

As in the previous section, let us consider two systems in thermal contact (fig. (3.1)). Their combined energy $U$, particle number $N$, and volume $V$ are fixed. The particle number and volume of system 1, $N_1$ and $V_1$, are also fixed. However, the systems may exchange energy, such that $U_1$ may fluctuate. Once again, the "number" of microstates for a given energy $U_1$ is given by the multiplication theorem,

$$\Gamma(U, U_1) = \Gamma_1(U_1) \cdot \Gamma_2(U - U_1) \ . \tag{3.44}$$

We now argue the following. If a microstate of system 1 allows for a relatively high number of microstates of the composite system, then that microstate of system 1 will have a relatively high probability. In other words, the number of microstates of the composite system per microstate of system 1 equals the (non-normalized) probability of that microstate of system 1:

$$\begin{aligned}\rho(U_1, N_1, V_1) &= \frac{\Gamma(U_1, V_1, N_1) \cdot \Gamma(U - U_1, V - V_1, N - N_1)}{\Gamma(U_1, V_1, N_1)} \\ &= \Gamma(U - U_1, V - V_1, N - N_1) \\ &= \exp\left[\frac{1}{k_B} S(U - U_1, V - V_1, N - N_1)\right] \\ &= \exp\left[\frac{1}{k_B} S(U) - \frac{U_1}{k_B} S'(U) + \frac{U_1^2}{2k_B} S''(U) + \dots\right] \ ,\end{aligned} \tag{3.45}$$

where $\rho$ is the non-normalized probability of a microstate of system 1. Here we used eq. (3.38) and expanded $S(U - U_1, V - V_1, N - N_1)$ around $U_1 = 0$. Let us now assume that system 2 is much larger than system 1, i.e. $N_2 = N - N_1 \gg N_1$, $V_2 = V - V_1 \gg V_1$, and $U_2 = U - U_1 \gg U_1$. Then, the second-order term of the Taylor expansion is negligible because

$$\frac{U_1^2}{2k_B} \frac{\partial^2 S(U)}{\partial U^2} \sim \frac{N_1^2}{N} \to 0 \quad (N_1 \ll N) \ .$$

Similar arguments hold for higher-order terms of the expansion. Furthermore, we know from the previous section that

$$\frac{dS(U)}{\mathrm{d}U} = \frac{1}{T} \ ,$$

where $T$ is the temperature of system 2. Inserting this into eq. (3.45), we obtain the *Boltzmann distribution*,

$$\boxed{\rho(U_1) \propto \exp\left(-\frac{U_1}{k_B T}\right)} \ . \tag{3.46}$$

Here we simply discarded the constant factor $e^{S(U)/k_B}$ coming from the zeroth order of the expansion in eq. (3.45), as the distribution is not normalized anyway.

Above we assumed that system 2 is much larger than system 1, such that $N - N_1 \approx N$. In that case, we call system 2 a *reservoir* or heat bath – a system which is so large that its extensive properties like $N, V, U$ essentially do not change when put in contact with a small system like system 1. The Boltzmann distribution, sometimes termed canonical distribution, thus gives the probability distribution for a closed system that may exchange energy with a reservoir. It defines the so-called *canonical ensemble* which is characterized by the macroscopic variables $N, V, T$. The fixed temperature $T$ of the reservoir controls the energy of the closed system. All states are possible, even states with extremely high energy $U_1$, but they will be extremely unlikely unless the heat bath is very, very hot.

**Expectation values and variances.** We now want to calculate the mean energy and its variance for a system governed by the canonical distribution $\rho(U_i)$. Let us suppose the system has discrete states $i$ with energy $U_i$. Then the expectation value of the energy reads

$$\langle U \rangle = \frac{\sum_i U_i \, \rho(U_i)}{\sum_i \rho(U_i)} = \frac{\sum_i U_i e^{-\frac{U_i}{k_B T}}}{\sum_i e^{-\frac{U_i}{k_B T}}} \ . \tag{3.47}$$

It is convenient to define $\beta := \frac{1}{k_B T}$ for increased simplicity. In terms of $\beta$, we write

$$\begin{aligned}\langle U \rangle &= \frac{\sum_i U_i e^{-\beta U_i}}{\sum_i e^{-\beta U_i}} \\ &= \frac{-\frac{\partial}{\partial \beta}\sum_i e^{-\beta U_i}}{\sum_i e^{-\beta U_i}} \\ &= -\frac{\partial}{\partial \beta} \ln\left(\sum_i e^{-\beta U_i}\right) \ , \end{aligned} \tag{3.48}$$

where, in the final step, we have used the chain rule "backwards" to arrive at the logarithm. Thus, the expectation value of the energy in the canonical ensemble is given by

$$\boxed{\langle U \rangle = -\frac{\partial}{\partial \beta} \ln Z \ , \qquad Z = \sum_i e^{-\beta U_i}} \ . \tag{3.49}$$

Here we introduced the *partition function* $Z$. It corresponds to the sum of Boltzmann weights $e^{-\beta U_i}$ over all microstates. The partition function is the central object in statistical mechanics; it allows to calculate any expectation values, variances, etc. by means of suitable derivatives. To obtain the variance of the energy, for example, we calculate

$$\begin{aligned}\frac{\partial^2}{\partial\beta^2}\ln(Z) &= -\frac{\partial}{\partial\beta}\langle U\rangle \\ &= -\frac{\partial}{\partial\beta}\left(\frac{\sum_i U_i e^{-\beta U_i}}{\sum_i e^{-\beta U_i}}\right) \\ &= \frac{\sum_i U_i^2 e^{-\beta U_i}}{\sum_i e^{-\beta U_i}} + \frac{\sum_i U_i e^{-\beta U_i}}{(\sum_i e^{-\beta U_i})^2}\frac{\partial}{\partial\beta}\sum_i e^{-\beta U_i} \\ &= \frac{\sum_i U_i^2 e^{-\beta U_i}}{\sum_i e^{-\beta U_i}} - \frac{(\sum_i U_i e^{-\beta U_i})^2}{(\sum_i e^{-\beta U_i})^2} \\ &= \langle U^2\rangle - \langle U\rangle^2 = \Delta U^2 \ . \end{aligned} \tag{3.50}$$

**Connection to Thermodynamics.** The expectation value of the energy $\langle U\rangle$, as derived here from Statistical Mechanics, is a macroscopic observable that we would also deal with in Thermodynamics. How does the variance, which describes deviations from the mean, connect to Thermodynamics?

Remembering that $\beta$ depends on the temperature $T$, the variance can be written as

$$\begin{aligned}\langle U^2\rangle - \langle U\rangle^2 &= -\frac{\partial}{\partial\beta}\langle U\rangle \\ &= -\frac{\partial T}{\partial\beta}\frac{\partial}{\partial T}\langle U\rangle \\ &= -\left(\frac{\partial\beta}{\partial T}\right)^{-1}\frac{\partial}{\partial T}\langle U\rangle \\ &= k_B T^2\frac{\partial}{\partial T}\langle U\rangle \ . \end{aligned} \tag{3.51}$$

Moreover, we introduce the *heat capacity* $C_V$ at constant volume as the derivative of energy by temperature,

$$C_V = \left.\frac{\partial\langle U\rangle}{\partial T}\right|_{V,N} \ . \tag{3.52}$$

The heat capacity quantifies how the system's energy increases with increasing temperature when the system volume is held fixed. More specifically, it states the amount of heat needed to increase the temperature by one Kelvin. $C_V$ is always positive and extensive; we need to double the heat to warm up double the amount of material!

*Example 3.1.* **Heating water**

At $15^X$C, the specific heat capacity of water is $\tilde{C}_V = 4.2\frac{\mathrm{kJ}}{\mathrm{kg\ K}}$. So to heat up 1 kg of water from $T = 0^X$C (273 K) to $T = 100^X$C (373 K), we need roughly 420 kJ of energy (neglecting for simplicity that $\tilde{C}_V$ is temperature-dependent). A 1000 W heater adds 1 kJ per second and would thus take 7 minutes to bring water from $0^X$C to boiling. In comparison, the same amount of energy would suffice to lift up a weight of 1 kg by 42 kilometers (1 kg excerts 10 N; 1 J=1 N·m; 420 kJ=10 N · 42 km). This demonstrates

> that heat is costly, requiring solutions to avoid wasting precious energy for heating. In chapter 4 we will return to this issue in the context of heat pumps.

Coming back to the variance, we now combine eqs. (3.51) and (3.52) to obtain

$$\langle U^2 \rangle - \langle U \rangle^2 = k_B T^2 C_V \ . \tag{3.53}$$

Accordingly, energy deviations are given by

$$\Delta U = \sqrt{\langle U^2 \rangle - \langle U \rangle^2} = T\sqrt{k_B C_V} \ , \tag{3.54}$$

and the relative energy deviations become

$$\frac{\Delta U}{U} = \frac{T\sqrt{k_B C_v}}{U} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \to 0 \quad (N \to \infty) \ . \tag{3.55}$$

Once again, this result reflects the law of large numbers: as $N \to \infty$, relative deviations in the energy approach zero. In the thermodynamic limit, the canonical ensemble (where the energy may fluctuate) and the microcanonical ensemble (where the energy is fixed) are equivalent because fluctuations around the mean vanish. Thermodynamics does not know about these fluctuations, but Statistical Mechanics does! Variances are determined by so-called response functions (see section 4.3 – which is a consequence of the general fluctuation-dissipation theorem).

## Concept of free energy

We have introduced the canonical partition function $Z(T,V,N) = \sum_i e^{-\beta \mathcal{H}_i}$, where $\beta = (k_B T)^{-1}$ and the index $i$ sums over all microstates. Calculating or approximating this sum is difficult. Therefore, we look for an expression of the partition function which circumvents the explicit summation over microstates. Let us insert unity, i.e.

$$1 = \int_{-\infty}^{\infty} \mathrm{d}U \, \delta(U - \mathcal{H}_i) \ , \tag{3.56}$$

into the expression of the partition function:

$$\begin{aligned} Z &= \sum_i \int_{-\infty}^{\infty} \mathrm{d}U \, \delta(U - \mathcal{H}_i) e^{-\beta \mathcal{H}_i} \\ &= \int_{-\infty}^{\infty} \mathrm{d}U \sum_i \delta(U - \mathcal{H}_i) e^{-\beta U} \\ &= \int_{-\infty}^{\infty} \mathrm{d}U \, \omega(U) e^{-\beta U} \\ &= \int_{-\infty}^{\infty} \mathrm{d}U \, e^{\ln \omega(U) - \beta U} \ . \end{aligned} \tag{3.57}$$

Here $\omega(U) := \sum_i \delta(U - \mathcal{H}_i)$ denotes the density of states, which we may interpret as the number of states with energy $U$. To verify this, consider the following "intuitive proof." The total number of states with energy $\mathcal{H}_i < U$ is given by the function $\Sigma(U,V,N)$, and should likewise be found by summing 1 over all possible states. Using eq. (3.36), we show that[4]

$$\begin{aligned}\Sigma(U) &= \int_{-\infty}^{U} \mathrm{d}U'\, \omega(U') \\ &= \int_{-\infty}^{U} \mathrm{d}U' \sum_i \delta(U' - \mathcal{H}_i) \\ &= \sum_{\substack{i \\ \mathcal{H}_i < U}} \int_{-\infty}^{\infty} \mathrm{d}U'\, \delta(U' - \mathcal{H}_i) \\ &= \sum_{\substack{i \\ \mathcal{H}_i < U}} 1 \;, \end{aligned} \tag{3.58}$$

as required. In section 3.4, we defined the entropy $S(U)$ as

$$\begin{aligned} \frac{S(U)}{k_B} &:= \ln \Gamma(U) = \ln(\omega(U)\Delta) \\ \Rightarrow \quad \frac{S(U)}{k_B} &= \ln \omega(U) + \cancelto{\text{const.}}{\ln \Delta} \;. \end{aligned} \tag{3.59}$$

Here we simply discard the non-extensive term $\ln \Delta$ because it merely adds an irrelevant constant. Therefore we can define the entropy based on the number of states or on the density of states. Note that $\omega(U)$ has units of inverse energy; as will be demonstrated in section 3.8 this is of no concern either. Now, inserting $\ln \omega(U) = S(U)/k_B$ into eq. (3.57), the partition function reads

$$Z = \int_{-\infty}^{\infty} \mathrm{d}U\, e^{-\beta[U - TS(U)]} \;. \tag{3.60}$$

We define $F(U) := U - TS(U)$, yielding

$$\boxed{Z = \int_{-\infty}^{\infty} \mathrm{d}U\, e^{-\beta F(U)} = \int_{-\infty}^{\infty} \mathrm{d}U\, \rho(U) \;, \qquad F = U - TS} \;. \tag{3.61}$$

This expression does not include a sum over all microstates anymore. The partition function is now given in terms of the *free energy* $F$, which is the relevant potential in the canonical ensemble.

To learn more about the free energy, let us Taylor expand $F$ around the most probable energy $U^*$, as we did earlier with the entropy $S$. For the first derivate evaluated at $U^*$, we find

$$\begin{aligned} \left.\frac{\mathrm{d}F(U)}{\mathrm{d}U}\right|_{U^*} &= \left.\frac{\mathrm{d}}{\mathrm{d}U}(U - TS(U))\right|_{U^*} \\ &= 1 - T \left.\frac{dS(U)}{\mathrm{d}U}\right|_{U^*} \\ &= 1 - T\,\frac{1}{T} \\ &= 0 \;. \end{aligned} \tag{3.62}$$

---

[4] Do not get confused with the function $\Sigma$ and the sum $\sum_i$.

The fact that the first derivative vanishes implies that the most probable energy $U^*$ also extremizes the free energy $F$. Note that we deal with two kinds of temperatures here. We must distinguish between the temperature of the reservoir, $T = T(U^*)$, which is independent of $U$, and the temperature of the canonical system, $T_{can} = T(U)$. In thermal equilibrium (at $U^*$), both temperatures coincide and we simply denote them by $T$. Let us also calculate the second derivative,

$$\begin{aligned}
\left.\frac{\mathrm{d}^2F(U)}{\mathrm{d}U^2}\right|_{U^*} &= -T\left.\frac{\mathrm{d}^2S(U)}{\mathrm{d}U^2}\right|_{U^*} \\
&= -T\left.\frac{\mathrm{d}}{\mathrm{d}U}\frac{1}{T(U)}\right|_{U^*} \\
&= \left.\frac{T}{T^2(U)}\,\frac{\mathrm{d}T(U)}{\mathrm{d}U}\right|_{U^*} \\
&= \left.\frac{T}{T^2(U)}\left(\frac{\mathrm{d}U}{\mathrm{d}T}\right)^{-1}\right|_{T(U^*)} \\
&= \frac{1}{T\cdot C_V} \sim \frac{1}{N} > 0\ . 
\end{aligned} \tag{3.63}$$

The inequality in the last line holds for any substance; energy must be added to raise the temperature of a substance. We draw the following conclusions from the preceding investigation.

- The most probable energy $U^*$ is determined by the extremum of the free energy $F$ where $\left.\frac{\mathrm{d}F}{\mathrm{d}U}\right|_{U^*} = 0$. At this energy, the temperature of the canonical system coincides with the temperature $T$ of the reservoir: $\left.\frac{\mathrm{d}S}{\mathrm{d}U}\right|_{U^*} = \frac{1}{T}$.
- We know that the most probable energy $U^*$ exists because $\left.\frac{\mathrm{d}^2F}{\mathrm{d}U^2}\right|_{U^*} > 0$. This result also implies, together with $\left.\frac{\mathrm{d}F}{\mathrm{d}U}\right|_{U^*} = 0$, that $F$ has a minimum at $U^*$.
- The variance of the energy, $\langle (U-U^*)^2\rangle \approx C_V \sim N$ is extensive.
- The relative variance becomes negligible for large $N$:

  $$\frac{\left\langle (U-U^*)^2\right\rangle}{U^{*2}} = \left\langle \left(\frac{U}{U^*}-1\right)^2\right\rangle \sim \frac{1}{N} \to 0 \quad (N\to\infty)\ .$$

- We have shown that $\frac{\mathrm{d}^2S}{\mathrm{d}U^2} < 0$, as used in the derivation of the entropy as an extensive function (see sec. 3.4). Thus, the curvature of the entropy around its most probable value is positive. In the canonical ensemble, the most probable state of the system is characterized by a balance between minimizing the energy and maximizing the entropy. At this equilibrium point, the free energy is minimal.

Since the relative variance of the energy $U$ approaches zero for very large $N$, the distribution of energies is sharply peaked at the dominating energy $U^*$. In the thermodynamic limit, in fact, energies other than $U^*$ become irrelevant; the distribution approaches a $\delta$-distribution. For the partition function $Z$ this means

$$Z = \int \mathrm{d}U\, e^{-\beta F(U)} \overset{N\to\infty}{=} e^{-\beta F(U^*)}\ . \tag{3.64}$$

Corrections to this limit can be calculated with a saddle-point approximation, using a Taylor expansion and Gaussian integration as we did when deriving eq. (3.41) in section 3.4. Rearranging eq. (3.64) for $F$ yields

$$\boxed{F = -k_B T \ln Z} \; . \tag{3.65}$$

Though derived in the thermodynamic limit, this result for the free energy $F$ also holds for finite $N$. The mean energy $\langle U \rangle = U^*$ can by obtained by the following recipe: We combine $\beta F = -\ln Z$ (eq. (3.65)) with the previously established result,

$$\begin{aligned} \langle U \rangle &= -\frac{\partial \ln Z}{\partial \beta} \\ &= \frac{\int \mathrm{d}U \, U e^{-\beta F(U)}}{\int \mathrm{d}U \, e^{-\beta F(U)}} \\ &= \frac{\int \mathrm{d}U \, U e^{-\beta U + S(U)/k_B}}{\int \mathrm{d}U \, e^{-\beta U + S(U)/k_B}} \; , \end{aligned}$$

and obtain

$$\langle U \rangle = \frac{\partial (F\beta)}{\partial \beta} = F + \beta \frac{\partial F}{\partial \beta} = F + \frac{1}{k_B T} \frac{\partial T}{\partial \beta} \frac{\partial F}{\partial T} \; . \tag{3.66}$$

The derivative $\partial T / \partial \beta$ is the reciprocal of $\partial \beta / \partial T$, which becomes

$$\frac{\partial \beta}{\partial T} = \frac{\partial (1/(k_B T))}{\partial T} = -\frac{1}{k_B T^2} \; .$$

Thus we find that $\langle U \rangle$, often simply written as $U$ while tacitly referring to the mean value, is given by

$$U = F - T \frac{\partial F}{\partial T} \; . \tag{3.67}$$

Together with $F = U - TS$ this implies

$$\boxed{\frac{\partial F}{\partial T} = -S} \; . \tag{3.68}$$

The boxed equation states an important thermodynamic relation between free energy and entropy. Another central relation that we already know is $\partial S / \partial U = 1/T$ (eq. (3.43)).

In the canonical ensemble, the equilibrium energy $U \equiv \langle U \rangle = U^*$ is a function of the temperature of the reservoir, $U(T)$. Therefore, functions like entropy or the free energy depend on temperature $T$, particle number $N$, and volume $V$:

$$S = S(T, V, N) \; , \quad F = F(T, V, N) \; , \quad U = U(T, V, N) \; , \quad Z = Z(T, V, N) \; , \quad \ldots$$

**Shannon entropy.** The term *entropy* also appears in information theory, where it quantifies the amount of *missing information*. In this context, the common quantity is the *Shannon entropy* defined as

$$\boxed{\mathcal{S} := -\sum_i \tilde{p}_i \ln(\tilde{p}_i)} \; , \tag{3.69}$$

where $\tilde{p}_i$ denotes the normalized probability of the event (or state) $i$ and the sum goes over all events/states. In this little excursion, we want to find out how the Shannon entropy relates to the entropy as defined in Thermodynamics in terms of the canonical partition function.

According to eq. (3.49), the partition function $Z$ of the canonical ensemble is given by the sum over all Boltzmann weights,

$$Z = \sum_i e^{-\beta H_i} = \sum_i p_i \ ,$$

where $H_i$ represents the energy of the state $i$ and $p_i$ is the non-normalized (!) probability of this state. From the partition function we obtain the free energy according to

$$F = -k_B T \ln Z = -k_B T \ln \left( \sum_i e^{-\frac{H_i}{k_B T}} \right) \ ,$$

and the entropy follows from differentiating by temperature, eq. (3.68), as

$$S = -\frac{\partial F}{\partial T} = k_B \ln \left( \sum_i p_i \right) + \frac{1}{T} \frac{\sum_i H_i p_i}{\sum_i p_i} \ .$$

Since $p_i = \exp(-\beta H_i)$ implies $H_i = -k_B T \ln p_i$, we may rewrite the entropy as

$$\frac{S}{k_B} = \ln \left( \sum_i p_i \right) - \frac{\sum_i p_i \ln p_i}{\sum_j p_j} \ .$$

In terms of the normalized probability $\tilde{p}_i := \frac{p_i}{\sum_j p_j}$, this becomes

$$\begin{aligned}
\frac{S}{k_B} &= \ln \left( \sum_i p_i \right) - \sum_i \tilde{p}_i \ln p_i \\
&= \ln \left( \sum_i p_i \right) - \sum_i \tilde{p}_i \ln \left( \tilde{p}_i \sum_j p_j \right) \\
&= \ln \left( \sum_i p_i \right) - \sum_i \tilde{p}_i \ln \tilde{p}_i - \underbrace{\sum_i \tilde{p}_i}_{=1} \ln \left( \sum_j p_j \right) \\
&= -\sum_i \tilde{p}_i \ln(\tilde{p}_i) = \mathcal{S} \ .
\end{aligned}$$

Thus we have shown that the entropy in the canonical ensemble and the Shannon entropy from information theory are indeed closely related concepts ($\mathcal{S} \leftrightarrow S/k_B$). They differ only by a prefactor corresponding to the Boltzmann constant.

## 3.6 Examples of canonical distributions

After introducing the canonical ensemble as a fundamental concept in Statistical Mechanics, we want to discuss what the canonical distribution, or Boltzmann distribution, implies for the velocity distribution of gas particles and for a gas in a gravitational field. The ideal gas will serve as the underlying model.

### 3.6.1 Velocity distribution of ideal gas atoms

The Hamiltonian $\mathcal{H}_{\text{tot}}$ of a gas composed of $N$ particles may be written as

$$\mathcal{H}_{\text{tot}} = \underbrace{\sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}}_{\text{kinetic}} + \underbrace{\sum_{i=1}^{N} V(\vec{q}_i)}_{\text{potential}} + \underbrace{\sum_{i=1}^{N} \sum_{j=i+1}^{N} V_{\text{pair}}(\vec{q}_i, \vec{q}_j)}_{\text{interactions}} \ . \tag{3.70}$$

The first term is the total kinetic energy; the second term describes the potential energy due to an external potential. Finally, the third term represents two-body interactions between gas particles. This could include gravitational interaction, Coulomb interaction, dipole-dipole, interaction, and more. In principle, even three-body interactions are feasible but we refrain from including them here.

**Ideal gas.** The full Hamiltonian (eq. (3.70)) is often very difficult to handle, particularly due to the complicated nature of pair interactions (not even to speak of three-body interactions). Therefore it is very common to work with the *ideal gas*, defined by the following assumptions:

- No interactions between gas particles;
- The gas consists of point particles which do not take up volume.

Thus any gas atom moves around without being influenced by other gas atoms. Although this is clearly an idealization, the ideal gas is capable of describing many fundamental properties of real gases. If we additionally assume the absence of an external potential, the ideal gas Hamiltonian just contains the kinetic energy terms,

$$\mathcal{H}_{\text{ideal}} = \sum_{i=1}^{N} \left( \frac{\vec{p}_i^{\,2}}{2m} \right) \ . \tag{3.71}$$

The canonical partition function of the ideal gas is then given by

$$\begin{aligned} Z &= \int_{-\infty}^{\infty} \mathrm{d}\vec{p}_1 \, \mathrm{d}\vec{p}_2 \cdots \mathrm{d}\vec{p}_N \int_V \mathrm{d}\vec{q}_1 \, \mathrm{d}\vec{q}_2 \cdots \mathrm{d}\vec{q}_N \ e^{-\beta \mathcal{H}_{\text{ideal}}} \\ &= \int_{-\infty}^{\infty} \mathrm{d}\vec{p}_1 \, \mathrm{d}\vec{p}_2 \cdots \mathrm{d}\vec{p}_N \int_V \mathrm{d}\vec{q}_1 \, \mathrm{d}\vec{q}_2 \cdots \mathrm{d}\vec{q}_N \ e^{-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}} \\ &= \int \mathrm{d}\vec{p}_1 \, V e^{-\frac{\beta p_1^2}{2m}} \int \mathrm{d}\vec{p}_2 \, V e^{-\frac{\beta p_2^2}{2m}} \cdots \int \mathrm{d}\vec{p}_N \, V e^{-\frac{\beta p_N^2}{2m}} \\ &= (Z_X)^N \ , \end{aligned} \tag{3.72}$$

where $Z_X$ represents the single-particle partition function. Note that the partition function factorizes completely, which should not surprise us since we neglected interactions.

**Equipartition theorem.** The kinetic energy of a single gas atom in three-dimensional space is

$$E_{\text{kin}} = \frac{\vec{p}^{\,2}}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \ .$$

For an isotropic system, where no direction is preferred, the expectation values of the momenta must be equal in all directions, i.e.

$$\langle p_x^2 \rangle = \langle p_y^2 \rangle = \langle p_z^2 \rangle \ .$$

Furthermore, the Boltzmann distribution factorizes with respect to the different directions such that

$$e^{-\beta \frac{\vec{p}^2}{2m}} = e^{-\beta \frac{p_x^2}{2m}} \, e^{-\beta \frac{p_y^2}{2m}} \, e^{-\beta \frac{p_z^2}{2m}} \; . \tag{3.73}$$

Since all directions are equivalent, let us now focus on the $x$ direction without loss of generality. The expectation value of the kinetic energy is

$$\begin{aligned} \left\langle \frac{p_x^2}{2m} \right\rangle &= \frac{\displaystyle\int \mathrm{d}p_x \, \frac{p_x^2}{2m} e^{-\beta \frac{p_x^2}{2m}}}{\displaystyle\int \mathrm{d}p_x \, e^{-\beta \frac{px^2}{2m}}} \\ &= -\frac{\partial}{\partial \beta} \ln \left( \int_{-\infty}^{\infty} \mathrm{d}p_x \, e^{-\beta \frac{p_x^2}{2m}} \right) \\ &= -\frac{\partial}{\partial \beta} \ln \sqrt{\frac{2\pi m}{\beta}} \\ &= \frac{\partial}{\partial \beta} \frac{1}{2} \Big( \ln \beta - \ln(2\pi m) \Big) \\ &= \frac{1}{2\beta} \\ &= \frac{k_B T}{2} \; . \end{aligned} \tag{3.74}$$

Thus, we have shown that the kinetic energy along one coordinate axis is, on average, $k_B T/2$. This generalizes into the *equipartition theorem*.

**Equipartition theorem.** A degree of freedom $x$, described by a quadratic energy $\mathcal{H}_x = \alpha x^2$, has an average energy of $\langle \mathcal{H}_x \rangle = k_B T/2$. For a system with $f$ degrees of freedom this implies that the total energy is

$$U = \langle \mathcal{H} \rangle = \frac{f}{2} k_B T \; . \tag{3.75}$$

In the monoatomic ideal gas, each atom has three degrees of freedom $(p_x, p_y, p_z)$.[5] Therefore, each atom contributes a mean kinetic energy of

$$E_{\text{kin}} = 3 \left\langle \frac{p_x^2}{2m} \right\rangle = \frac{3}{2} k_B T \; , \tag{3.76}$$

and an ideal gas of $N$ particles has the total energy

$$\boxed{U = \frac{3}{2} N k_B T} \; . \tag{3.77}$$

---

[5] For an ideal gas in a vanishing external potential, the Hamiltonian does not depend on the position coordinates of the gas particles, so the position coordinates do not count as degrees of freedom. Thus, for a monoatomic gas $f = 3N$. On the other hand, a diatomic gas such as $O_2$ has $(6+1)N$ degrees of freedom ($2 \times 3$ momentum coordinates and 1 inter-atomic scalar distance coordinate).

As a consequence, the heat capacity of an ideal gas does not depend on temperature nor on the volume:

$$C = \frac{\mathrm{d}U}{\mathrm{d}T} = \frac{f k_B}{2} = \frac{3 N k_B}{2} \ . \tag{3.78}$$

But what do these results tell us about the velocity distribution in an ideal gas? Using eq. (3.76), we know that

$$\begin{aligned} \left\langle \frac{m \vec{v}^2}{2} \right\rangle &= \left\langle \frac{\vec{p}^2}{2m} \right\rangle = \frac{3}{2} k_B T \\ \Rightarrow \quad \bar{v} &:= \sqrt{\langle \vec{v}^2 \rangle} = \sqrt{\frac{3 k_B T}{m}} \ , \end{aligned} \tag{3.79}$$

where $\bar{v}$ denotes the average speed of a gas molecule and $m$ is its mass. Thus, the absolute value of the mean particle velocity is proportional to the square root of the temperature. Note, however, that the expectation value of the velocity $\vec{v}$ itself must vanish, $\langle \vec{v} \rangle = 0$. Otherwise the gas as a whole would move in a certain direction, which violates our assumption of isotropy.

*Example 3.2.* **Gas molecules are fast!**

At room temperature $T = 300\,\mathrm{K}$, the mean kinetic energy of a gas molecule is of the order $k_B T \approx 4 \times 10^{-21}\,\mathrm{J}$. As already calculated in the introductory example of section 1.4, the resulting speeds for typical gases like $O_2$ or $H_2$ amount to several hundred meters per second (according to eq. (3.79)). For example, we found

$$\bar{v}_{O_2} \approx 460\,\mathrm{m\,s^{-1}} \ ,$$

which is comparable to the speed of sound. Thus, the air molecules around you fly about very fast! This result is exact and is not modified in the presence of interaction.

### 3.6.2 Maxwell-Boltzmann distribution

We already know the mean squared velocity of ideal gas molecules – but what does the shape of the speed distribution actually look like? According to the Boltzmann distribution, the velocity component $v_x$ follows the distribution

$$\rho(v_x) \propto \exp\left(-\beta \frac{p_x^2}{2m}\right) = \exp\left(-\beta \frac{m v_x^2}{2}\right) \ . \tag{3.80}$$

We reemphasize that this distribution is not normalized. The components $v_y$ and $v_z$ follow analogously. Based on eq. (3.80), we compute the expectation value of the second moment of $\vec{v}$,

$$\begin{aligned} \left\langle \vec{v}^2 \right\rangle &= \frac{\int \mathrm{d}\vec{v}\, \vec{v}^2 \rho(\vec{v}_x) \rho(\vec{v}_y) \rho(\vec{v}_z)}{\int \mathrm{d}\vec{v}\, \rho(\vec{v}_x) \rho(\vec{v}_y) \rho(\vec{v}_z)} \\ &= \frac{\int_{-\infty}^{\infty} \mathrm{d}v_x \mathrm{d}v_y \mathrm{d}v_z \, (v^2 + v_y^2 + v_z^2) e^{-\frac{\beta m}{2}(v_x^2 + v_y^2 + v_z^2)}}{\int_{-\infty}^{\infty} \mathrm{d}v_x \mathrm{d}v_y \mathrm{d}v_z \, e^{-\frac{\beta m}{2}(v_x^2 + v_y^2 + v_z^2)}} \ . \end{aligned} \tag{3.81}$$

This expression simplifies when we switch to spherical coordinates. Writing $v \equiv ||\vec{v}||$ and using the relation between volume elements $\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z = v^2\mathrm{d}v\mathrm{d}\Omega$, we find

$$\begin{aligned}\left\langle \vec{v}^2 \right\rangle &= \frac{\int_\Omega \mathrm{d}\Omega \int_0^\infty \mathrm{d}v\, v^4 e^{-\frac{\beta m v^2}{2}}}{\int_\Omega \mathrm{d}\Omega \int_0^\infty \mathrm{d}v\, v^2 e^{-\frac{\beta m v^2}{2}}} \\ &= \frac{\int_0^\infty \mathrm{d}v\, v^4 e^{-\frac{\beta m v^2}{2}}}{\int_0^\infty \mathrm{d}v\, v^2 e^{-\frac{\beta m v^2}{2}}} \\ &\equiv \int_0^\infty \mathrm{d}v\, v^2 \rho_{MB}(v) \ . \end{aligned} \tag{3.82}$$

Here we have introduced the *Maxwell-Boltzmann distribution* $\rho_{MB}$, defined by

$$\boxed{\rho_{MB}(v) := \frac{v^2 \exp\left(-\frac{\beta m v^2}{2}\right)}{\frac{1}{4\pi}\left(\frac{2\pi}{\beta m}\right)^{3/2}}} \ . \tag{3.83}$$

The Maxwell-Boltzmann distribution is normalized in the sense that[6]

$$\int_0^\infty \mathrm{d}v\, \rho_{MB}(v) = 1 \ . \tag{3.85}$$

Thus, it expresses the probability that a gas particle with mass $m$ in an ideal gas at temperature $T$ moves around with the speed $v$. What is the most probable speed? To answer this question, we must find the maximum of $\rho_{MB}$. Equating the first derivative with zero yields

$$\begin{aligned} 0 &= \left.\frac{\mathrm{d}\rho_{MB}(v^2)}{\mathrm{d}(v^2)}\right|_{v^2=v^2_{\max}} \\ \Rightarrow \quad 0 &= 1 - \frac{\beta m}{2} v^2_{\max} \\ \Rightarrow \quad & \boxed{v_{\max} = \sqrt{\frac{2}{\beta m}} = \sqrt{\frac{2k_BT}{m}}} \ . \end{aligned} \tag{3.86}$$

Let us compare this result with the mean of the distribution (see eq. (3.79)). Since $\langle v^2 \rangle = 3k_BT/m$, we find

$$\frac{\langle v^2 \rangle}{v^2_{\max}} = \frac{3}{2} \ . \tag{3.87}$$

---

[6] Let us prove that $\rho_{MB}$ is normalized. Define the normalization constant $C := 4\pi\left(\frac{2\pi}{\beta m}\right)^{-3/2}$. Then, substituting $a := \beta m/2$, we have

$$\begin{aligned}\int_0^\infty \mathrm{d}v\, \rho_{MB} &= \frac{1}{2}\int_{-\infty}^\infty \mathrm{d}v\, C v^2 e^{-av^2} \\ &= -\frac{C}{2}\frac{\mathrm{d}}{\mathrm{d}a}\int_{-\infty}^\infty \mathrm{d}v\, e^{-av^2} = -\frac{C}{2}\frac{\mathrm{d}}{\mathrm{d}a}\sqrt{\frac{\pi}{a}} \\ &= \frac{C}{2}\cdot\frac{\sqrt{\pi}}{2}a^{-3/2} = C\frac{1}{4\pi}\left(\frac{2\pi}{\beta m}\right)^{3/2} \\ &= C \cdot \frac{1}{C} = 1 \qquad \text{q.e.d.} \end{aligned} \tag{3.84}$$

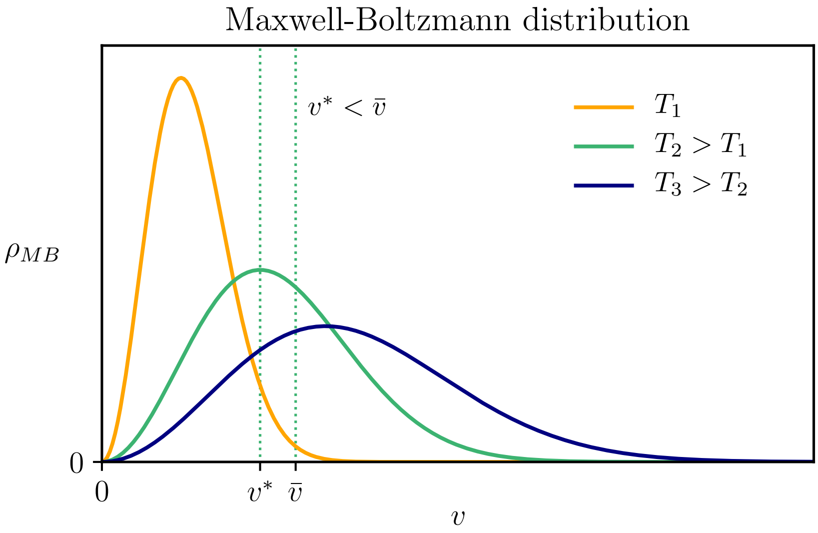

**Figure 3.2: Maxwell-Boltzmann distribution** as a function of velocity $v$ for three different temperatures. With increasing temperature, the distribution broadens and shifts towards larger velocities. Note the asymmetry of the distribution: the mean $\bar{v}$ exceeds the maximum value $v^* \equiv v_{\mathsf{max}}$ (shown for the green line here).

This means that the distribution is asymmetric because its mean differs from its maximum. In other words, the average speed of a gas particle does not coincide with the most probable speed. Indeed, the law of large numbers does not apply here since the Maxwell-Boltzmann distribution merely describes a single-particle property. This is highlighted by the fact that $\rho_{MB}$ does not depend on the particle number $N$. Figure 3.2 illustrates the distribution for three different temperatures.

### 3.6.3 Barometric height formula

The canonical distribution also allows for a rough estimate of the height of Earth's atmosphere. For this purpose, we consider a non-interacting gas in a uniform gravitational field. Sufficiently close to the Earth's surface, the Hamiltonian of the system reads

$$\mathcal{H} = \sum_{i=1}^{N} \left( \frac{\vec{p}_i^{\,2}}{2m} + mgz_i \right) . \tag{3.88}$$

Here $z_i \equiv q_{z,i}$ denotes the $z$ position (height above surface of Earth) of the $i$-th particle above the surface and $g \approx 9.81\,\mathrm{m\,s^{-2}}$ is the acceleration due to gravity. In the corresponding Boltzmann weight $e^{-\beta\mathcal{H}}$, all positions $z_i$ and momenta $\vec{p}_i$ factorize into separate exponentials. Then, the unnormalized height distribution of a single air molecule is

$$\rho(z) = e^{-\beta mgz} . \tag{3.89}$$

This is known as the *barometric height formula*. It allows a basic estimate of atmospheric pressure as a function of altitude. From eq. (3.89) we may calculate the mean altitude $z$

of an air molecule,

$$\begin{aligned}
\langle z\rangle &= \frac{\int_0^\infty \mathrm{d}z\, z e^{-\beta mgz}}{\int_0^\infty \mathrm{d}z\, e^{-\beta mgz}} \\
&= -\frac{\mathrm{d}}{\mathrm{d}(\beta mg)} \ln\left(\int_0^\infty dz e^{-\beta mgz}\right) \\
&= -\frac{\mathrm{d}}{\mathrm{d}(\beta mg)} \ln\left(\frac{1}{\beta mg}\right) \\
&= \frac{k_B T}{mg} \ . \qquad (3.90)
\end{aligned}$$

For a nitrogen molecule at around $0^X$C, this yields an average height of about 15 km above sea level, which seems reasonable for the Earth's atmosphere. However, the barometric height distribution remains a rather crude approximation. Firstly, we fully ignored the fact that the atmospheric temperature varies significantly as a function of altitude; secondly, we neglected that $g$ decreases with increasing height. At large altitudes compared to the radius $R$ of the Earth, we must in fact consider the exact potential,

$$V(z) = \frac{GMm}{R+z} \ ,$$

where $G$ denotes the gravitational constant and $M$ is the Earth's mass. If $z > R$, the exponential $e^{-\beta V(z)}$ approaches unity, and the integral $\int_0^\infty \mathrm{d}z\, e^{-\beta GMm/(R+z)}$ diverges. Hence the atmosphere evaporates to space and has not yet reached equilibrium.

## 3.7 Ideal gas in the canonical ensemble

In this section we will apply the toolbox of the canonical ensemble (section 3.5) to the ideal gas, which we introduced in section 3.6.1.

The partition function of an ideal gas composed of $N$ identical mono-atomic particles, confined in a volume $V$, is given by

$$Z(N,V,T) = \frac{1}{N!}\prod_{j=1}^{N}\left[\frac{1}{h^3}\int_V \mathrm{d}^3 q_j \int \mathrm{d}^3 p_j\right] e^{-\beta \mathcal{H}(\vec{q}_{3N},\vec{p}_{3N})} \ . \qquad (3.91)$$

To obtain this expression, we "borrowed" some knowledge from quantum mechanics (see chapter 6):

- Since gas atoms or molecules are indistinguishable particles, we must include the factor $\frac{1}{N!}$ to avoid over-counting of microstates. This is because there are $N!$ possible permutations of particle indices which all describe exactly the same state. It does not matter which particle is at which position because we *cannot* tell the difference. If we would not correct for over-counting, this would lead to the *Gibbs paradox* of non-extensive entropy, which we will address in a problem set.
- Planck's constant $h = 6.626 \times 10^{-34}$ Js ($1\,\mathrm{Js} = 1\,\mathrm{kg\,m^2\,s^{-1}}$) appears in Quantum Statistics. More specifically, the factor $h^3$ emerges when transforming from a sum over discrete quantum states to a continuous phase space integral (see section 6.3). Planck's constant has units of an action and causes the integral over phase space,

and thus $Z$ itself, to become unitless. In any case, the value of $h$ is irrelevant for any physical observable since we only use the logarithm of $Z$ (e.g. $F = -k_B T \ln(Z)$).

For a free ideal gas, the Hamiltonian $\mathcal{H}$,

$$\mathcal{H}(q_{3N}, p_{3N}) = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} \ ,$$

only contains the kinetic energy term and does not depend on the position coordinates $\vec{q}_i$. Therefore the three-dimensional position integral simply yields the total volume $V$,

$$\int_V \mathrm{d}^3 q_i \, 1 = \iiint \mathrm{d}q_{x,i} \mathrm{d}q_{y,i} \mathrm{d}q_{z,i} \, 1 = V \ .$$

Since the ideal gas partition function factorizes, we may calculate it explicitly:

$$\begin{aligned} Z &= \frac{1}{N!} \prod_{j=1}^{N} \left[ \frac{1}{h^3} \int_V \mathrm{d}^3 q_j \int \mathrm{d}^3 p_j \right] e^{-\beta \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m}} \\ &= \frac{1}{N!} \left[ \frac{1}{h^3} \int_V \mathrm{d}^3 q \int \mathrm{d}^3 p e^{-\frac{\beta \vec{p}^2}{2m}} \right]^N \\ &= \frac{1}{N!} \left( \frac{V}{h^3} \right)^N \left[ \int_{-\infty}^{\infty} \mathrm{d}p \, e^{-\frac{\beta p^2}{2m}} \right]^{3N} \\ &= \frac{1}{N!} \left( \frac{V}{h^3} \right)^N \left( \sqrt{\frac{2\pi m}{\beta}} \right)^{3N} \\ &= \frac{1}{N!} \left( \frac{V}{\lambda_t^3} \right)^N \ . \end{aligned} \tag{3.92}$$

In the final step, we have defined the *thermal wavelength* $\lambda_t$,

$$\boxed{\lambda_t := \frac{h}{\sqrt{2\pi m k_B T}}} \ . \tag{3.93}$$

We may think of the thermal wavelength as the de Broglie wavelength $\lambda = h/p$ of a particle with thermal energy $\pi k_B T$. Indeed, if $E_t = \pi k_B T = p_t^2/(2m)$, then $\lambda_t = h/p_t$.

From eq. (3.92), we clearly see that the canonical thermodynamic variables of the partition function are $T$, $V$, and $N$, i.e. $Z \equiv Z(T, V, N)$. The same holds for the free energy $F(T, V, N)$, which we compute in the following:

$$\begin{aligned} F &= -k_B T \ln(Z) \\ &= k_B T N \ln \left( \frac{\lambda_t^3}{V} \right) + k_B T \ln(N!) \ . \end{aligned} \tag{3.94}$$

Using Stirling's formula (eq. (2.19)), this approximates to

$$\boxed{F(T, V, N) = k_B T N \left[ \ln \left( \frac{N}{V} \lambda_t^3 \right) - 1 \right] + \mathcal{O}(\ln N)} \ . \tag{3.95}$$

We see that the free energy scales like the system size $N$; thus, $F$ is an extensive quantity. If we had not included the factorial pre-factor to avoid over-counting, $F$ would scale like $N \ln N$.

From the free energy, we obtain many thermodynamic quantities by taking partial derivatives. For instance, we have derived (eq. (3.68))

$$S = -\frac{\partial F}{\partial T} \; .$$

To calculate the derivative it may help to split the logarithm into several terms:

$$\begin{aligned} F &= k_B T N \left[ \ln \left( \frac{N}{V} h^3 \left( 2\pi m k_B T \right)^{-\frac{3}{2}} \right) - 1 \right] \\ &= k_B T N \left[ \ln \left( \frac{N}{V} h^3 \right) - \frac{3}{2} \ln \left( 2\pi m k_B \right) - \frac{3}{2} \ln \left( T \right) - 1 \right] \; . \end{aligned}$$

Now we easily find the entropy of the ideal gas,

$$\begin{aligned} S &= -\frac{F}{T} + \frac{3}{2} k_B N \\ &= -k_B N \left[ \ln \left( \frac{N}{V} \lambda_t^3 \right) - 1 \right] + \frac{3}{2} k_B N \\ \Rightarrow \quad & \boxed{S(T,V,N) = -k_B N \left[ \ln \left( \frac{N}{V} \lambda_t^3 \right) - \frac{5}{2} \right]} \; . \end{aligned} \tag{3.96}$$

Knowing $F$ and $S$, the internal energy $U = F + TS$ (from eq. (3.61)) follows as

$$\boxed{U(T,N) = \frac{3}{2} N k_B T} \; . \tag{3.97}$$

This result perfectly agrees with the equipartition theorem (see eq. (3.75)). Note that the energy is volume-independent as it only receives contributions from the kinetic energy ($\propto k_B T$) of all $N$ particles.

We established that the change of free energy under variation of the temperature defines the entropy. Apart from $T$, the free energy also depends on $V$ and $N$. In the canonical ensemble, $N$ remains constant. But what is $(\partial F/\partial V)_{T,N}$? Differentiating eq. (3.95) by volume, we get

$$\frac{\partial F}{\partial V} = \frac{\partial}{\partial V} k_B T N \left[ \ln \left( N \lambda_t^3 \right) - \ln V - 1 \right] = -\frac{N k_B T}{V} \; . \tag{3.98}$$

A comparison with the ideal gas law, which we previously derived in section 1.4, shows that

$$PV = N k_B T \quad \Leftrightarrow \quad \frac{N k_B T}{V} = P \; . \tag{3.99}$$

Therefore we define the pressure $P$ as[7]

$$\boxed{P := -\left( \frac{\partial F}{\partial V} \right)_{T,N}} \; . \tag{3.100}$$

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[7] You may know the pressure by its mechanical definition $P = \mathcal{F}/A$, where $\mathcal{F}$ is the force acting on the surface area $A$. To see how this relates to the thermodynamic definition of pressure $P = -\partial F/\partial V$, we refer back to the derivation of the Boyle-Mariotte law in section 1.4.

Let us now write down the total differential of $F$:

$$\mathrm{d}F(T,V,N) = \left(\frac{\partial F}{\partial T}\right)_{V,N}\mathrm{d}T + \left(\frac{\partial F}{\partial V}\right)_{T,N}\mathrm{d}V + \left(\frac{\partial F}{\partial N}\right)_{T,V}\mathrm{d}N\ . \tag{3.101}$$

As mentioned, $N$ is fixed in the canonical ensemble, so the total differential reduces to

$$\mathrm{d}F(T,V,N) = -S(T,V,N)\mathrm{d}T - P(T,V,N)\mathrm{d}V \qquad (N \text{ fixed})\ . \tag{3.102}$$

Using $U = F + TS$, we obtain the total differential of $U$ via a Legendre transform,

$$\begin{aligned}\mathrm{d}U &= \mathrm{d}F + T\mathrm{d}S + S\mathrm{d}T\\ &= -S\mathrm{d}T - P\mathrm{d}V + T\mathrm{d}S + S\mathrm{d}T\\ &= T\mathrm{d}S - P\mathrm{d}V\ .\end{aligned} \tag{3.103}$$

The result reveals that the canonical variables of the internal energy are entropy and volume. Given $U(S,V)$, we have

$$\boxed{P = -\left(\frac{\partial U}{\partial V}\right)_S}\ ,\quad \boxed{T = -\left(\frac{\partial U}{\partial S}\right)_V}\ . \tag{3.104}$$

By deriving eq. (3.103), we have obtained the *First Law of Thermodynamics* in differential form,

$$\mathrm{d}U = \Delta Q - \Delta W = T\mathrm{d}S - P\mathrm{d}V\ . \tag{3.105}$$

The law states that the internal energy of a gas may change in two ways:

- The gas can perform mechanical work $\Delta W = P\mathrm{d}V$ *on* its surroundings.
- There may be a heat transfer $\Delta Q = T\mathrm{d}S$ *from* the surroundings *to* the gas.

Thus $\mathrm{d}U$ is given by the balance of absorbed heat minus work done. Note that the definition of mechanical work $\Delta W = P\mathrm{d}V$ also indicates that the relation (3.100) makes sense. We will continue with a systematic discussion of total differentials, derivatives of thermodynamic potentials, and the laws of Thermodynamics in chapter 4. For now, we direct our focus back towards the ideal gas. To get the explicit function $U(S,V)$ for an ideal gas, we take eq. (3.96) and replace the temperature by

$$k_BT = \frac{2}{3}\frac{U}{N}\ ,$$

as follows from eq. (3.97). This yields the *Sackur-Tetrode equation*,

$$\boxed{S(U,V,N) = -k_BN\left[\ln\left(\frac{h^3N}{V\left(2\pi m\frac{2U}{3N}\right)^{3/2}}\right) - \frac{5}{2}\right]}\ . \tag{3.106}$$

From this formula, we derive $U(S,V,N)$ by inversion, i.e. by solving for $U$. In turn, $U(S,V,N)$ enables us to calculate the temperature $T(S,V,N) = (\partial U/\partial S)_{V,N}$, which leads back to the free energy $F = U - TS$. This means that the conversion from $F(T,V,N)$ via $S(U,V,N)$ to $U(S,V,N)$ is reversible. All these so-called *thermodynamic potentials* contain the complete information about the system and we may switch back and forth between them as we wish.

As a last check, let us see whether

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

holds as it should. The Sackur-Tetrode equation (3.106) gives

$$S(U,V,N) = k_B N \frac{3}{2} \ln U + f(V,N)$$
$$\Rightarrow \quad \frac{\partial S}{\partial U} = \frac{3}{2}\frac{k_B N}{U} \overset{*}{=} \frac{1}{T} \qquad \text{q.e.d.} \tag{3.107}$$

At the equality marked by $*$ we have inserted the ideal gas result $U = \frac{3}{2} N k_B T$. Thus everything is consistent!

## 3.8 Ideal gas in the microcanonical ensemble

The framework of the canonical ensemble allowed us to determine the thermodynamic properties of an ideal gas, e.g. entropy, energy, and free energy. Now we want to study the ideal gas in the microcanonical ensemble. Will we get the same results?

In the microcanonical ensemble, the total energy $U$ is fixed and all microstates with that energy are equally probable. Recall that the density of states $\omega(U)$ is defined as

$$\omega(U,V) = \lim_{\Delta \to 0} \frac{\Gamma(U,V)}{\Delta} \ , \tag{3.108}$$

where $\Gamma$ denotes the phase space volume (see section 3.4) and $\Delta$ represents a small energy range around $U$. If we know the density of states, we can find the entropy using eq. (3.59),

$$S = k_B \ln \omega \ . \tag{3.109}$$

Our task is thus to calculate the density of states $\omega(U,V,N)$ of the ideal gas,

$$\omega(U,V,N) = \frac{1}{N!} \prod_{j=1}^{N} \left[ \frac{1}{h^3} \int_V \mathrm{d}^3 q_j \int \mathrm{d}^3 p_j \right] \delta\left( \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} - U \right) \ . \tag{3.110}$$

Here the factor $N!$ avoids over-counting and $h^3$ originates from quantum mechanics (see previous section). The position integral extends over the volume $V$ that confines the gas. Furthermore, the $\delta$ distribution restricts the integral over phase space to a hyper surface on which the energy of the gas, given by its total kinetic energy, equals $U$.

First, we perform the integral over all positions and rescale the momenta according to $\vec{x}_j := \sqrt{\frac{1}{2m}} \vec{p}_j$. This leads to

$$\omega = \frac{1}{N!} \left( \frac{V (2m)^{3/2}}{h^3} \right)^N \int \mathrm{d}x_1 \mathrm{d}x_2 \cdots \mathrm{d}x_{3N} \delta \left( \sum_{i=1}^{3N} x_i^2 - U \right) \ , \tag{3.111}$$

where we used the notation $\vec{x}_1 = (x_1, x_2, x_3)$, $\vec{x}_2 = (x_4, x_5, x_6)$, $\vec{x}_N = (x_{3N-2}, x_{3N-1}, x_{3N})$. Notice that the $3N$-dimensional integral corresponds to the surface “area” of a $3N$-dimensional hyper-sphere with radius $R = \sqrt{\sum_{i=1}^{3N} x_i^2} = \sqrt{U}$.

**Hyper-surface of a $D$-dimensional sphere.** Let $S_D$ denote the surface "area" of a sphere in $D$ dimensions. From basic geometry we know that $S_2 = 2\pi R$ (circumference of a circle) and $S_3 = 4\pi R^2$. But what is $S_4, S_5$, etc.?

If we want to calculate a Gaussian integral in $D$ dimensions, we may do this in two different ways.

1) We use the fact that the exponentials factorize:

$$I = \int_{-\infty}^{\infty} \mathrm{d}x_1 \int_{-\infty}^{\infty} \mathrm{d}x_2 \cdots \int_{-\infty}^{\infty} \mathrm{d}x_D \; e^{-x_1^2-x_2^2-\cdots-x_D^2} = \left[\int_{-\infty}^{\infty} \mathrm{d}x\, e^{-x^2}\right]^D = \pi^{D/2} \; .$$

(A proof of this integral is provided in Appendix A.1.)

2) Alternatively, we switch to spherical coordinates by defining $R := \sqrt{x_1^2 + \cdots + x_D^2}$:

$$I = \int_{-\infty}^{\infty} \mathrm{d}x_1 \int_{-\infty}^{\infty} \mathrm{d}x_2 \cdots \int_{-\infty}^{\infty} \mathrm{d}x_D \; e^{-(x_1^2+x_2^2+\cdots+x_D^2)} = \int_0^{\infty} \mathrm{d}R\, S_D(R) e^{-R^2} \; ,$$

where $S_D(R)$ generalizes the surface area of a sphere to $D$ dimensions.

In fact, we know that the dimension of the hyper-surface must be $D-1$, leading us to define

$$S_D(R) := R^{D-1} C_D \; . \tag{3.112}$$

The factor $C_D$ is to be determined. Inserting this definition into integration method 2), we obtain

$$I = C_D \int_0^{\infty} \mathrm{d}R\, R^{D-1} e^{-R^2} \; .$$

Substituting $t = R^2$, $\mathrm{d}t = 2\sqrt{t}\,\mathrm{d}R = 2R\mathrm{d}R$ yields

$$\begin{aligned} I &= \frac{C_D}{2} \int_0^{\infty} \mathrm{d}t\, R^{D-2}\, e^{-t} \\ &= \frac{C_D}{2} \int_0^{\infty} \mathrm{d}t\, t^{D/2-1}\, e^{-t} \\ &= \frac{C_D}{2} \Gamma(D/2) \; , \end{aligned} \tag{3.113}$$

where we have introduced the *Gamma function* $\Gamma(x) := (x-1)!$ . If we compare the result from 1) with eq. (3.113), we find

$$I = \pi^{D/2} = \frac{C_D}{2}\Gamma(D/2) \qquad \Rightarrow \qquad C_D = \frac{2\pi^{D/2}}{\Gamma(D/2)} \; .$$

Hence the surface "area" of a $D$-dimensional hyper-sphere with radius $R$ is given by

$$\boxed{S_D(R) = R^{D-1}\frac{2\pi^{D/2}}{\Gamma(D/2)}} , \tag{3.114}$$

with $\Gamma(D/2) = \left(\frac{D}{2}-1\right)!$ . This result indeed reproduces $S_3 = 4\pi R^2$. For $D = 4$, for example, we find $S_4 = 2\pi^2 R^3$.

After this little excursion far beyond the limitations of our three-dimensional perception, we are prepared to tackle the integral in eq. (3.111). Switching to spherical coordinates, the density of states becomes

$$\omega = \frac{1}{N!}\left(\frac{V(2m)^{3/2}}{h^3}\right)^N \int_0^\infty \mathrm{d}R\, S_{3N}(R)\delta(R^2-U) . \tag{3.115}$$

Now we define the integration variable $t := R^2$, which gives $\frac{\mathrm{d}t}{\mathrm{d}R} = 2R = 2\sqrt{t}$ and thus

$$\begin{aligned}
\omega &= \frac{1}{N!}\left(\frac{V(2m)^{3/2}}{h^3}\right)^N \int_0^\infty \frac{\mathrm{d}t}{2\sqrt{t}} S_{3N}\left(\sqrt{t}\right)\delta(t-U) \\
&= \frac{1}{N!}\left(\frac{V(2m)^{3/2}}{h^3}\right)^N \frac{S_{3N}\left(\sqrt{U}\right)}{2\sqrt{U}} \\
&= \frac{1}{N!}\left(\frac{V(2m)^{3/2}}{h^3}\right)^N \frac{U^{(3N-1)/2}}{2\sqrt{U}} C_{3N} \\
&= \frac{1}{N!}\left(\frac{V(2m)^{3/2}}{h^3}\right)^N \frac{U^{3N/2}}{2U}\frac{2\pi^{3N/2}}{\Gamma(3N/2)} \\
&= \left(\frac{V(2\pi mU)^{3/2}}{h^3}\right)^N \frac{1}{UN!\left(\frac{3N}{2}-1\right)!} .
\end{aligned} \tag{3.116}$$

In fact, we need the logarithm of the density of states,

$$\ln\omega = N\ln\left(\frac{V(2\pi mU)^{3/2}}{h^3}\right) - \ln U - \ln N! - \ln\left(\frac{3N}{2}-1\right)! . \tag{3.117}$$

First of all, we drop the term $\ln U$ since it scales as $\ln N$ and is thus negligible compared to the leading term. Secondly, as $N\to\infty$, we may safely approximate $\frac{3N}{2}-1 \approx \frac{3N}{2}$. Applying Stirling's approximation (eq. (2.19)) to the factorial terms, we rewrite

$$\begin{aligned}
\frac{-\ln N! - \ln\left(\frac{3N}{2}-1\right)!}{N} &\approx \frac{-\ln N! - \ln\left(\frac{3N}{2}\right)!}{N} \\
&\approx \frac{-N\ln N + N - \frac{3}{2}N\ln\left(\frac{3N}{2}\right) + \frac{3}{2}N}{N} \\
&= -\ln N - \ln\left[\left(\frac{3N}{2}\right)^{3/2}\right] + \frac{5}{2} \\
&= -\ln\left[N\left(\frac{3N}{2}\right)^{3/2}\right] + \frac{5}{2} .
\end{aligned} \tag{3.118}$$

Reinserting the approximate result of eq. (3.118) into eq. (3.117), we obtain an expression for the entropy,

$$S = k_B \ln \omega = k_B N \left[ \ln \left( \frac{V(2\pi m U)^{3/2}}{h^3} \right) - \ln \left( N \left( \frac{3N}{2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

$$\Rightarrow \quad \boxed{S(U,V,N) = -k_B N \left[ \ln \left( \frac{N}{V} \frac{h^3}{\left( 2\pi m \frac{2U}{3N} \right)^{3/2}} \right) - \frac{5}{2} \right]} \, . \tag{3.119}$$

A comparison with eq. (3.106) shows that this is precisely the Sackur-Tetrode equation we derived in the canonical ensemble. From here, the ideal gas law and other properties of the ideal gas follow. The Sackur-Tetrode equation gives the leading part of the entropy which is extensive and valid for large $N$. Thus, we draw the important conclusion:

> **Equivalence of canonical and microcanonical ensembles.** In the thermodynamic limit ($N \to \infty$), the canonical ensemble and the microcanonical ensemble are equivalent.

As it turned out, the calculation in the microcanonical ensemble, at fixed energy $U$, is more complicated than the corresponding derivation in the canonical ensemble where the energy may fluctuate.

## 3.9 Grand canonical ensemble

Let us recapitulate how we transitioned from the microcanonical to the canonical ensemble. The microcanonical ensemble fixes the total energy to a certain value. In most physical systems, however, the total energy is not precisely constant. Instead it is controlled by the ambient temperature which ensures that the energy attains a constant *average* value. The canonical ensemble conceptualizes this situation and allows the energy to fluctuate. For large systems, however, energy fluctuations around the mean are in fact so small that both ensembles yield equivalent results.

In reality, we will also never know the exact number of particles in a thermodynamic system. Just like the total energy, the particle number will fluctuate when the system exchanges particles with its surroundings or during chemical reactions. This motivates us to introduce another statistical ensemble – the *grand canonical ensemble*.

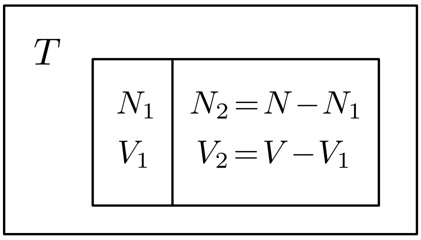

**Figure 3.3:** A system with volume $V_1$ in contact with a reservoir of volume $V_2$. The total number of particles is constant, $N = N_1 + N_2$, but the system 1 can exchange particles with the reservoir. The reservoir is much larger than system 1, i.e. $V_1 \ll V_2$ and $N_1 \ll N_2$ (even though the figure cannot show this). Both system 1 and the reservoir are surrounded by a heat reservoir of temperature $T$.

Figure 3.3 provides a schematic drawing of the grand canonical ensemble. The system connects to a reservoir with which it may exchange energy and particles. Both the system (1) and the reservoir (2) are surrounded by a large thermal reservoir with constant temperature $T$.

**Grand canonical partition function.** Assume a weak interaction between the system and the reservoir, such that the total Hamiltonian is approximately given by the sum of the individual Hamiltonians,

$$\mathcal{H}\left(q^{3N},p^{3N}\right) \approx \mathcal{H}\left(q_1^{3N_1},p_1^{3N_1}\right) + \mathcal{H}\left(q_2^{3N_2},p_2^{3N_2}\right) \ . \tag{3.120}$$

Here the coordinates $(q_k^{3N_k}, p_k^{3N_k})$ refer to the set of particles contained in system $k \in \{1,2\}$. The total (canonical) partition function of systems 1 and 2 combined reads

$$\begin{aligned} Z(N,V,T) &= \frac{1}{h^{3N}N!}\int \mathrm{d}^{3N}q\,\mathrm{d}^{3N}p\, e^{-\beta H(q^{3N},p^{3N})} \\ &= \frac{1}{h^{3N}N!}\sum_{N_1=0}^{N}\frac{N!}{N_1!N_2!}\int \mathrm{d}\vec{q}_1\,\mathrm{d}\vec{q}_2\,\mathrm{d}\vec{p}_1\,\mathrm{d}\vec{p}_2\, e^{-\beta\mathcal{H}(\vec{p}_1,\vec{q}_1,N_1)}\, e^{-\beta\mathcal{H}(\vec{p}_2,\vec{q}_2,N_2)} \\ &= \sum_{N_1=0}^{N} Z_{N_1}(V_1,T)\, Z_{N_2}(V_2,T) = Z_N(V,T) \ . \end{aligned} \tag{3.121}$$

Here we have used the notation $\vec{q}_k \equiv q_k^{3N_k}$, $k \in \{1,2\}$, for brevity. The sum $\sum_{N_1=0}^{N}$ runs through all possible particle numbers in system 1. Moreover, the factorial term counts all possibilities for selecting $N_1$ particles from $N$ particles. Due to the factorization of the Boltzmann distributions, the total partition function equals the product of the individual partition functions. We now define the probability distribution $\rho$,

$$\rho(\vec{q}_1,\vec{p}_1,N_1) := \frac{Z_{N_2}(V_2,T)}{Z_N(V,T)}\frac{e^{-\beta\mathcal{H}(\vec{q}_1,\vec{p}_1,N_1)}}{h^{3N_1}N_1!} \ . \tag{3.122}$$

This distribution is normalized, i.e.

$$\sum_{N_1=0}^{N}\int \mathrm{d}^{3N_1}\vec{q}_1\,\mathrm{d}^{3N_1}\vec{p}_1\,\rho(p_1,q_1,N_1) = 1 \ , \tag{3.123}$$

which we confirm using eq. (3.121). With the result from section 3.5,

$$F(N,V,T) = -k_BT\ln Z_N(V,T) \quad \Leftrightarrow Z_N(V,T) = e^{-\beta F(N,V,T)} \ ,$$

we write the ratio of the partition functions $Z_{N_2}/Z_N$ as

$$\frac{Z_{N_2}(V_2,T)}{Z_N(V,T)} = \exp\left[-\beta\Big(F(N-N_1,V-V_1,T) - F(N,V,T)\Big)\right] \ , \tag{3.124}$$

where we inserted $N_2 = N - N_1$. At this point we invoke our assumption $N_1 \ll N$, which means that the particle reservoir is very large compared to system 1. In this case it is sufficient, to a good approximation, to consider the Taylor expansion of $F(N-N_1,V-V_1,T)$ up to first order. The first derivatives define the quantities

$$\boxed{P := -\frac{\partial F(N,V,T)}{\partial V}} \ , \quad \boxed{\mu := \frac{\partial F(N,V,T)}{\partial N}} \ . \tag{3.125}$$

Here $P$ is the pressure, as previously defined in eq. (3.100). The thermodynamic quantity $\mu$ is termed *chemical potential*. It describes the change in free energy when adding one particle to the system. In these terms, the Taylor expansion gives

$$F(N-N_1,V-V_1,T)=F(N,V,T)-N_1\mu+V_1P+\mathcal{O}\left(\frac{N_1}{N}\right)\ . \tag{3.126}$$

Using eqs. (3.124) and (3.126), the probability distribution $\rho$ becomes

$$\rho(\vec{q}_1,\vec{p}_1,N_1)=\frac{1}{h^{3N_1}N_1!}e^{-\beta\left(PV_1-\mu N_1+\mathcal{H}(\vec{q}_1,\vec{p}_1,N_1)\right)}\ . \tag{3.127}$$

In the following, we drop the subscript 1, since the expression exclusively contains variables referring to system 1 now. After all, system 2 only serves as a reservoir for particle exchange. It enters indirectly via the temperature $T$ of the heat reservoir, the pressure $P$, as well as the chemical potential $\mu$. In fact, we make the particle reservoir infinitely large such that the thermodynamic limit ($N\to\infty$) applies.

Let us now define the *grand canonical partition function* $\mathcal{Z}$,

$$\boxed{\mathcal{Z}(\mu,V,T):=\sum_{N=0}^{\infty}e^{\beta N\mu}Z_N(V,T)}\ , \tag{3.128}$$

where $Z$ represents the canonical partition function of the system. Using the first line of eq. (3.121) and the distribution $\rho$ in eq. (3.127), the grand canonical partition function equates to

$$\begin{aligned}\mathcal{Z}&=\sum_{N=0}^{\infty}e^{\beta N\mu}\int\frac{\mathrm{d}q^{3N}\,\mathrm{d}p^{3N}}{h^{3N}N!}\,e^{-\beta\mathcal{H}(q^{3N},p^{3N})}\\&\overset{(3.127)}{=}e^{\beta PV}\sum_{N=0}^{\infty}\int\mathrm{d}q^{3N}\,\mathrm{d}p^{3N}\,\rho\left(q^{3N},p^{3N},N\right)\\&\overset{(3.123)}{=}e^{\beta PV}\ .\end{aligned} \tag{3.129}$$

This result leads to the *grand canonical equation of state*,

$$\boxed{\ln\mathcal{Z}(\mu,V,T)=\beta PV=\frac{PV}{k_BT}}\ . \tag{3.130}$$

Furthermore, we define the *grand canonical potential*, or *grand potential*, $\Omega$,

$$\boxed{\Omega(\mu,V,T):=-k_BT\ln\mathcal{Z}(\mu,V,T)=-VP(\mu,V,T)}\ . \tag{3.131}$$

Note the structural similarity to the definition of the free energy as the thermodynamic potential of the canonical ensemble, $F=-k_BT\ln Z$. While the natural variables of the canonical ensemble are $(N,V,T)$, the variables of the grand canonical ensembles are $(\mu,V,T)$.

**Mean particle number and fluctuations.** From the definition of $\mathcal{Z}$ (eq. (3.128)) we derive the mean particle number $\langle N\rangle$ in the grand canonical ensemble,[8]

$$\langle N\rangle = \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}(\mu, V, T)}{\partial \mu} \; . \tag{3.132}$$

Next, we want to calculate the particle number fluctuations around the mean, quantified by the variance $\sigma_N^2 = \langle N^2\rangle - \langle N\rangle^2$. That works by taking two derivatives with respect to the chemical potential:

$$\begin{aligned}
\frac{\partial}{\beta\partial\mu}\frac{\partial}{\beta\partial\mu}\ln \mathcal{Z}(\mu, V, T) &= \frac{\partial}{\beta\partial\mu}\frac{\partial}{\beta\partial\mu}\ln\left(\sum_{N=0}^{\infty} e^{\beta N\mu} Z_N(V,T)\right)\\
&= \frac{\partial}{\beta\partial\mu}\frac{\sum_N N e^{\beta N\mu} Z_N}{\sum_N e^{\beta N\mu} Z_N}\\
&= \frac{\sum_N N^2 e^{\beta N\mu} Z_N}{\sum_N e^{\beta N\mu} Z_N} - \left(\frac{\sum_N N e^{\beta N\mu} Z_N}{\sum_N e^{\beta N\mu} Z_N}\right)^2\\
&= \langle N^2\rangle - \langle N\rangle^2 \; .
\end{aligned} \tag{3.133}$$

Based on the grand canonical equation of state (eq. (3.130)), the variance is given by

$$\langle N^2\rangle - \langle N\rangle^2 = \left.\frac{\partial}{\beta\partial\mu}\right|_{V,T} \left.\frac{\partial}{\beta\partial\mu}\right|_{V,T} \frac{PV}{k_B T} = k_B T V \left.\frac{\partial^2 P}{\partial \mu^2}\right| \; . \tag{3.134}$$

We will explicitly calculate the derivative $(\partial^2 P/\partial\mu^2)_{V,T}$ at the end of this section. For now, we make the following argument. From the grand canonical equation of state, we see that the variance scales extensively because $\beta PV \sim \mathcal{O}(N)$ ($P$ and $\mu$ are intensive; $V$ is extensive). This implies that the relative deviation around the mean scales as

$$\frac{\sqrt{\langle N^2\rangle - \langle N\rangle^2}}{\langle N\rangle} \sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}} \xrightarrow{N\to\infty} 0 \; . \tag{3.135}$$

We conclude that particle number fluctuations become negligible in the thermodynamic limit, confirming the law of large numbers (see eq. (2.17) in section 2.3). Most of the time, the system will have a particle number close to the most probable particle number $N^*$, which is much more probable than any other particle number. Therefore we may approximate

$$\mathcal{Z}(\mu, V, T) = \sum_N \underbrace{e^{\beta N\mu} Z(N, V, T)}_{\rho(N)} \approx e^{\beta N^*\mu} Z(N^*, V, T) \; . \tag{3.136}$$

In fact, for large systems there is no need to distinguish between the mean $\langle N\rangle$ and the maximally likely $N^*$; we simply write $N = \langle N\rangle = N^*$.

**Grand potential vs. free energy.** Eq. (3.136) implies that in the thermodynamic limit

$$-\ln \mathcal{Z}(\mu, V, T) = -\beta N\mu - \ln Z(N, V, T).$$

---

[8] If we would differentiate by $\beta$ here, we would also get a factor $N$ in front of the exponential. But $\beta = (k_B T)^{-1}$ and the canonical partition function $Z$ also depends on temperature! Thus we must choose the derivative by $\mu$.

With $\Omega = -k_B T \ln \mathcal{Z}$ and $F = -k_B T \ln Z$, we find (by multiplying $k_B T$ on both sides)

$$\boxed{\Omega(\mu, V, T) = F(N, V, T) - \mu N} \ . \tag{3.137}$$

This equation relates the grand potential $\Omega$ to the canonical potential, the free energy $F$. Note the analogy to $F = U - TS$ (eq. (3.61)) and the Legendre transform structure. We can write eq. (3.137) in terms of the independent variables $(\mu, V, T)$, or $(N, V, T)$, or any other triplet!

Equating $\Omega = -PV$ (eq. (3.131)) with eq. (3.137), we obtain

$$F = -PV + N\mu \ ,$$

and with $F = U - TS$, this yields the *fundamental equation of Thermodynamics*,

$$\boxed{U = TS - PV + N\mu} \ . \tag{3.138}$$

The fundamental equation is a bilinear form of intensive state variables $(T, P, \mu)$, each multiplied with an extensive state variable $(S, V, N)$. In fact, all thermodynamic potentials – such as the internal energy $U$, the free energy $F$, the grand potential $\Omega$, the Gibbs free energy $G$ and the enthalpy $H$ (which we will come across later) – are expressed in a bilinear form as functions of a combination of state variables. More on this will follow in chapter 4, where the fundamental equation of Thermodynamics will play a central role.

**Gibbs-Duheme equation.** What is the total differential of the grand potential? We already know that

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

where

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} \ , \quad P = -\left(\frac{\partial F}{\partial V}\right)_{N,T} \ , \text{ and } \quad S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \ .$$

Combining this with eq. (3.137) yields

$$\begin{aligned} \mathrm{d}\Omega = \mathrm{d}(F - \mu N) &= \mathrm{d}F - \mathrm{d}(\mu N) \\ &= \mu \mathrm{d}N - P\mathrm{d}V - S\mathrm{d}T - \mu \mathrm{d}N - N\mathrm{d}\mu \\ &= -P\mathrm{d}V - S\mathrm{d}T - N\mathrm{d}\mu \\ &= \mathrm{d}\Omega(\mu, T, V) \ . \end{aligned} \tag{3.139}$$

At the same time, eq. (3.131) tells us that

$$\Omega = -PV \quad \Rightarrow \quad \mathrm{d}\Omega = -P\mathrm{d}V - V\mathrm{d}P \ .$$

Since both expressions for the total differential $\mathrm{d}\Omega$ must be true, they must be equal to each other:

$$\begin{aligned} \mathrm{d}\Omega = -P\mathrm{d}V - V\mathrm{d}P &\overset{!}{=} -P\mathrm{d}V - S\mathrm{d}T - N\mathrm{d}\mu \\ \Rightarrow \quad &\boxed{0 = V\mathrm{d}P - S\mathrm{d}T - N\mathrm{d}\mu} \ . \end{aligned} \tag{3.140}$$

The boxed equation is known as the *Gibbs-Duheme equation*. By relating all intensive differentials to each other, it implies that we cannot find a potential $\Theta(P, T, \mu)$. A thermodynamic potential must be extensive, and it is impossible to “create” an extensive potential from intensive variables only.

**Explicit calculation of particle number variance.** When discussing the particle number fluctuations above, we skipped over the explicit calculation of the derivative $(\partial^2 P/\partial\mu^2)_{V,T}$. We make good for this now.

We may write the free energy as $F(N,V,T) = Nf(v,T)$, where $f$ denotes the free energy per particle. By construction $f$ is intensive; it can only depend on the volume per particle $v := \frac{V}{N}$. Using the definition in eq. (3.125), the chemical potential becomes

$$\begin{aligned}\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} &= \frac{\partial\Big(Nf(v,T)\Big)}{\partial N}\\ &= f(v,T) - v\frac{\partial f(v,T)}{\partial v}\\ &= \mu(v,T)\ .\end{aligned} \tag{3.141}$$

Similarly, the pressure $P$ is

$$\begin{aligned}P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} &= -\frac{\partial\Big(Nf(v,T)\Big)}{\partial V}\\ &= -\frac{\partial f(v,T)}{\partial V}\\ &= P(v,T) = P(v(\mu,T),T)\ ,\end{aligned} \tag{3.142}$$

where $v(\mu,T)$ is the inverse of $\mu(v,T)$. The first derivative of the pressure with respect to $\mu$ follows with the chain rule,

$$\left.\frac{\partial P}{\partial\mu}\right|_T = \left.\frac{\partial P}{\partial v}\right|_T \left.\frac{\partial v}{\partial\mu}\right|_T\ . \tag{3.143}$$

With eq. (3.141), we write the derivative $\partial v/\partial\mu$ as

$$\left.\frac{\partial\mu}{\partial v}\right|_T = \left.\frac{\partial f}{\partial v}\right|_T - \left.\frac{\partial f}{\partial v}\right|_T - v\left.\frac{\partial^2 f}{\partial v^2}\right|_T = -v\left.\frac{\partial^2 f}{\partial v^2}\right|_T\ , \tag{3.144}$$

and from eq. (3.142) we get

$$\left.\frac{\partial P}{\partial v}\right|_T = -\left.\frac{\partial^2 f}{\partial v^2}\right|_T\ , \tag{3.145}$$

which implies

$$\left.\frac{\partial\mu}{\partial v}\right|_T = v\left.\frac{\partial P}{\partial v}\right|_T\ . \tag{3.146}$$

Based on all this, eq. (3.143) becomes

$$\left.\frac{\partial P}{\partial\mu}\right|_{T,V} = \frac{1}{v}\ . \tag{3.147}$$

The second derivative is then given by

$$\left.\frac{\partial^2 P}{\partial\mu^2}\right|_{V,T} = \left.\frac{\partial(1/v)}{\partial\mu}\right|_T = -\left.\frac{1}{v^2}\frac{\partial v}{\partial\mu}\right|_T = -\left.\frac{1}{v^3}\frac{\partial v}{\partial P}\right|_T\ . \tag{3.148}$$

Switching back to the variables $T, V$, and $N$, we write

$$\left.\frac{\partial^2 P}{\partial \mu^2}\right|_{T,V} = -\left.\frac{N^2}{V^3}\frac{\partial V(P,T,N)}{\partial P}\right|_{T,N} = \frac{N^2}{V^2}\kappa_T(P,T) \ , \tag{3.149}$$

where we have defined the *isothermal compressibility* $\kappa_T$,

$$\kappa_T := -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} \ . \tag{3.150}$$

The isothermal compressibility measures by how much the relative volume decreases when increasing the pressure at constant $T$ and $N$. For physical reasons, $\kappa_T \geq 0$ and $\kappa_T$ is intensive by construction. Being intensive, it cannot depend on $N$.

Now that we have calculated the second derivative, the variance of $N$ in the grand canonical ensemble (see eq. (3.134)) is explicitly given by

$$\begin{aligned} \langle N^2 \rangle - \langle N \rangle^2 &= k_B T V \left.\frac{\partial^2 P}{\partial \mu^2}\right|_{T,V} \\ &= k_B T \frac{N^2}{V}\kappa_T(P,T) \\ &= k_B T N n(P,T)\kappa_T(P,T) \ \sim \mathcal{O}(N) \ . \end{aligned} \tag{3.151}$$

Here $n(P,T)$ denotes the particle number density, which is an intensive quantity. The only non-intensive variable on the RHS of eq. (3.151) is $N$, so the variance scales like $N$. Thus we have confirmed our argument above.

## 3.10 Ideal gas in the grand canonical ensemble

After introducing the grand canonical ensemble, the ideal gas will again serve as our paradigmatic example to test the theory and compare results with our previous findings for the canonical and the microcanonical ensemble.

We begin with the grand canonical partition function, defined in eq. (3.128) as

$$\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta N \mu} Z(N, V, T) \ . \tag{3.152}$$

This expression involves the canonical partition function $Z(N, V, T)$ of the ideal gas, which we calculated in eq. (3.92) to be

$$Z(N,V,T) = \frac{1}{N!}\left(\frac{V}{\lambda_t^3}\right)^N \ ,$$

where the thermal wavelength is defined in eq. (3.93). Inserting into the grand canonical partition function yields

$$\mathcal{Z} = \sum_{N=0}^{\infty}\frac{1}{N!}\left(\frac{V}{\lambda_t^3}e^{\beta\mu}\right)^N = \exp\left(\frac{V}{\lambda_t^3}e^{\beta\mu}\right) \ . \tag{3.153}$$

Knowing $\mathcal{Z}$, we obtain the grand potential $\Omega$ by computing

$$\begin{aligned}\Omega(\mu, V, T) &= -k_B T \ln(\mathcal{Z}(\mu, V, T)) \\ &= -k_B T \frac{V}{\lambda_t^3} e^{\beta\mu} \\ &\overset{!}{=} -PV \ , \end{aligned} \tag{3.154}$$

where the last equality follows from eq. (3.131). Furthermore, in section 3.7 we derived the free energy of the ideal gas,

$$F(N, V, T) = k_B T N \ln\left(\frac{N\lambda_t^3}{V}\right) - k_B T N \ ,$$

(and $F(N, V, T) = N f(v, T)$ as assumed in the derivation of $(\partial^2 P/\partial\mu^2)_{V,T}$ in the previous section). The chemical potential $\mu$ then follows as

$$\mu = \frac{\partial F}{\partial N} = k_B T \ln\left(\frac{N\lambda_t^3}{V}\right) \ . \tag{3.155}$$

From this relation we conclude

$$e^{\beta\mu} = \frac{N\lambda_t^3}{V} \ , \tag{3.156}$$

and combining eq. (3.156) with eq. (3.154) leads to

$$N k_B T = PV \ . \tag{3.157}$$

This result is the – by now familiar – ideal equation of state, which we have thus re-derived in the grand canonical ensemble. In the thermodynamic limit, the description of the ideal gas is consistent regardless of which ensemble we use.

## 3.11 Chemical reactions and the law of mass action

We have introduced the grand canonical ensemble as a framework to describe systems with variable numbers of particles. An important application are chemical reactions, where the involved types of particles constantly change their amounts. In this section, we will focus on bimolecular reactions of the type

$$A + A \rightleftharpoons B \ .$$

For example, this simple case occurs in a hydrogen gas when two hydrogen atoms recombine to molecular hydrogen or vice versa ($H + H \rightleftharpoons H_2$).

We consider a gas confined in the volume $V$ at temperature $T$, comprised of particles of the two types $A$ and $B$. The total particle number is given by the sum of individual particle numbers, $N = N_A + N_B$. Furthermore, we denote the chemical potentials of the types by $\mu_A$ and $\mu_B$, respectively.

The grand partition function of the reacting system is the product of the two individual grand partition functions (see sec. 3.9),

$$\mathcal{Z}(\mu_A, \mu_B, V, T) = \sum_{N_A=0}^{\infty} \sum_{N_B=0}^{\infty} e^{\beta\mu_A N_A} e^{\beta\mu_B N_B} \, Z_A(N_A, V, T) \, Z_B(N_B, V, T) \ . \tag{3.158}$$

Let us assume that the canonical partition functions $Z_A$ and $Z_B$ each describe an ideal gas, i.e.

$$Z_X(N_X, V, T) = \frac{1}{N_X!}\left(\frac{V}{\lambda_{t,X}^3}\right)^{N_X} \quad , \qquad X \in \{A, B\} \ . \tag{3.159}$$

Then, eq. (3.158) becomes

$$\begin{aligned}\mathcal{Z} &= \sum_{N_A=0}^{\infty}\frac{1}{N_A!}\left(e^{\beta\mu_A}\frac{V}{\lambda_{t,A}^3}\right)^{N_A}\sum_{N_B=0}^{\infty}\frac{1}{N_B!}\left(e^{\beta\mu_B}\frac{V}{\lambda_{t,B}^3}\right)^{N_B} \\ &= \exp\left[e^{\beta\mu_A}\frac{V}{\lambda_{t,A}^3} + e^{\beta\mu_B}\frac{V}{\lambda_{t,B}^3}\right] \ . \end{aligned}\tag{3.160}$$

The expectation values of $N_A$ and $N_B$ are

$$\langle N_X\rangle = \frac{1}{\beta}\frac{\partial \ln(\mathcal{Z})}{\partial \mu_X} = e^{\beta\mu_X}\frac{V}{\lambda_{t,X}^3} \ , \qquad X \in \{A, B\} \ . \tag{3.161}$$

In the following, we omit the brackets for the expectation value (i.e. $\langle N_X\rangle \equiv N_X$).

During the chemical reaction $A + A \to B$, one particle of type $B$ is created while two particles of type $A$ are destroyed. This requires the chemical energy $\Delta\mu = \mu_B - 2\mu_A$. Rewriting $N_B$ (eq. (3.161)) in terms of $\Delta\mu$ and $\mu_A$, we obtain

$$\begin{aligned} N_B &= e^{\beta(\Delta\mu + 2\mu_A)}\frac{V}{\lambda_{t,B}^3} \\ &= e^{\beta\Delta\mu}\left(N_A^2\frac{\lambda_{t,A}^6}{V^6}\right)\frac{V}{\lambda_{t,B}^3} \ , \end{aligned}\tag{3.162}$$

where in the second equality we have used eq. (3.161) for type $A$.

Let us now define the *concentrations* $C_A := N_A/V$ and $C_B := N_B/V$ of the types $A$ and $B$, respectively. According to the *law of mass action*, the rate of a chemical reaction is proportional to the concentrations of the involved reactants. In equilibrium, we expect the recombination $A + A \to B$ to occur as frequently as the dissociation $B \to A + A$, such that the ratio of the products of involved reactants is constant. This ratio is termed the *equilibrium reaction constant* $K$. In our case, it is given by

$$K := \frac{\text{product of concentrations of reactants for } B \to A + A}{\text{product of concentrations of reactants for } A + A \to B} = \frac{C_B}{C_A^2} \ . \tag{3.163}$$

Note that in the denominator we get the concentration of $A$ to the power of two because two particles of type $A$ are needed for the reaction. Generally, the powers of reactants' concentrations are given by their multiplicity in the reaction.

Using eqs. (3.161) and (3.162), we get

$$\boxed{K := \frac{C_B}{C_A^2} = e^{\beta\Delta\mu}\left(\frac{\lambda_{t,A}^6}{\lambda_{t,B}^3}\right)} \ . \tag{3.164}$$

Let $C_A^{\text{tot}} := C_A + 2C_B$ denote the maximal concentration of particle type $A$. In terms of the hydrogen example ($H + H \rightleftharpoons H_2$), if $C_A = C_A^{\text{tot}}$ then the gas consists purely of atomic hydrogen $H$, whereas all particles are molecular hydrogen $H_2$ if $C_A = 0$ and $C_B = C_A^{\text{tot}}/2$. Thus $C_A^{\text{tot}}V$ states the total number of hydrogen atoms contained in the volume $V$ (no matter whether they are single or bound as a molecule). Starting from $K = C_B/(C_A^{\text{tot}} - 2C_B)^2$, we compute

$$\begin{aligned} \frac{C_B}{K} &= (C_A^{\text{tot}} - 2C_B)^2 \\ &= (C_A^{\text{tot}})^2 + 4C_B^2 - 4C_B C_A^{\text{tot}} \\ \Leftrightarrow \qquad 0 &= C_B^2 - C_B\left(C_A^{\text{tot}} + \frac{1}{4K}\right) + \frac{(C_A^{\text{tot}})^2}{4} \,. \end{aligned} \tag{3.165}$$

The solution to this quadratic equation reads

$$C_{B,\pm} = \frac{C_A^{\text{tot}} + \frac{1}{4K}}{2} \pm \sqrt{\frac{\left(C_A^{\text{tot}} + \frac{1}{4K}\right)^2}{4} - \frac{(C_A^{\text{tot}})^2}{4}} \,. \tag{3.166}$$

Since $C_B$ cannot exceed $C_A^{\text{tot}}/2$, we can physically exclude the larger root, leaving us with

$$C_B = \frac{C_A^{\text{tot}}}{2} + \frac{1}{8K} - \sqrt{\frac{1}{64K^2} + \frac{C_A^{\text{tot}}}{8K}} \,. \tag{3.167}$$

This result is plotted in fig. **??**. We conclude with an asymptotic analysis of the molecular concentration $C_B$ in the limit of low and high total concentration of atoms.

- **Low concentration limit.**
- **High concentration limit.**

# 4 Thermodynamics

In the previous chapter, we started out from microscopic properties of a large number of individual particles and employed a statistical description to derive macroscopic properties of the whole system. The derivation prompted us to define concepts like entropy and temperature, and to introduce thermodynamic potentials for the different statistical ensembles.

Historically, Thermodynamics was developed before the framework of Statistical Mechanics. Based on physical experiments, researchers deduced phenomenological relations between Thermodynamic quantities – such as energy, temperature, pressure, volume, or entropy – without involving any microscopic information. The most fundamental generalizations of the empirical findings were formulated as Laws of Thermodynamics. While not mathematically derived, these laws offer an axiomatic basis for a consistent mathematical description.

This chapter takes axiomatic Thermodynamics as a starting point to derive various relations between thermodynamic quantities. We calculate response functions such as the heat capacity and introduce Maxwell relations as powerful tools. These results will allow us to discuss thermodynamic processes, e.g. adiabatic processes, the expansion of a gas, and the Carnot cycle. Finally, we will study phase transitions.

## 4.1 Laws of Thermodynamics

We have occasionally come across the Laws of Thermodynamics in chapter 3 because the derivation of Statistical Mechanics produces corresponding results. In the context of Classical Thermodynamics, they are simply postulated:

- **Zeroth Law.** At equilibrium, two systems in heat contact with each other have the same temperature. If a system A is in thermal equilibrium with a system B, and if B is in thermal equilibrium with a third system C, then A and C must also be in thermal equilibrium.
- **First Law.** In an isolated system, the total energy is constant. If a closed system exchanges heat with its environment, its change of internal energy $U$ is given by

  $$\mathrm{d}U = \Delta Q - \Delta W \ , \tag{4.1}$$

  where $\Delta Q$ and $\Delta W$ denote the heat absorbed and work done *by* the system, respectively. (Here d denotes a total differential, while $\Delta$ represents an inexact differential.[1])

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[1] The internal energy $U$ and entropy $S$ are state functions and can thus be written as a total differential. Conversely, quantities like heat $Q$ or work $W$ cannot be expressed in total differential form since they are path-dependent quantities. We discuss this further below (see sections 4.5 and 4.6).

- **Second Law.** The total entropy of an isolated system cannot decrease. For a closed system undergoing a reversible heat exchange with its environment, the entropy change is given by
$$\mathrm{d}S = \frac{\Delta Q}{T} \ . \tag{4.2}$$
- **Third Law.** For any system, the entropy approaches a universal constant $S \to S_0$ as the temperature approaches absolute zero ($T \to 0$).

## 4.2 Axiomatic Thermodynamics

The laws of Thermodynamics may be seen as axioms which allow formulating Thermodynamics in a versatile, yet consistent manner.[2]

We begin with the *fundamental equation* in Thermodynamics,

$$U = TS - PV + \mu N \ , \tag{4.3}$$

which we already encountered in eq. (3.138) when discussing the grand canonical ensemble. In total differential form, the fundamental equation becomes

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N \ . \tag{4.4}$$

This formula also follows from the first law of Thermodynamics (when generalized to an open system where the particle number may vary).

From eq. (4.4), we can derive $T(S,V,N)$, $P(S,V,N)$ and $\mu(S,V,N)$. This means that the internal energy $U(S,V,N)$, as a function of entropy, volume, and particle number, contains complete information; everything can be derived from it. In contrast, $T(S,V,N)$ does not contain all information because we additionally require the functions $P(S,V,N)$ and $\mu(S,V,N)$ to reconstruct $U(S,V,N)$. Geometrically, we may visualize $T(S,V,N)$, $P(S,V,N)$, and $\mu(S,V,N)$ as the slopes of the three-dimensional function $U$ along the three respective directions.

Let us now perform a Legendre transform in order to switch from the energy differential $\mathrm{d}U$ to the free energy differential $\mathrm{d}F$. Since $F = U - TS$ (see section 3.5) we have, using eq. (4.4),

$$\begin{aligned}\mathrm{d}F &= \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T \\ &= -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N \ .\end{aligned} \tag{4.5}$$

From this we see that the free energy is now expressed as a function of $T$, $V$, and $N$; explicitly,

$$\mathrm{d}F(T,V,N) = -S(T,V,N)\,\mathrm{d}T - P(T,V,N)\,\mathrm{d}V + \mu(T,V,N)\,\mathrm{d}N \ . \tag{4.6}$$

In practice, the Legendre transform is done by

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[2] The axiomatic description of Thermodynamics goes back to the mathematician Constantin Carathéodory. See his original work [1] (in German language) for further background.

1. inverting $T(S,V,N)$ to obtain $S(T,V,N)$ and
2. replacing $S$ by $S(T,V,N)$ wherever it occurs in $U(S,V,N)$, such that

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

Just like $U(S,V,N)$, the function $F(T,V,N)$ contains all thermodynamic information. The same holds for the inversions $T(F,V,N)$, $V(T,F,N)$, and $N(F,T,V)$. For example, from the total differential $\mathrm{d}F$ we can derive an expression for $\mathrm{d}V$:

$$\mathrm{d}V = -\frac{S}{P}\mathrm{d}T - \frac{1}{P}\mathrm{d}F + \frac{\mu}{P}\mathrm{d}N\ , \tag{4.7}$$

which in turn yields the functions $S(T,F,N)$, $P(T,F,N)$, and $\mu(T,F,N)$. In conclusion, there exist many ways of formulating Thermodynamics, although we mostly deal with the most important ones.

## 4.3 Equations of state, response functions

Let us revisit eq. (4.6). Since we can write the function $F(T,V,N)$ as a total differential, it contains complete information about the thermodynamic system. However, the functions $S(T,V,N)$, $P(T,V,N)$, and $\mu(T,V,N)$ do not. This does not mean we should not care about them; they contain useful information and are named *equations of state*. Generally, equations of state are first derivatives of thermodynamic potentials (e.g. $F$, $\Omega$).

For example, we see from eq. (4.6) that

$$P(T,V,N) = -\frac{\partial F(T,V,N)}{\partial V}\ . \tag{4.8}$$

This equation is termed *thermal equation of state*. The functions $P(T,V,N)$, $V(P,T,N)$, and $N(P,T,V)$ are equivalent. In fact, since the pressure is intensive, we may write $P$ in terms of the volume per particle $v = V/N$ such that $P(T,V,N) = P(T,v)$.

For a second example of an equation of state, we return to the fundamental equation (4.4), which we may rearrange to yield

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN\ . \tag{4.9}$$

This implies the so-called *caloric equation of state*,

$$\frac{1}{T(U,V,N)} = \frac{\partial S(U,V,N)}{\partial U}\ . \tag{4.10}$$

$T(U,V,N)$ connects the variables $T,U,V$, and $N$. Typically one writes $U(T,V,N)$, which is derived by inversion.

We may also take second derivatives of thermodynamic potentials. The resulting functions constitute an important class called *response functions*.

Consider the thermal equation of state (4.8). Transforming, via a Legendre transform, from the free energy $F(T,V,N)$ to the *Gibbs free energy* $G(T,P,N)$, we have

$$\begin{aligned} G &= F + PV \\ &= U - TS + PV \ , \end{aligned} \tag{4.11}$$

and thus

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}N \ . \tag{4.12}$$

. With this, the thermal equation of state takes the form

$$V(P,T,N) = \frac{\partial G(P,T,N)}{\partial P} \ . \tag{4.13}$$

Now we compute the total differential of $V(P,T,N)$,

$$\mathrm{d}V = \left.\frac{\partial V}{\partial P}\right|_{T,N} \mathrm{d}P + \left.\frac{\partial V}{\partial T}\right|_{P,N} \mathrm{d}T + \left.\frac{\partial V}{\partial N}\right|_{P,T} \mathrm{d}N \ . \tag{4.14}$$

Eq. (4.14) elucidates that second derivatives of thermodynamic potentials describe how state variables change – or “respond” – under variation of other state variables. Since they are easily measured in practice, response functions are extremely important to characterize systems and have many applications.

The total differential in eq. (4.14) contains three response functions. The first one is

$$-V\kappa_T(P,T) = \frac{\partial V(P,T,N)}{\partial P} = \frac{\partial^2 G(P,T,N)}{\partial P^2} \ , \tag{4.15}$$

which defines the *isothermal compressibility* $\kappa_T$,

$$\kappa_T(P,T) = -\frac{1}{V}\frac{\partial V(P,T,N)}{\partial P} \ . \tag{4.16}$$

Since $\kappa_T$ is intensive by construction, it cannot depend on $N$. The last equality in eq. (4.15) makes it explicit that $\kappa_T$ is given by a second derivative of the thermodynamic potential $G$. The next second derivative is linked to the *expansion coefficient* $\alpha$,

$$\alpha(P,T) = \frac{1}{V}\frac{\partial V(P,T,N)}{\partial T} = \frac{1}{V}\frac{\partial^2 G(P,T,N)}{\partial T \partial P} \ . \tag{4.17}$$

Finally, the third response function states the volume per particle $v$, or *inverse density*,

$$\frac{\partial^2 G(P,T,N)}{\partial N \partial P} = \frac{\partial V(N,P,T)}{\partial N} = \frac{\partial N v(P,T)}{\partial N} = v(P,T) \ . \tag{4.18}$$

Combining these formulas, eq. (4.14) becomes

$$\mathrm{d}V = -V\kappa_T \mathrm{d}P + V\alpha \mathrm{d}T + v\mathrm{d}N \ . \tag{4.19}$$

Thus, total differentials of equations of state define response functions.

To summarize:

| | | |
|---|---|---|
| Equation of state | ↔ | First partial derivative of thermodynamic potential |
| Response function | ↔ | Second partial derivative of thermodynamic potential. |

## 4.4 Maxwell relations

In Thermodynamics, Maxwell relations[3] establish connections between different state variables by relating partial derivatives of these variables.

Consider the fundamental equation for a closed system (i.e. $N =$ constant),

$$dU = TdS - PdV \ .$$

This implies

$$T = T(S,V,N) = \frac{\partial U(S,V,N)}{\partial S} \ , \tag{4.20}$$

$$P = P(S,V,N) = -\frac{\partial U(S,V,N)}{\partial V} \ . \tag{4.21}$$

According to Schwarz's theorem, which states that second partial derivatives are symmetric in the order of differentiation, we have

$$\left.\frac{\partial}{\partial V}\right|_{S,N} \left.\frac{\partial U}{\partial S}\right|_{V,N} = \left.\frac{\partial}{\partial S}\right|_{V,N} \left.\frac{\partial U}{\partial V}\right|_{S,N} \tag{4.22}$$

Using eqs. (4.20) and (4.21) in eq. 4.22 yields *one* Maxwell relation:

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}} \ . \tag{4.23}$$

Note that numerous other Maxwell relations exist; this is merely one example. Their derivation, however, always follows the same recipe:

1. Take a pair of thermodynamic variables and express each of them in terms of a partial derivative of a thermodynamic potential.
2. Use Schwarz's theorem to relate them.

Just from $U(S,V,N)$, we can form several other pairs besides $T$ and $P$, and many more Maxwell relations arise from the other thermodynamic potentials, e.g. from

$$F(T,V,N), \ G(T,P,N), \ H(S,P,N), \ \Omega(T,V,\mu), \ \ldots$$

Thus, Maxwell relations are a powerful concept in Thermodynamics.

## 4.5 Adiabatic processes and the TdS equations: Thermodynamic calculus

A thermodynamic process is *adiabatic* if no heat is exchanged between the system and its surroundings, i.e. $\Delta Q = 0$. In practice, this might be (approximately) achieved if the process occurs quickly, such that there is no time to conduct heat to or away from the system. (Note that when a process is conducted very quickly, it will become irreversible.)

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[3] Maxwell relations should not be confused with Maxwell's equations of Electrodynamics.

The fundamental equation (4.4), which expresses the First Law of Thermodynamics combined with eq. (4.2), states:

$$\Delta Q = T\mathrm{d}S = \mathrm{d}U + P\mathrm{d}V - \mu\mathrm{d}N \ . \tag{4.24}$$

We reemphasize that $\Delta Q \neq \mathrm{d}Q$, i.e. heat is not a potential or state function and cannot be written as a total differential. For an adiabatic process, eq. (4.24) reduces to

$$0 = \mathrm{d}U + P\mathrm{d}V - \mu\mathrm{d}N \ . \tag{4.25}$$

**TdS equations.** To describe typical adiabatic processes like the compression of a gas, it is often useful to switch from the independent variables $(U, V, N)$ to, say, $(V, P, N)$ or $(V, T, N)$. Our aim in the following calculation is thus to express the RHS[4] of eq. (4.24) in terms of different variable combinations. This is interesting because the LHS vanishes in the adiabatic case, $T\mathrm{d}S = 0$ . To keep it simple, we assume that the particle number is constant and omit the $\mathrm{d}N$ term.

By suitable variable transformation, we may write the caloric equation of state (see eq. (4.10)) as $U(P, V)$, $U(P, T)$, or $U(V, T)$. For instance, we obtain $U(P, V)$ from the equations of state $U(V, T)$ and $T(V, P)$ (eqs. (4.8) and (4.10) with constant $N$). Let us look at these cases consecutively:

- Using $U(P, V)$, we write the total differential of $U$ as

  $$\mathrm{d}U = \left(\frac{\partial U}{\partial P}\right)_V \mathrm{d}P + \left(\frac{\partial U}{\partial V}\right)_P \mathrm{d}V \ .$$

  Inserting this in eq. (4.24) gives the *first TdS equation*,

  $$T\mathrm{d}S = \left(\frac{\partial U}{\partial P}\right)_V \mathrm{d}P + \left[P + \left(\frac{\partial U}{\partial V}\right)_P\right] \mathrm{d}V \ . \tag{4.26}$$

- Using the equations of state $U(P, T)$ and $V(P, T)$, we may write the total differentials of $U$ and $V$ as

  $$\mathrm{d}U = \left(\frac{\partial U}{\partial P}\right)_T \mathrm{d}P + \left(\frac{\partial U}{\partial T}\right)_P \mathrm{d}T \ ,$$
  $$\mathrm{d}V = \left(\frac{\partial V}{\partial P}\right)_T \mathrm{d}P + \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}T \ .$$

  With this, $T\mathrm{d}S$ in eq. (4.24) is expressed in terms of $\mathrm{d}P$ and $\mathrm{d}T$, yielding the *second TdS equation*:

  $$T\mathrm{d}S = \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] \mathrm{d}P + \left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] \mathrm{d}T \ . \tag{4.27}$$

- Finally, using $U(V, T)$ to write $T\mathrm{d}S$ with respect to $\mathrm{d}V$ and $\mathrm{d}T$, the *third TdS equation* becomes

  $$T\mathrm{d}S = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \mathrm{d}V \ . \tag{4.28}$$

---

[4] RHS – right hand side, LHS – left hand side (of an equal sign in an equation)

Note that the *canonical* variables of d$S$ are the energy $U$ and volume $V$ (together with the particle number $N$ in case $\mu \mathrm{d}N \neq 0$). These are the "natural" variables of d$S$ which also appear in the fundamental equation (4.4). In terms of $U$ and $V$, the total differential d$S$ thus contains complete information. In contrast, the expressions in eqs. (4.26)-(4.28) in terms of non-canonical variables do *not* include all thermodynamic information about the system. Note, however, that $T\mathrm{d}S$ in eq. (4.28) becomes an exact differential if $\mathrm{d}V = 0$.

The TdS equations (4.26)–(4.28) feature several partial derivatives of equations of state which we now want to relate to response functions such as heat capacity or the thermal expansion coefficient (see section 4.3).

**Heat capacity.** The heat capacity at constant volume is defined as

$$C_V := \left(\frac{\Delta Q}{\Delta T}\right)_V , \tag{4.29}$$

where $\Delta T$ denotes the temperature increase associated with adding the amount of heat $\Delta Q$ to the system. Looking at infinitesimal changes in heat and temperature, we can use the TdS equation (4.28) together with $\Delta Q = T\mathrm{d}S$ to deduce

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V . \tag{4.30}$$

Similarly, we define the heat capacity at constant pressure as

$$C_P := \left(\frac{\Delta Q}{\Delta T}\right)_P . \tag{4.31}$$

Combining $\Delta Q = T\mathrm{d}S$ with eq. (4.27), this yields

$$\begin{aligned} C_P &= \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \\ &= \left(\frac{\partial (U+PV)}{\partial T}\right)_P \\ &= \left(\frac{\partial H}{\partial T}\right)_P , \end{aligned} \tag{4.32}$$

where we have defined the *enthalpy* $H := U + PV$.

*Example 4.1.* **Heat capacity of ideal gas**

For an ideal gas, the internal energy is given by $U = \frac{3}{2}Nk_BT$, and the state variables volume, pressure, and temperature are related according to the ideal gas law (1.10), $PV = Nk_BT$. This implies

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{k_B N}{P}$$

and hence

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}k_B N \tag{4.33}$$

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = \frac{5}{2}k_B N \tag{4.34}$$

> We thus see that $C_P > C_V$.

In general, the heat capacity at constant pressure is never smaller than the heat capacity at constant volume:

$$C_P \geq C_V \ .$$

The reason is that when adding heat at constant pressure, a fraction of the absorbed heat gets converted into mechanical work, thus not contributing to an increase in temperature. At constant volume, the system does not perform any mechanical work.

**Isothermal Compressibility and expansion coefficient.** To relate the remaining expressions in the TdS equations to other known response functions, we make use of a Maxwell relation. Dividing eq. (4.28) by temperature, we obtain

$$\mathrm{d}S = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left[\frac{P}{T} + \frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T\right]\mathrm{d}V \ . \tag{4.35}$$

Using Schwarz's theorem, we equate

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{\partial^2 S}{\partial V \partial T} \ , \tag{4.36}$$

where the partial derivaties $\partial S/\partial T$ and $\partial S/\partial V$ are given by the total differential in eq. (4.35), such that eq. (4.36) becomes

$$\begin{aligned} \frac{\partial}{\partial V}\left(\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V\right)\Bigg|_T &= \frac{\partial}{\partial T}\left(\frac{P}{T} + \frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T\right)\Bigg|_V \\ \frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} &= -\frac{1}{T^2}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial V} \\ \Rightarrow \qquad P + \left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial P}{\partial T}\right)_V \ . \end{aligned} \tag{4.37}$$

With this Maxwell relation, we may now progress by relating $\left(\frac{\partial P}{\partial T}\right)_V$ to something already known. The thermal equation of state (relating $P, T, V$ at fixed $N$, see section 4.3) may be written as

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial V}{\partial P}\right)_T \mathrm{d}P = \mathrm{d}V(T,P) \ , \tag{4.38}$$

which we invert to find

$$\mathrm{d}P = \frac{1}{\left(\frac{\partial V}{\partial P}\right)_T}\mathrm{d}V - \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T}\mathrm{d}T = \mathrm{d}P(T,V) \ . \tag{4.39}$$

This result implies

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\alpha}{\kappa_T} \ , \tag{4.40}$$

where $\alpha$ and $\kappa_T$ denote the expansion coefficient and isothermal compressibility, respectively, as defined in eqs. (4.17) and (4.16). We remark that the first equal sign in eq. 4.40 may be seen as a second version of the chain rule. [5] Now that we have related all partial derivatives to known response function, we may write the TdS equation (4.28) as

$$\boxed{T\mathrm{d}S = C_V\mathrm{d}T + T\frac{\alpha}{\kappa_T}\mathrm{d}V}\ . \tag{4.41}$$

A similar procedure leads to the final expression for the other TdS equations (exercise):

$$\boxed{T\mathrm{d}S = C_P\mathrm{d}T - \alpha TV\mathrm{d}P} \tag{4.42}$$

$$\boxed{T\mathrm{d}S = \frac{C_V\kappa_T}{\alpha}\mathrm{d}P + \frac{C_P}{\alpha V}\mathrm{d}V} \tag{4.43}$$

When a system does not exchange any heat with its environment, we can set $T\mathrm{d}S = 0$ and obtain relations between $T$ and $V$, $P$ and $V$, or $T$ and $P$. This makes the TdS equations important especially for adiabatic processes.

When combined, the TdS equations (4.41)–(4.43) tell us something about how the response functions $C_V, C_P, \alpha$, and $\kappa_T$ relate to each other. Subtracting eq. (4.41) from eq. (4.42), we get

$$(C_P - C_V)\mathrm{d}T = \alpha TV\mathrm{d}P + \frac{\alpha T}{\kappa_T}\mathrm{d}V\ . \tag{4.44}$$

Now, we choose the state function $T(V,P)$ which implies the differential

$$\mathrm{d}T = \left(\frac{\partial T}{\partial V}\right)_P \mathrm{d}V + \left(\frac{\partial T}{\partial P}\right)_V \mathrm{d}P\ .$$

Invoking eqs. (4.17) and (4.40) finally leads to the equation

$$\left(\frac{C_P - C_V}{\alpha V} - \frac{\alpha T}{\kappa_T}\right)\mathrm{d}V + \left((C_P - C_V)\frac{\kappa_T}{\alpha} - \alpha TV\right)\mathrm{d}P = 0\ . \tag{4.45}$$

Since $V$ and $P$ are independent variables, the coefficients (in large parentheses) must vanish independently. Thus,

$$\boxed{C_P - C_V = \frac{\alpha^2 TV}{\kappa_T}}\ . \tag{4.46}$$

Since $\kappa_T \geq 0$, we see from this immediately that $C_P \geq C_V$, in agreement with the physical argument above.

---

[5] The chain rule, as you probably know it, states that

$$\begin{aligned}\left(\frac{\partial P}{\partial T}\right)_V &= \left.\frac{\partial P(T,V)}{\partial T}\right|_V = \left.\frac{\partial P\big(U(T,V),V\big)}{\partial T}\right|_V \\ &= \left(\frac{\partial P}{\partial U}\right)_V \Big/ \left(\frac{\partial T}{\partial U}\right)_V = \left(\frac{\partial P}{\partial U}\right)_V \cdot \left(\frac{\partial U}{\partial T}\right)_V\ ,\end{aligned}$$

where $U$ is an arbitrary function.

As another application of the TdS equations, imagine an adiabatic process described by the variables volume and temperature. Adiabaticity requires $T\mathrm{d}S = 0$, and eq. (4.41) describes the process in terms of $V$ and $T$,

$$C_V \mathrm{d}T + T\frac{\alpha}{\kappa_T}\mathrm{d}V = 0 \ . \tag{4.47}$$

From this we infer that

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\frac{T\alpha}{\kappa_T C_V}} \ , \tag{4.48}$$

where all quantities on the RHS are functions of $T$ and $V$. In general, $C_V > 0$ and $\kappa_T \geq 0$. For most systems, also $\alpha > 0$, from which we conclude that for most systems $(\partial T/\partial V)_S < 0$, i.e. the temperature rises upon compression. You may know this from every-day experience when using an air pump. Water is a prominent exception: for $H_2O$ the expansion coefficient can be negative for certain temperatures, leading to the well-known anomaly that causes icebergs to float.

## 4.6 Different ways of expanding gas

There exist many different paths for a gas to expand from an initial volume $V_i$ to a final volume $V_f$. For example, the pressure might stay constant while expanding the gas (isobaric) or the temperature might be held fixed (isothermal), or the temperature and pressure might change in complicated ways as the gas expands. The mechanical work $W$ performed *by* the gas during the expansion is described by the integral

$$W_{i\to f} = \int_{V_i}^{V_f} P(V)\,\mathrm{d}V \ . \tag{4.49}$$

Here we assume that all state changes are quasistatic, i.e. so slow that at each point in state space we can describe the gas by the three state variables $P, V$, and $T$. Since the equation of state $T(P,V)$ exists (see section 4.3), any point in a P-V diagram completely specifies the system. Fig. 4.1 shows a P-V diagram including important paths a gas may take in a thermodynamic process. Curves along constant temperature are termed *isotherms*. The work $W$ corresponds to the area under the path in the P-V diagram.

Consider the isothermal expansion of an ideal gas ($T$ =const., $T_i = T_f$) corresponding to path 1 in fig. 4.1. From the ideal gas law (eq. (1.10)) we obtain

$$P(V) = \frac{Nk_BT}{V} \ .$$

Thus, the work $W^{(1)}_{i\to f}$ along this path is

$$W^{(1)}_{i\to f} = Nk_BT\int_{V_i}^{V_f}\frac{\mathrm{d}V}{V} = Nk_BT\ln\left(\frac{V_f}{V_i}\right) \ . \tag{4.50}$$

This shows that the gas does positive work, $W^{(1)}_{i\to f} \geq 0$. For the paths 2 and 3, we find

$$W^{(2)}_{i\to f} = P_i(V_f - V_i) = \frac{Nk_BT}{V_i}(V_f - V_i) = Nk_BT\left(\frac{V_f}{V_i} - 1\right) \ , \tag{4.51}$$

$$W^{(3)}_{i\to f} = P_f(V_f - V_i) = \frac{Nk_BT}{V_f}(V_f - V_i) = Nk_BT\left(1 - \frac{V_i}{V_f}\right) \ . \tag{4.52}$$

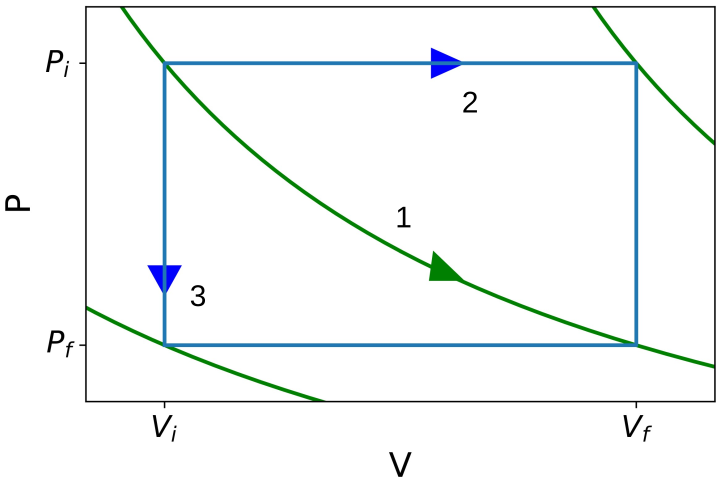


**Figure 4.1:** P-V diagram of expanding a gas from initial volume $V_i$ to final volume $V_f$. Green lines are isotherms and blue lines are isochors (vertical) and isobars (horizontal).

These paths are a combination of isochoric and isobaric processes. While they are certainly not isothermal, their gas ends up with the same temperature as in the beginning, i.e. $T_i = T_f$. Comparing the areas under the curves when taking paths 1, 2, and 3, we see that

$$W^{(2)}_{i\to f} \geq W^{(1)}_{i\to f} \geq W^{(3)}_{i\to f} \ .$$

We can confirm this mathematically by defining $x := V_f/V_i$ in eqs. (4.50)-(4.52) and showing that

$$x - 1 \geq \ln x \geq 1 - \frac{1}{x} \qquad (\text{for } x > 0) \ .$$

All these considerations show clearly that work is a path-dependent quantity. Therefore work cannot be an exact (total) differential, i.e. we must write $\Delta W$ instead of $\mathrm{d}W$. For this reason, work is not a state function. We can see this by writing down the total work $W_{\text{tot}}$ done in a cyclic process,

$$W_{\text{tot}} = \oint \Delta W = \oint P\,\mathrm{d}V \neq 0 \ , \tag{4.53}$$

which is generally nonzero as it corresponds to the area enclosed by the cycle beginning and ending at the same point in a P-V diagram. Thus, a work function $W(P,V)$ has no meaning.

From the path-dependence of mechanical work in a thermodynamic process, we draw the following conclusions.

- The First Law of Thermodynamics states that $\mathrm{d}U = \Delta Q - \Delta W$ (eq. (4.1)). Now we take a closed contour integral,

  $$\oint \mathrm{d}U = \oint \Delta Q - \oint \Delta W = 0 \ , \tag{4.54}$$

  which vanishes since the internal energy $U$ is a state function, $U(V,P)$ (and, equivalently, because $\mathrm{d}U$ is an exact differential). It follows from this and eq. (4.53) that $\oint \Delta Q \neq 0$. Thus heat is also not a state function. Moreover, the total absorbed heat in a cyclic process equals the total work done.

- In our example of expanding an ideal gas as illustrated by fig. 4.1, the process starts and ends at the same temperature. Thus we have $U_f - U_i = 0$ because $U = \frac{3}{2}Nk_BT$ for an ideal mono-atomic gas. Consequently, the heat absorbed during the process equals the work performed (even though the process is not cyclic): $Q_{i\to f} = W_{i\to f}$.
- For an adiabatic process where $\Delta Q = T\mathrm{d}S = 0$, i.e. the system does not exchange heat with its surroundings, we find that

  $$\mathrm{d}U = -\Delta W = -\mathrm{d}W \ .$$

  Thus, for $\mathrm{d}S = 0$, the work becomes an exact differential $\mathrm{d}W$.

**Adiabatic expansion of an ideal gas.** In the first part of this section, we have discussed the expansion of a gas in an isothermal process ($T$ =const.) as well as in a combination of isobaric ($P$ =const.) and isochoric ($V$ =const.) processes, using the example of an ideal gas. Now we consider the *adiabatic* expansion of an ideal gas ($\mathrm{d}S = 0$). What path in a P-V diagram describes an adiabatic process?

To address this question, we need a TdS equation that relates $\mathrm{d}P$ and $\mathrm{d}V$ to each other. From eq. (4.43) we get

$$0 = \frac{C_V\kappa_T}{\alpha}\mathrm{d}P + \frac{C_P}{\alpha V}\mathrm{d}V \ . \tag{4.55}$$

Here the response functions depend on volume and pressure, i.e. $C_V(P,V)$, $C_P(P,V)$, $\alpha(P,V)$, and $\kappa_T(P,V)$. Furthermore, the equation of state for the ideal gas is given by eq. (1.10); $PV = Nk_BT$. The thermal compressibility is then given by

$$\begin{aligned}\kappa_T &= -\frac{1}{V}\left(\frac{\partial V(P,T)}{\partial P}\right)_T \\ &= \frac{Nk_BT}{VP^2} \\ &= \frac{1}{P} \ .\end{aligned} \tag{4.56}$$

In example 4.1 we have already calculated the heat capacities for an ideal mono-atomic gas,

$$C_V = \frac{3}{2}Nk_B \ , \qquad C_P = \frac{5}{2}Nk_B \ .$$

Note that $C_V$ and $C_P$ do not depend on $P$ or $V$.

Now, inserting the result for $\kappa_T$ into eq. (4.55) yields

$$\begin{aligned}C_V\frac{\mathrm{d}P}{P} &= -C_P\frac{\mathrm{d}V}{V} \\ \frac{\mathrm{d}P}{P} &= -\gamma\frac{\mathrm{d}V}{V} \ ,\end{aligned} \tag{4.57}$$

where we have defined the *adiabatic exponent* $\gamma := C_P/C_V \geq 1$. For an ideal gas, the adiabatic exponent is $\gamma = 5/3$. Integrating both sides of eq. (4.57) from the initial state $i$

to the final state $f$ gives

$$\begin{aligned} \ln P\Big|_i^f &= -\gamma \ln V\Big|_i^f \\ \ln\left(\frac{P_f}{P_i}\right) &= \ln\left(\frac{V_i}{V_f}\right)^\gamma \\ \Rightarrow \quad \frac{P_f}{P_i} &= \left(\frac{V_i}{V_f}\right)^\gamma . \end{aligned} \tag{4.58}$$

This result is an important relation describing adiabatic processes. Since the initial and final state were chosen arbitrarily, we have derived

$$PV^\gamma = \text{const.} \tag{4.59}$$

Since for any expansion $\gamma > 1$, the adiabatic $P(V)$ curves in a P-V diagram drop faster than the isotherms.

Note that like isotherms, adiabatic curves (sometimes called adiabates) never cross each other in a P-V diagram. However, adiabates cross with isotherms.

## 4.7 Carnot cycle

The Carnot cycle is a cyclic thermodynamic process which serves as an idealization of real heat engines converting heat to work. To give an example of a real heat engine, fig. 4.2 illustrates a scheme of the Otto engine and its corresponding cycle.

The Carnot cycle consists of four steps as depicted in fig. 4.3:

- $a \to b$: isothermal expansion at temperature $T_1$;
- $b \to c$: adiabatic reversible expansion;
- $c \to d$: isothermal compression at $T_2 < T_1$;
- $d \to a$: adiabatic reversible compression.

The Carnot cycle is approximately realized by periodically moving a cylinder between two heat reservoirs of different temperatures. As a result, heat gets transferred from the hot ($T_1$) to the cold reservoir ($T_2$). Figures 4.4 and 4.5 provide an illustration of the four distinct steps in this heat engine.

As for any cycle, the integral over the internal energy is zero,

$$\oint \mathrm{d}U = 0 \ .$$

It follows that the total work $W_{\text{tot}}$ done in the Carnot cycle is

$$W_{\text{tot}} = \oint \Delta W = \oint \Delta Q = Q_{\text{tot}} = Q_{a\to b} + Q_{c\to d} \ , \tag{4.60}$$

where $Q_{a\to b}$ and $Q_{c\to d}$ denote the heat transfer *to* the system during the respective isothermal processes. Note that no heat is exchanged along the adiabates. The quantity $Q_{a\to b}$ corresponds to the amount of heat the (idealized) engine absorbs from the hot

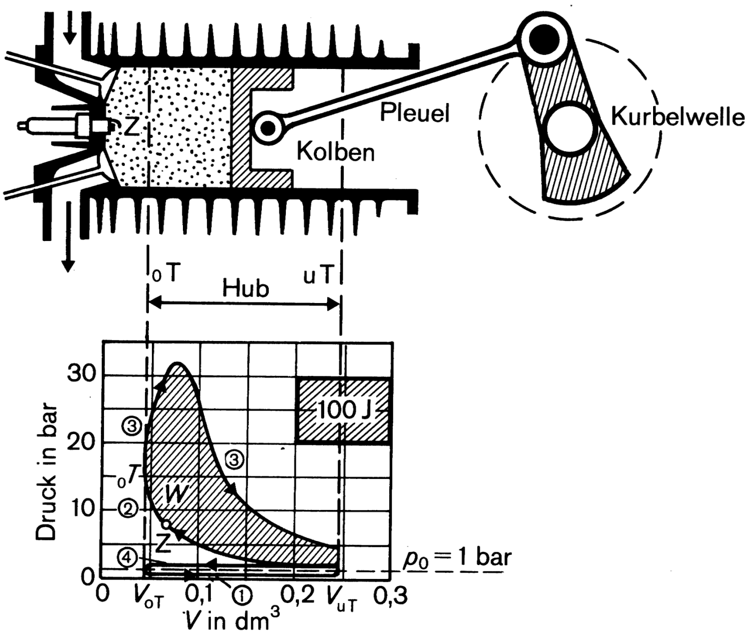


**Figure 4.2: Four-stroke Otto engine and Otto cycle** as an example of a real heat engine.

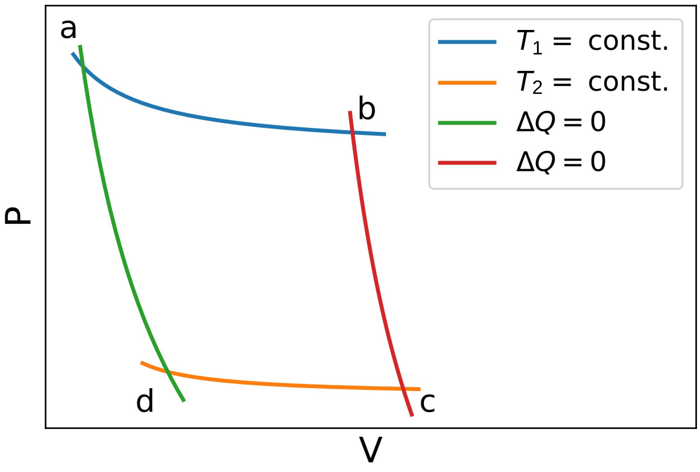


**Figure 4.3: $PV$ diagram of the Carnot cycle.**

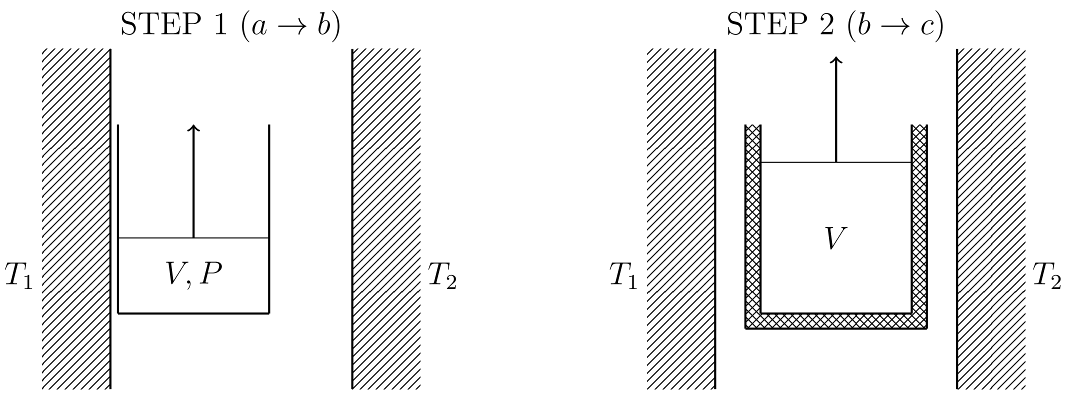


**Figure 4.4:** Carnot process steps 1 and 2: isothermal and adiabatic expansion. (In step 2 the cylinder is thermally insulated, as shown by the cross-hatched pattern).

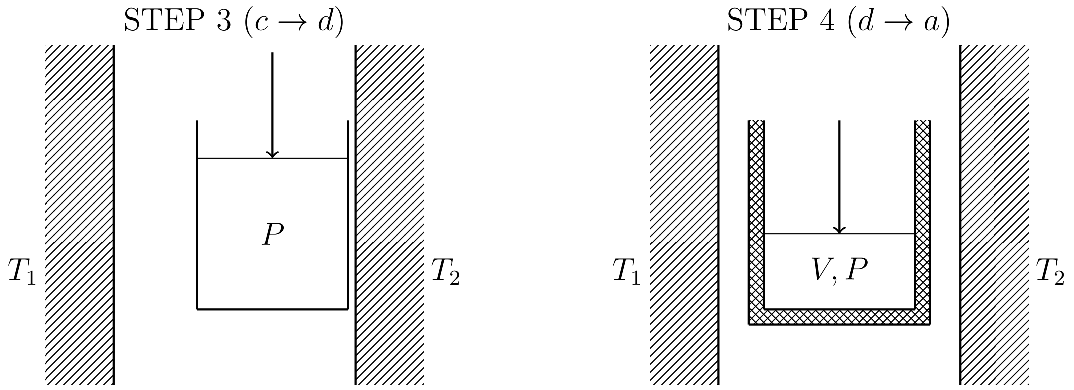


**Figure 4.5:** Carnot process steps 3 and 4: isothermal and adiabatic compression. (In step 4 the cylinder is thermally insulated, as shown by the cross-hatched pattern.)

reservoir ($T_1$) during isothermal expansion. Similarly, $-Q_{c\to d}$ represents the heat emitted to the cold reservoir at $T_2$ during isothermal compression.

Let us now look at the entropy of the system. As a state function, $S$ must satisfy[6]

$$\oint \mathrm{d}S = 0 \; , \tag{4.61}$$

and $\mathrm{d}S$ is an exact differential given by eq. (4.2) according to the Second Law of Thermodynamics. This implies

$$0 = \oint \mathrm{d}S = \frac{Q_{a\to b}}{T_1} + \frac{Q_{c\to d}}{T_2}$$

and thus

$$Q_{c\to d} = -\frac{T_2}{T_1} Q_{a\to b} \; . \tag{4.62}$$

Notice the negative sign on the RHS, showing that indeed is transferred from the system *to* the cold reservoir at $T_2$. Combining eqs. (4.60) and (4.62), we derive that the total work done in the Carnot cycle is given by

$$\boxed{W_{\text{tot}} = Q_{a\to b}\left(1 - \frac{T_2}{T_1}\right)} \; . \tag{4.63}$$

Hence the work done by the idealized Carnot engine depends on the temperature ratio between the reservoirs. We define the *efficiency* of the Carnot heat engine as

$$\eta := \frac{W_{\text{tot}}}{Q_{a\to b}} = 1 - \frac{T_2}{T_1} \; . \tag{4.64}$$

---

[6] The entropy balance refers to the heat engine itself (which we call system), not including the two reservoirs. For the reservoirs, the total entropy change is given by

$$\oint \mathrm{d}S = -\frac{Q_{a\to b}}{T_1} - \frac{Q_{c\to d}}{T_2} \; ,$$

which must equal to zero for a reversible process. Thus, as soon as the heat emitted $-Q_{c\to d}$ becomes slightly larger than $\frac{T_2}{T_1} Q_{a\to b}$, the process is irreversible.

The efficiency expresses the net work done per absorbed heat. Since $0 < T_2 < T_1$, the efficiency can take values between zero and one; $0 < \eta < 1$. If $T_1$ is very high and $T_2$ very small, the total work will be large. Conversely, if both reservoirs have the same temperature $T_2 = T_1$, the engine performs no work and the efficiency is zero. We can visualize this considering that the total work corresponds to the area enclosed by the cycle in the P-V diagram. The further the isotherms are apart, the larger the enclosed area will be.

**Carnot heat pump.** As an ideal process, the Carnot cycle is reversible. This means that instead of using it as a heat engine that converts heat into work, we might reverse the process and use the machine as a heat pump which converts work into heat. The P-V diagram of the reversed Carnot cycle looks just the same and consists of the same steps, only running in the opposite direction.

A Carnot heat pump transports heat from the cold reservoir at $T_2$ to the hot reservoir at $T_1$. Specifically, the heat $Q_1 := -Q_{b\to a}$ transferred to the hot reservoir during isothermal compression is given by

$$Q_1 = \frac{-W_{\mathrm{tot}}}{\eta} , \tag{4.65}$$

where $-W_{\mathrm{tot}}$ represents the work done *on* the system. To measure how powerful the heat pump is, we define the *coefficient of performance* $\varepsilon$ as the inverse of the Carnot efficiency,

$$\varepsilon := \frac{1}{\eta} = \frac{T_1}{T_1 - T_2} . \tag{4.66}$$

Thus, to get a lot of heat from a heat pump, the temperatures $T_1$ and $T_2$ should not be too different. We will calculate an example in the following when discussing the principle of cogeneration of heat and electricity.

**Cogeneration of heat and electricity.** How do you heat a house as efficiently as possible? Suppose that your house features a tank of natural gas and has access to a ground water reservoir beneath. The most direct way would be to simply burn the gas to produce heat. 1J (one Joule) of burned gas would then yield 1J of heat. However, you can do much better by using a Carnot engine. First, you would burn the gas to power the Carnot machine. If the gas burns at 600°C ≈ 870K and the heating panels have a temperature of 40°C ≈ 313K, the ideal efficiency is

$$\eta = 1 - \frac{T_2}{T_1} \approx 0.64 .$$

In other words, 1J of burned gas supplies 0.64J of work (e.g. electricity) and 0.36J of heat to the house. With the 0.64J of work, you can now run a heat pump. This is where the ground water comes into play. Suppose the ground water is 10°C ≈ 283K cold. Then, the heat pump's ideal coefficient of performance is

$$\varepsilon = \frac{T_1}{T_1 - T_2} \approx 10.4 .$$

Feeding 0.64J into the heat pump, this means that you will get $10.4 \cdot 0.64\text{J} \approx 6.7\text{J}$ for heating the house. Together with the 0.36J of heat coming directly from the Carnot engine, you will obtain a total heat of 7.6J from burning just 1J of gas!

At first glance, this looks suspiciously like a violation of energy conservation. However, a large amount of energy was extracted from the ground water during the process, which makes up for the seemingly missing part. Since the ground water reservoir is large, its temperature decrease will not be noticeable.

The principle described here is known as *cogeneration of heat and electricity.* It is applied in many private and public buildings.

## 4.8 Transfer and creation of entropy

Now we discuss why real engines are less efficient than the idealised Carnot process. $\Delta Q$ is the heat transfer from reservoir 1 at $T_1$ to reservoir 2 at $T_2$. The two reservoirs are connected via a wire that conducts heat (see Fig. 4.6).

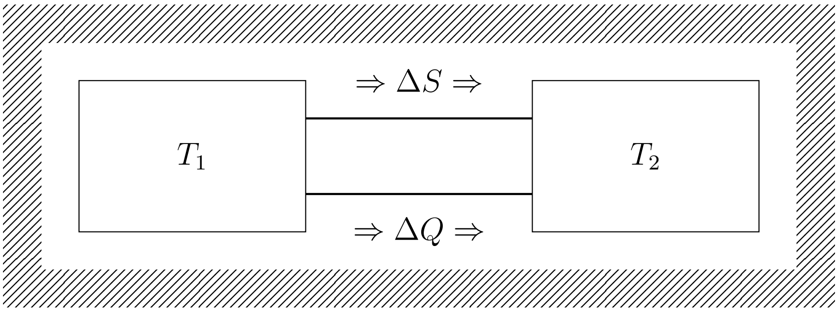


**Figure 4.6:** Two reservoirs with temperatures $T_1$ and $T_2$ can exchange heat and entropy via wires. (The striped pattern represents thermal insulation from the environment.)

### Reversible Case

The entropy changes in the reservoirs are $\Delta S_1 = -\frac{\Delta Q}{T_1} < 0$ and $\Delta S_2 = \frac{\Delta Q}{T_2} > 0$. For $T_1 = T_2$ the total entropy change $\Delta S_{\text{tot}} = \Delta S_1 + \Delta S_2 = 0$ is zero. This is an example of a reversible heat transfer. Heat is transferred, but the total entropy stays constant. The second law of thermodynamics allows these kinds of reversible processes to happen.

### Irreversible Case

Opposite to the reversible case, here the assumption is that $T_1 > T_2$. The heat will flow from the hot to the cold reservoir. $\Delta Q$ is assumed so small that $T_1$ and $T_2$ stay quasi constant. The entropy however increases:

$$\begin{aligned}\Delta S_{\text{tot}} &= \Delta S_1 + \Delta S_2 && (4.67)\\ &= \Delta Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right) && (4.68)\\ &= \Delta Q\frac{T_1 - T_2}{T_1 T_2} && (4.69)\\ &> 0, && (4.70)\end{aligned}$$

and thus this process is irreversible. Note that the opposite process, i.e. heat flowing from the cold to the hot reservoir meaning $T_1 < T_2$, would increase the entropy and is not allowed.

### Comments

- The Carnot process is reversible if no heat leaks from the hot to the cold reservoir.
- The heat flow from the hot to the cold reservoir without conversion to mechanical work is the main reason for the low efficiency of real heat engines compared to the ideal Carnot efficiency.
- There is no heat engine with a higher efficiency than the Carnot engine.

## 4.9 Extremal properties of thermodynamic potentials

- In an insulated system $U$, $V$, and $N$ are constant and the entropy $S(U,V,N)$ is maximized with respect to all non-conserved quantities, as shown in section 3.5.
- If energy transfer is allowed between a small system and a reservoir (see Fig. 4.7), we have

$$\begin{aligned}dU &= TdS - PdV + \mu dN && (4.71)\\ dS &= \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN && (4.72)\\ S_{\text{tot}} &= S(U_1, V_1, N_1) + S(U - U_1, V - V_1, N - N_1)\\ &\approx S(U_1, V_1, N_1) + S(U, V, N) - \frac{U_1}{T} + \mathcal{O}\left(\frac{1}{N}\right)\\ &= S(U_1, V_1, N_1) - \frac{U_1}{T} + \text{const.}\\ &= -\frac{1}{T}(U_1 - S_1 T) + \text{const.} && (4.73)\end{aligned}$$

  So from the second law of thermodynamics follows that $S_1 - \frac{U_1}{T}$ is maximized. And thus $U_1 - TS_1$ is minimized. We conclude that the free energy $F = U - TS$ is minimized when $T, V, N$ are fixed.

- Now let us allow energy transfer and volume transfer: $V_1$ and $U_1$ can change (see

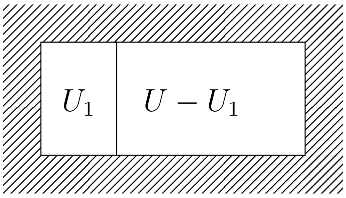


**Figure 4.7:** A small reservoir in heat contact with a reservoir (The stripy pattern represents thermal insulation).

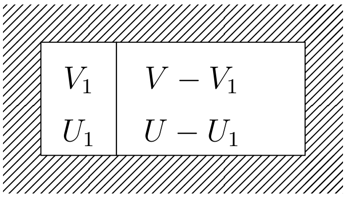


**Figure 4.8:** A small reservoir in contact with a reservoir, but now $V_1$ and $U_1$ can change (The stripy pattern represents thermal insulation).

Fig. 4.8):

$$\begin{aligned} S_{\text{tot}} &= S(U_1, V_1, N_1) + S(U - U_1, V - V_1, N - N_1) \\ &= S_1 + S(U, V, N) - \frac{U_1}{T} - \frac{V_1 P}{T} + \mathcal{O}\left(\frac{1}{N}\right) \; . \end{aligned} \tag{4.74}$$

The total entropy $S_{\text{tot}}$ is maximized, and thus $TS_1 - U_1 - V_1P$ is maximized. With that the Gibbs free energy (free enthalpy) $G(T, P, N) = U - TS + PV$ is minimised for a system at fixed $T, P, N$.

## 4.10 Thermodynamics of phase transitions

Simple substances can exist in one of three phases: solid, liquid, gas (vapor). A phase diagram of such a substance (see fig. 4.9) illustrates in which phase the substance exists depending on temperature and pressure.

Along the lines in the diagram, two phases coexist, meaning there are two solutions to the equation of state with different volumes $v = \frac{V}{N}$ per particle. On the two-phase coexistence lines, for a given volume, the system splits into two coexisting phases (phase separation / phase equilibrium). At the triple point all three phases coexist. At the critical point the difference between two phases (liquid/vapour) vanishes.

### 4.10.1 Thermodynamic stability at the phase transition

Consider a two-phase system like liquid-vapour at constant $T$ and $P$. As shown in section 4.9, at constant $T$,$P$, equilibrium is characterised by a minimum of the Gibbs free energy (free enthalpy)

$$G = U - TS + PV \tag{4.75}$$

$$= \sum_i \mu_i N_i . \tag{4.76}$$

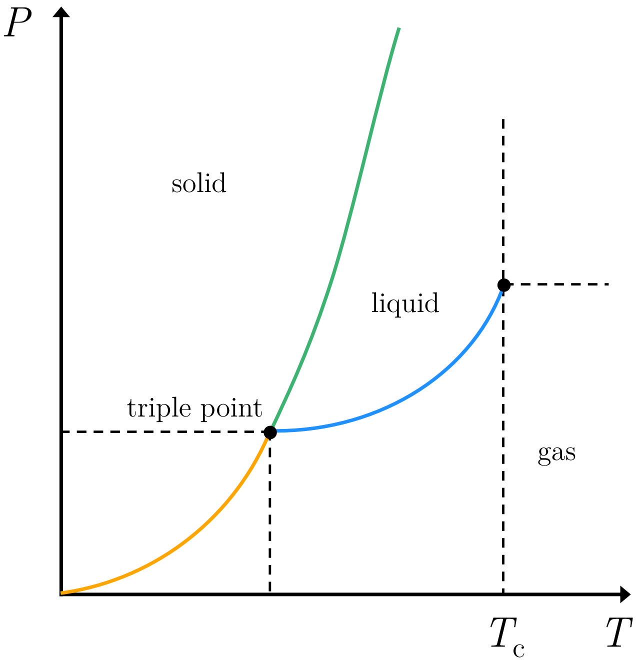


**Figure 4.9:** Example of a phase diagram for a simple substance (not water).

Now let $N = N_1 + N_2$, where $N_1$ is the number of particles in phase 1 and $N_2$ the number of particles in phase 2.

$$\begin{aligned} G &= N_1\mu_1 + N_2\mu_2 && (4.77)\\ &= N_1\mu_1 + (N - N_1)\mu_2 && (4.78) \end{aligned}$$

This can be minimised with respect to $N_1$

$$\begin{aligned} \frac{\partial G}{\partial N_1} &= \frac{\partial}{\partial N_1}(N_1\mu_1 + (N - N_1)\mu_2) && (4.79)\\ &= \mu_1 - \mu_2 && (4.80)\\ &\overset{!}{=} 0. && (4.81) \end{aligned}$$

We see that in equilibrium the chemical potential has to be equal for the two phases.

### 4.10.2 Clausius-Clapeyron equation

Consider two coexisting phases $i = 1, 2$. For each phase we can write

$$\begin{aligned} dG_i &= -S_i dT + V_i dP + \mu_i dN_i && (4.82)\\ &= d(\mu_i N_i) && (4.83)\\ &= \mu_i dN_i + N_i d\mu_i && (4.84)\\ d\mu_i &= -\frac{S_i}{N_i}dT + \frac{V_i}{N_i}dP. && (4.85) \end{aligned}$$

With the definition of the total differential this yields

$$\left.\frac{\partial\mu_i}{\partial T}\right|_P = -\frac{S_i}{N_i} \tag{4.86}$$

$$\left.\frac{\partial\mu_i}{\partial P}\right|_T = \frac{V_i}{N_i} \tag{4.87}$$

$$\left.\frac{\partial(\mu_2-\mu_1)}{\partial T}\right|_P = -\left(\frac{S_2}{N_2}-\frac{S_1}{N_1}\right) \tag{4.88}$$

$$= -\Delta s. \tag{4.89}$$

Here $s=\frac{S}{N}$ is the entropy per particle.

$$\left.\frac{\partial(\mu_2-\mu_1)}{\partial P}\right|_T = \frac{V_2}{N_2}-\frac{V_1}{N_1} \tag{4.90}$$

$$= \Delta v \tag{4.91}$$

Here $v=\frac{V}{N}$ is the volume per particle. With $\Delta\mu=\mu_2-\mu_1$ and using the differential chain rule[7] this becomes

$$-\left.\frac{\partial P}{\partial T}\right|_{\Delta\mu} = \frac{\left.\frac{\partial\Delta\mu}{\partial T}\right|_P}{\left.\frac{\partial\Delta\mu}{P}\right|_T} = -\frac{\Delta s}{\Delta v} \tag{4.96}$$

$$\frac{dP_{co}(T)}{dT} = \left.\frac{\partial P}{\partial T}\right|_{\Delta\mu=0} = \frac{\Delta s}{\Delta v}\ , \tag{4.97}$$

where $P_{co}(T)$ describes the coexistence curve in the phase diagram. With $\Delta q_i = T\Delta s$, which is the latent heat required for the phase change, this becomes

$$\frac{dP_{co}}{dT}(T) = \frac{\Delta q_i}{T\Delta v}\ . \tag{4.98}$$

This is the *Clausius-Clapeyron equation.*

---

[7] The total differential of $\Delta\mu$ as a function of pressure and temperature reads

$$\mathrm{d}\Delta\mu = \left(\frac{\partial\Delta\mu}{\partial P}\right)_T \mathrm{d}P + \left(\frac{\partial\Delta\mu}{\partial T}\right)_P \mathrm{d}T\ , \tag{4.92}$$

which can be rewritten as

$$\mathrm{d}T = \frac{\mathrm{d}\Delta\mu}{\left(\frac{\partial\Delta\mu}{\partial T}\right)_P} - \frac{\left(\frac{\partial\Delta\mu}{\partial P}\right)_T \mathrm{d}P}{\left(\frac{\partial\Delta\mu}{\partial T}\right)_P}\ . \tag{4.93}$$

This implies

$$\left(\frac{\partial T}{\partial P}\right)_{\Delta\mu} = -\frac{\left(\frac{\partial\Delta\mu}{\partial P}\right)_T}{\left(\frac{\partial\Delta\mu}{\partial T}\right)_P} \tag{4.94}$$

and, using $\left(\frac{\partial\Delta\mu}{\partial P}\right)_T = \left(\frac{\partial P}{\partial\Delta\mu}\right)_T^{-1}$,

$$\left(\frac{\partial\Delta\mu}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_{\Delta\mu} \left(\frac{\partial P}{\partial\Delta\mu}\right)_T = -1\ . \tag{4.95}$$

We call this the differential chain rule.

*Example 4.2.* **Boiling water and the Clausius-Clapeyron equation**

At 100°C ($T = 373.15\,\mathrm{K}$), the latent heat for water is $\Delta q_i \approx 2.3\,\mathrm{MJ\,kg^{-1}}$. The liquid volume of water is $V_l \approx 0.001\,\mathrm{m^3\,kg^{-1}}$, whereas its gaseous volume is $V_g \approx 1.7\,\mathrm{m^3\,kg^{-1}}$. With these values, the RHS of the Clausius Clapeyron equation (4.98) amounts to

$$\frac{\Delta q_i}{T(V_g - V_l)} \approx 3600\,\mathrm{J\,K^{-1}\,m^{-3}}\ .$$

The LHS is found to be

$$\frac{\mathrm{d}P_{co}}{\mathrm{d}T} \approx 3618\,\mathrm{Pa\,K^{-1}} = 3618\,\mathrm{J\,K^{-1}\,m^{-3}}\ ,$$

which agrees well with the RHS.

*Example 4.3.* **The anomal coexistence curve of water**

When melting ice (i.e. frozen water), the change in volume $\Delta V$ is very small. The coexistence curve must therefore have a steep slope $\mathrm{d}P_{co}/\mathrm{d}T$. In fact, $\Delta V$ is negative in this case because ice contracts when melting (anomaly of water). This means that also the liquid–solid coexistence curve of water has a negative slope in the phase diagram!

# 5 Statistical Mechanics of interacting systems

Throughout the previous chapters, the ideal gas served as the standard example for any application or calculation. Indeed, the ideal gas is a powerful model that allows us to calculate many properties explicitly. However, this computability relies on ignoring all interactions between the particles. Real gases interact, and in some cases the ideal gas is too simple to recover the properties of a real physical system.

In this chapter, we turn on interactions in order to find out how this influences thermodynamic properties. After introducing the virial theorem and the virial expansion, we derive the Van der Waals equation of state, which provides insight into the behavior of a real gas – even when the liquid and gaseous phases coexist! The methods presented in this chapter also have applications in fields like Astrophysics.

## 5.1 Virial theorem

Consider a gas of $N$ interacting atoms. Let us suppose that the interaction is described by a power law, such that the Hamiltonian $\mathcal{H}$ of the gas is given by

$$\mathcal{H} = \mathcal{H}_{\text{kin}} + \mathcal{H}_{\text{pot}} \ , \tag{5.1a}$$

where the kinetic and potential contributions are, respectively,

$$\mathcal{H}_{\text{kin}} = \sum_{j=1}^{N} \frac{\vec{p}_j^{\,2}}{2m_j} \ , \tag{5.1b}$$

$$\mathcal{H}_{\text{pot}} = \sum_{j=1}^{N} \sum_{k=j+1}^{N} \left[(\vec{q}_j - \vec{q}_k)^2\right]^{\frac{n}{2}} a_{jk} \ . \tag{5.1c}$$

Here $\vec{p}_j$ and $\vec{q}_j$ symbolize the momentum and position of the $j$-th particle, respectively. In principle, the prefactors $a_{jk}$ and the particle masses $m_j$ may differ from particle to particle. In addition, the power law exponent $n$ may be any arbitrary number, which makes this model very general and versatile. Possible applications include:

- gravity, where $n = -1$ and the prefactor are proportional to the product of the masses, $a_{jk} \propto -m_j m_k$;
- a one-component plasma of equally charged particles of equal mass $m_j = m$, with exponent $n = -1$ and prefactors $a_{jk} \propto Q^2$, where $Q$ denotes the charge (found in e.g. heavy planets and white dwarfs); or
- a two-component plasma described by $n = -1$ and $a_{jk} \propto Q_j Q_k$, where the charge $Q_j$ of particle $j$ may be $\pm Q$.

As established in chapter 3, the partition function $Z$ plays a central role in calculating expectation values of state variables like the pressure $P$ or entropy $S$. For the interacting system (eq. (5.1)), it is given by

$$Z = \frac{1}{N!} \prod_{j=1}^{N} \left[ \frac{1}{h^3} \int_V \mathrm{d}^3 q_j \int \mathrm{d}^3 p_j \right] e^{-\beta \mathcal{H}} \ , \tag{5.2}$$

where $h$ denotes Planck's constant and $\beta$ represents the inverse temperature as usual. Essentially, the partition function contains the solution of the problem since we could derive all thermodynamic quantities from it. The bad news are that we cannot solve eq. (5.2) explicitly. Nonetheless, we may extract some important information analytically. To do this, let us rescale $T$, $p$ and $q$ using a rescaling factor $\lambda$. We define the rescaled quantities

$$\begin{aligned} \tilde{T} &= \lambda^{-n} T \ , \\ \tilde{q} &= \lambda^{-1} q \ , \\ \tilde{p} &= \lambda^{-n/2} p \ . \end{aligned}$$

This transformation leaves the exponential in the partition function, $\exp\{-\beta\mathcal{H}\}$, invariant:

$$\tilde{\beta}\tilde{\mathcal{H}} = \frac{\frac{\tilde{p}_j^2}{2m_j} + (\tilde{q}_j - \tilde{q}_k)^n a_{jk}}{k_B \tilde{T}} = \frac{\frac{p_j^2}{2m_j} + (q_j - q_k)^n a_{jk}}{k_B T} = \beta \mathcal{H} \ , \tag{5.3}$$

where $\tilde{\mathcal{H}}$ denotes the Hamiltonian in rescaled variables. The bounds of integration change according to

$$\int_0^L \mathrm{d}q = \int_0^{\frac{L}{\lambda}} \lambda \mathrm{d}\tilde{q} = \int_0^{\tilde{L}} \lambda \mathrm{d}\tilde{q} \ , \tag{5.4}$$

which follows from the fact that lengths are rescaled as $\tilde{L} = L/\lambda$. Thus the total volume $V$ is related to the rescaled volume $\tilde{V}$ according to $V = \lambda^3 \tilde{V}$.

In terms of the rescaled variables, the partition function now reads

$$Z(V,T,N) = \frac{1}{N!} \prod_{j=1}^{N} \left[ \frac{1}{h^3} \int_{\tilde{V}} \mathrm{d}^3 \tilde{q}_j \lambda^3 \int \mathrm{d}^3 \tilde{p}_j \lambda^{3n/2} \right] e^{-\frac{1}{k_B \tilde{T}} \tilde{\mathcal{H}}_{\mathrm{kin}}(\tilde{p}) + \tilde{\mathcal{H}}_{\mathrm{pot}}(\tilde{q})} \ . \tag{5.5}$$

From this we see that

$$Z(V,T,N) = \lambda^{3N\left(1+\frac{n}{2}\right)} Z(\tilde{V}, \tilde{T}, N) \ . \tag{5.6}$$

In other words, the rescaling merely adds a prefactor to the partition function. We now apply another redefinition: instead of using the three variables $V, T, N$, we substitute them with the new set of variables $VT^{-3/n}$, $T$, and $N$. In terms of these, we write $Z$ as

$$\begin{aligned} Z(V,T,N) &\equiv h(VT^{-3/n},\, T,\, N) \\ &= h(\lambda^3 \tilde{V} \lambda^{-3} \tilde{T}^{-3/n},\, \lambda^n \tilde{T},\, N) \\ &= h(\tilde{V}\tilde{T}^{-3/n},\, \lambda^n \tilde{T},\, N) \ . \end{aligned} \tag{5.7}$$

Here $h$ is an unknown function of the new variables. We note that $\lambda$ only appears as a prefactor of the variable $\tilde{T}$ in the last line of eq. (5.7); the variable $VT^{-3/n}$ remains invariant under scaling. Connecting eq. (5.7) with eq. (5.6), we conclude that the partition function must have the functional form

$$Z(V,T,N) = (\lambda^n \tilde{T})^{\frac{3N}{n}\left(1+\frac{n}{2}\right)} \phi(\tilde{V}\tilde{T}^{-3/n},\, N)\ , \tag{5.8}$$

where $\phi$ is yet another unknown function. This formula for $Z$ is exact since no approximations were made.

We have shown the following: Apart from the particle number $N$, the partition function depends on the variables $V$ and $T$. These two variables may be rescaled in a way that $Z$ is given by the product of a prefactor which contains the sole dependence on $\lambda$, multiplied by a scaling-independent function $\phi$.

We utilized the scale factor $\lambda$ to reveal certain symmetry relations. Since $\lambda$ holds no physical meaning, we may now safely set $\lambda = 1$. This yields

$$Z(V,T,N) = T^{\frac{3N}{n}\left(1+\frac{n}{2}\right)} \phi(VT^{-3/n}, N)\ . \tag{5.9}$$

Using this formula, let us compute some thermodynamic quantities. The free energy of the interacting gas is

$$F = -k_B T \ln Z = -k_B T \left[\frac{3N}{n}\left(1+\frac{n}{2}\right)\ln(T) + \ln\left(\phi(VT^{-3/n})\right)\right]\ . \tag{5.10}$$

Since $\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V$ (eq. (3.102)), the free energy in turn allows us to calculate pressure and entropy:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = k_B T \cdot T^{-3/n} \frac{\phi'\left(VT^{-3/n}\right)}{\phi\left(VT^{-3/n}\right)}\ , \tag{5.11}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\frac{F}{T} + k_B\left[\frac{3N}{n}\left(1+\frac{n}{2}\right) - \frac{3}{n}VT^{-3/n}\frac{\phi'\left(VT^{-3/n}\right)}{\phi\left(VT^{-3/n}\right)}\right]\ . \tag{5.12}$$

A comparison of eq. (5.11) and (5.12) shows that we can express $S$ in terms of $P$ to get rid of the unknown functions $\phi$ and $\phi'$ in the expression. Then, the internal energy $U = F + TS$ (see eq. (3.61)) is given by

$$\boxed{U = k_B T\frac{3N}{n}\left(1+\frac{n}{2}\right) - \frac{3}{n}VP}\ . \tag{5.13}$$

Eq. (5.13) is known as the *virial theorem*. Analyzing the scaling properties of the partition function, we have arrived at an exact relation between energy, temperature, volume, and pressure for an interacting gas of $N$ atoms – without the need to solve the partition function explicitly. However, the theorem requires that the particle interaction potential follows a power law; otherwise it does not hold. Note that eq. (5.13) is neither the thermal nor the caloric equation of state ($f(P,V,T) = 0$, respectively $f(U,V,T) = 0$) but rather of the form $f(U,P,V,T) = 0$.

Returning to the applications mentioned above, we immediately find the energy of a gas with gravitational or Coulomb interactions by setting $n = -1$, which yields

$$U = -\frac{3N}{2}k_B T + 3VP\ . \tag{5.14}$$

The first term on the RHS corresponds to the result for an ideal gas, as follows from the equipartition theorem (see section 3.6.1). The second term containing the product $VP$ is the *virial* term which results from the non-zero interactions. In fact, to be consistent with previous results, the virial theorem should reduce to the equation of state for the ideal gas if the interactions vanish. Setting $n = 0$ in eq. (5.13) indeed leads to

$$nU = 3Nk_BT\left(1+\frac{n}{2}\right) - 3VP \qquad \overset{n=0}{\Longrightarrow} \qquad VP = Nk_BT \ , \tag{5.15}$$

which states the ideal gas law (eq. (1.10)) as expected.

**Separation into mean kinetic and potential energy.** To separate the internal energy $U$ into its kinetic and potential energy contribution, we make use of the fact that the kinetic energy depends solely and exclusively on the momentum coordinates of the gas atoms. When discussing the equipartition theorem in section 3.6.1, we already derived the expectation value of the kinetic energy,

$$\langle E_{\text{kin}}\rangle = \left\langle \sum_{j=1}^{N} \frac{\vec{p}_j^{\,2}}{2m_j} \right\rangle = \frac{3N}{2}k_BT \ , \tag{5.16}$$

for $N$ atoms with equal mass. Writing

$$\langle U\rangle = \langle E_{\text{kin}}\rangle + \langle E_{\text{pot}}\rangle \ , \tag{5.17}$$

the virial theorem implies that the average potential energy of the interacting gas is

$$\langle E_{\text{pot}}\rangle = \langle U\rangle - \frac{3N}{2}k_BT = \frac{3N}{n}k_BT - \frac{3}{n}VP \ . \tag{5.18}$$

This underlines that the virial theorem allows to derive exact results for a large class of interacting systems.

## 5.2 Virial expansion

As discussed above, the partition function $Z$ of an interacting gas, given by eq. (5.2), cannot be solved explicitly. In this section we seek an approximate solution. Using a perturbative approach known as the *virial expansion*, we wish to derive a correction to the ideal gas equation of state which adequately describes a weakly interacting gas. The idea is that interactions in a real gas are weak if the particle concentration, or density, is low. In that case, the atoms are, on average, far away from other gas atoms, inhibiting strong interactions. Besides generalizing the ideal gas law, the aim of this section is thus also to discuss an important application of perturbation theory in Statistical Mechanics.

To reiterate, the partition function of an interacting gas reads

$$Z\left(T,V,N\right) = \frac{1}{N!}\prod_{j=1}^{N}\left[\int \frac{\mathrm{d}^3p_j\mathrm{d}^3q_j}{h^3}\right] e^{-\beta(\mathcal{H}_{\text{kin}}+\mathcal{H}_{\text{pot}})} \ , \tag{5.19}$$

where the Hamiltonian $\mathcal{H} = \mathcal{H}_{\text{kin}} + \mathcal{H}_{\text{pot}}$ is now – to keep things simple – given by

$$\mathcal{H}_{\text{kin}} = \sum_{l=1}^{N} \frac{\vec{p_l}^2}{2m} \tag{5.20a}$$

$$\mathcal{H}_{\text{pot}} = \sum_{l=1}^{N} \sum_{k=l+1}^{N} w(|\vec{q_l} - \vec{q_k}|) \ . \tag{5.20b}$$

Here the pair potential $w(q)$ may be an arbitrary function of the distance $q = |\vec{q_l} - \vec{q_k}|$ between any pair $(l, k)$ of atoms. Typical contributions to the potential include steric (hard core), Coulomb, and/or van der Waals interactions.

Firstly, we can directly perform the integration over the momenta $p_j$. This leads to

$$Z\left(T, V, N\right) = \frac{1}{N!} \prod_j \int \frac{\mathrm{d}^3 q_j}{\lambda_t^3} e^{-\beta \sum_{k>l}^{N} w(|\vec{q_l} - \vec{q_k}|)} \ , \tag{5.21}$$

where $\lambda_t$ represents the thermal wavelength as defined in eq. (3.93). Note that the pair potential prevents the factorization of the position integral. It is now useful to switch to the grand canonical ensemble. The grand canonical partition function $\mathcal{Z}$ is given by

$$\mathcal{Z}\left(\mu, V, T\right) = \sum_{N=0}^{\infty} e^{\beta N \mu} Z_N\left(V, T\right) \tag{5.22}$$

in terms of the canonical partition function $Z_N(V, T) \equiv Z(T, V, N)$ (eq. (5.21)). As derived in section 3.9, the grand canonical equation of state (eq. (3.130)) reads

$$PV = k_B T \ln\Big(\mathcal{Z}(\mu, V, T)\Big) \tag{5.23}$$

and the number of atoms follows from

$$N = \frac{1}{\beta} \frac{\partial \ln\Big(\mathcal{Z}\left(\mu, V, T\right)\Big)}{\partial \mu} \ . \tag{5.24}$$

We now define the *fugacity* $z := e^{\beta\mu}$; this allows us to write the grand canonical partition function as a power series in $z$:

$$\mathcal{Z}\left(\mu, V, T\right) = \sum_{N=0}^{\infty} z^N Z_N\left(V, T\right) \ . \tag{5.25}$$

Then, we may also write the equation of state (5.23) as a power series in $z$. We therefore demand

$$\frac{PV}{k_B T} = \ln\left(\mathcal{Z}\right) = \ln\left(\sum_{N=0}^{\infty} z^N Z_N\right) \overset{!}{=} V \sum_{\ell=1}^{\infty} \left(\frac{z}{\lambda_t^3}\right)^{\ell} b_\ell \ , \tag{5.26}$$

where the coefficients $b_\ell$ must be determined such that they satisfy the equality. The perturbation is hence described in terms of the fugacity. How do we know that $z$ is a small parameter, you might ask? We do not, but we will eventually replace $z$ by a different parameter, the concentration.

To find the coefficients $b_\ell$, we realize that $z^0 Z_0 = 1$ and invoke the Taylor expansion

$$\ln(1 + \epsilon) = \epsilon - \frac{1}{2}\epsilon^2 + \frac{1}{3}\epsilon^3 + \mathcal{O}(\epsilon^4)$$

in order to rewrite $\ln \mathcal{Z}$ as

$$\begin{aligned}
&\ln\left(\sum_{N=0}^{\infty} z^N Z_N\right)\\
&= \ln\left(1 + \underbrace{zZ_1 + z^2Z_2 + z^3Z_3 + \cdots}_{=:\epsilon}\right)\\
&= zZ_1 + z^2\left(Z_2 - \frac{1}{2}Z_1^2\right) + z^3\left(Z_3 - Z_1Z_2 + \frac{1}{3}Z_1^3\right) + \mathcal{O}\left(z^4\right) \ . \qquad (5.27)
\end{aligned}$$

Comparing coefficients between eq. (5.27) and the RHS of eq. (5.26), we see that

$$\begin{aligned}
b_1 &= \frac{\lambda_t^3}{V}Z_1\\
b_2 &= \frac{\lambda_t^6}{V}\left(Z_2 - \frac{1}{2}Z_1^2\right)\\
b_3 &= \frac{\lambda_t^9}{V}\left(Z_3 - Z_1Z_2 + \frac{1}{3}Z_1^3\right)\\
&\dots
\end{aligned} \qquad (5.28)$$

Next, we want to express the functions $Z_N$ in terms of the *Mayer function* $f_{ij}$ defined by

$$f_{ij} := \exp\Big(-\beta w(|\vec{q}_i - \vec{q}_j|)\Big) - 1 \ . \qquad (5.29)$$

The Mayer function possesses two beneficial properties: *a)* it remains finite even for infinitely repulsive potentials; and *b)* it approaches zero as $w \to 0$. Inserting eq. (5.29) into the $Z_N$, we get

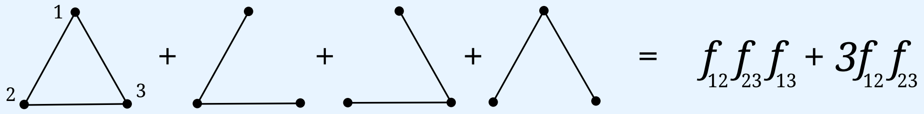
$$\begin{aligned}
Z_1 &= \int \frac{\mathrm{d}^3q}{\lambda_t^3}1 = \frac{V}{\lambda_t^3}\\
Z_2 &= \frac{1}{2!\lambda_t^6}\int \mathrm{d}^3q_1\mathrm{d}^3q_2\, e^{-\beta w(|\vec{q}_1-\vec{q}_2|)}\\
&= \frac{1}{2!\lambda_t^6}\int \mathrm{d}^3q_1\mathrm{d}^3q_2\,(1+f_{12})\\
Z_3 &= \frac{1}{3!\lambda_t^6}\int \mathrm{d}^3q_1\mathrm{d}^3q_2\mathrm{d}^3q_3\ (1+f_{12})(1+f_{23})(1+f_{13})\\
&\dots
\end{aligned} \qquad (5.30)$$

With this, the coefficients $b_\ell$ become

$$\begin{aligned}
b_1 &= 1\\
b_2 &= \frac{1}{2}\int \frac{\mathrm{d}^3q_1\mathrm{d}^3q_2}{V} f_{12}\\
b_3 &= \frac{1}{6}\int \frac{\mathrm{d}^3q_1\mathrm{d}^3q_2\mathrm{d}^3q_3}{V}\Big((1+f_{12})(1+f_{23})(1+f_{13}) - 3(1+f_{12}) + 2\Big)\\
&= \frac{1}{6}\int \frac{\mathrm{d}^3q_1\mathrm{d}^3q_2\mathrm{d}^3q_3}{V}\Big(f_{12}f_{23}f_{13} + f_{12}f_{23} + f_{12}f_{13} + f_{23}f_{13}\Big)\\
&= \frac{1}{6}\int \frac{\mathrm{d}^3q_1\mathrm{d}^3q_2\mathrm{d}^3q_3}{V}\Big(f_{12}f_{23}f_{13} + 3f_{12}f_{23}\Big)\\
&\dots
\end{aligned} \qquad (5.31)$$

Since the integrals are proportional to the Mayer functions, they converge (as long as $f_{ij}$ falls off to zero fast enough).

**Virial diagrams.** We can keep track of the Mayer function terms in the coefficients $b_\ell$ by drawing diagrams. This technique known as *diagrammatic expansion* allows a quick calculation of the terms and is very helpful for bookkeeping. The idea is the following: first, you draw $\ell$ points. Then, you connect the points pairwise in all possible ways. A connecting line between points $i$ and $j$ corresponds to $f_{ij}$, and you multiply all lines in the same diagram. Only the irreducible diagrams, i.e. the diagrams where all points are directly or indirectly connected to each other, contribute a term to $b_\ell$. For example, the virial diagram for $b_3$ has four irreducible diagrams of which the last three are equivalent:



We can invoke the chain rule to write the particle number (eq. (3.132)) as

$$\begin{aligned} N &= \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}(\mu)}{\partial \mu} \\ &= \frac{1}{\beta}\frac{\partial z}{\partial \mu}\frac{\partial \ln \mathcal{Z}}{\partial z} \\ &= z\frac{\partial \ln \mathcal{Z}}{\partial z} \ . \end{aligned} \tag{5.32}$$

Thus, based on eq. (5.26), we have

$$N = z\frac{\partial \ln \mathcal{Z}}{\partial z} = V\sum_{\ell=1}^{\infty} \ell \left(\frac{z}{\lambda_t^3}\right)^{\ell} b_\ell \ . \tag{5.33}$$

Defining the *particle concentration* $c := N/V$, we arrive at the formula

$$\boxed{c = \sum_{\ell=1}^{\infty} \ell \left(\frac{z}{\lambda_t^3}\right)^{\ell} b_\ell} \ . \tag{5.34}$$

We have derived an expression for the concentration $c$ in terms of a power series in $z$. As mentioned at the beginning of the calculation, we are looking for an equation of state that, in good approximation, describes an interacting gas with low concentration. In other words, $c$ is (physically) the small parameter, and we would like to expand the equation of state in powers of $c$. To achieve this, we must invert the function $c(z)$ to obtain $z(c)$ and insert this into the equation of state $P(z)$.

**Mathematical intermezzo: Inversion of power series.** Consider a power series $c(z)$ of the form[a]

$$c = \sum_{\ell=1}^{\infty} d_\ell z^\ell \ . \tag{5.35}$$

Such a series is always invertible. To find the inverse function $z(c)$, we make the ansatz

$$z = n_1 c + n_2 c^2 + n_3 c^3 + \cdots = \sum_{\ell=1}^{\infty} n_\ell c^\ell \ . \tag{5.36}$$

Inserting this ansatz into eq. (5.35) yields

$$\begin{aligned} c &= d_1 z + d_2 z^2 + d_3 z^3 + \cdots \\ &= d_1 \left(n_1 c + n_2 c^2 + n_3 c^3 + \cdots\right) + d_2 \left(n_1 c + n_2 c^2 + \ldots\right)^2 + d_3 \left(n_1 c\right)^3 + \mathcal{O}(c^4) \\ &= d_1 n_1 c + \left(d_1 n_2 + d_2 n_1^2\right) c^2 + \left(d_1 n_3 + 2 d_2 n_1 n_2 + d_3 n_1^3\right) c^3 + \cdots \end{aligned} \tag{5.37}$$

up to third order in $c$. In the last line of eq. (5.37) we have sorted the RHS by powers of $c$. Since the RHS must equal $c$, we necessarily conclude:

$$\begin{aligned} c = d_1 n_1 c \quad &\Rightarrow \quad n_1 = \frac{1}{d_1} \\ \left(d_1 n_2 + d_2 n_1^2\right) c^2 = 0 \quad &\Rightarrow \quad n_2 = -\frac{d_2 n_1^2}{d_1} = -\frac{d_2}{d_1^3} \\ \left(d_1 n_3 + 2 d_2 n_1 n_2 + d_3 n_1^3\right) c^3 = 0 \quad &\Rightarrow \quad n_3 = -\frac{2{d_2}^2 - d_3 d_1}{d_1^5} \\ &\ldots \end{aligned}$$

These are the coefficients of the inverse power series $z(c)$ in terms of the coefficients of $c(z)$, which means that we successfully inverted the original power series.

---

[a] If the sum would start at zero, we would have a constant term $d_0$ which would raise an issue for the inversion. However, we can solve this problem by defining a new power series $y := c - d_0$. This eliminates the constant term and we can proceed by inverting $y$. Later, the coefficients of the inverse of the original power series $c$ can be found by re-summation.

Now that we know how to invert a power series, we can invert eq. (5.34) to obtain the fugacity in powers of the concentration:

$$c = b_1 \frac{z}{\lambda_t^3} + 2 b_2 \left(\frac{z}{\lambda_t^3}\right)^2 + \mathcal{O}\left(\left(\frac{z}{\lambda_t^3}\right)^3\right) \quad \Rightarrow \quad \frac{z}{\lambda_t^3} = c - 2 b_2 c^2 + \mathcal{O}(c^3)\ . \tag{5.38}$$

Note that we have used $b_1 = 1$ here (eq. (5.31)). Finally, we use this result to rewrite the equation of state given in eq. (5.26), yielding

$$\begin{aligned} \frac{P}{k_B T} &= \frac{z}{\lambda_t^3} + b_2 \left(\frac{z}{\lambda_t^3}\right)^2 + \mathcal{O}\left(\left(\frac{z}{\lambda_t^3}\right)^3\right) \\ &= c - 2 b_2 c^2 + b_2 \left(c - 2 b_2 c^2\right)^2 + \mathcal{O}(c^3)\ . \end{aligned} \tag{5.39}$$

Expanding the square and omitting all terms with $c^3$ or a higher order leads to the *virial expansion* of the pressure in powers of the particle concentration,

$$\boxed{\frac{P}{k_B T} = c - b_2 c^2 + \mathcal{O}(c^3)}\ , \tag{5.40}$$

where $b_2$ is given in eq. (5.31). This approximation is relatively good for gases with low particle concentration. Generally, the equation of state for an interacting gas is written as

$$\frac{P}{k_B T} = \sum_{\ell=1}^{\infty} a_\ell c^\ell\ , \tag{5.41}$$

where the coefficients $a_\ell$ are termed *virial coefficients*. The first two virial coefficients are $a_1 = 1$ and $a_2 = -b_2$.

In the following, we apply the virial expansion to two examples.

*Example 5.1.* **Ideal gas limit**

The ideal gas is characterized by the absence of interactions, i.e. $w(q) = 0$. This implies that the Mayer function between any pair of particles vanishes, $f_{ij} = \exp\left(-\beta w(|\vec{q}_i - \vec{q}_j|)\right) - 1 = 0$. Consequently, all coefficients $b_\ell$ and all virial coefficients $a_\ell$ vanish except for $a_1 = b_1 = 1$. The equation of state for the pressure thus becomes

$$\frac{P}{k_B T} = c \ ,$$

and with $c = N/V$ we arrive, once again, at the exact equation of state for the ideal gas.

The ideal gas limit of the virial expansion shows that the leading term in eq. (5.40) represents the ideal gas while the second term provides a first-order correction in the presence of non-zero interactions. In the next example, we calculate this correction explicitly.

*Example 5.2.* **A gas of hard spheres**

Consider a gas of solid spheres with diameter $d$, interacting with each other according to the pair potential

$$w(|\vec{q}_i - \vec{q}_j|) = \begin{cases} \infty & |\vec{q}_i - \vec{q}_j| < d \\ 0 & |\vec{q}_i - \vec{q}_j| \geq d \ . \end{cases} \tag{5.42}$$

The second virial coefficient is then given by

$$\begin{aligned} a_2 &= -\frac{1}{2}\int \frac{\mathrm{d}^3 q_1 \mathrm{d}^3 q_2}{V}\left(e^{-\beta w(|\vec{q}_1 - \vec{q}_2|)} - 1\right) \\ &= \frac{1}{2}\int \mathrm{d}^3 q \left(1 - e^{-\beta w(q)}\right) \\ &= \frac{1}{2} 4\pi \int_0^d \mathrm{d}q\, q^2 \\ &= \frac{1}{2}\frac{4\pi}{3} d^3 = \frac{1}{2} V_\circ \ , \end{aligned} \tag{5.43}$$

where $V_\circ$ denotes the excluded volume around each sphere. In this case, the first-order correction to the non-interacting gas is thus proportional to the excluded volume created by one particle. Since $a_2 > 0$ here, the pressure is larger than that of a comparable ideal gas. Intuitively we can understand this as a consequence of the excluded volume.

## 5.3 Van der Waals equation of state

With the virial expansion at hand, let us now explore the thermodynamic properties of a real gas. Virtually all real gases behave like hard spheres for very short distances between

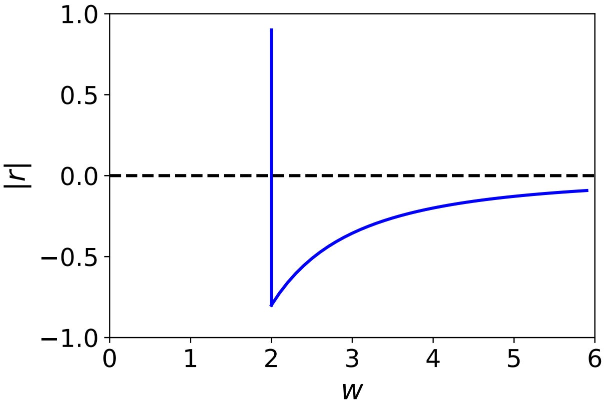


**Figure 5.1:** Typical pair potential (Here for example: $D = 2$, $s = 2$)

gas molecules, while exhibiting attractive forces between molecules at larger distances to each other. This characteristic may be described fairly well by the pair potential $w(r)$,

$$w(r) = \begin{cases} \infty & |r| < R_0 \\ -w_0 \left(\frac{R_0}{|r|}\right)^S & |r| \geq R_0 \ . \end{cases} \tag{5.44}$$

Here $r$ denotes the distance between two gas molecules and $S$, $R_0$, and $w_0 > 0$ are gas-specific constants. The potential causes particles to repel for separations of $r < R_0$ and attract for larger separations due to inter-molecular forces. For example, these forces might be Van der Waals attractions characterized by $S = 6$. Figure 5.1 shows the graph of $w(r)$.

The first non-trivial virial coefficient is $a_2$; for the given potential we find

$$\begin{aligned} a_2 &= \frac{1}{2} \int_0^\infty \mathrm{d}r \, 4\pi r^2 \left(1 - e^{-\beta w(r)}\right) \\ &= 2\pi \int_0^{R_0} \mathrm{d}r \, r^2 + 2\pi \int_{R_0}^\infty \mathrm{d}r \, r^2 \left(1 - e^{\frac{w_0}{k_B T}\left(\frac{R_0}{r}\right)^S}\right) \ . \end{aligned} \tag{5.45}$$

The second integral cannot be solved in closed form. However, if we assume[1] $\frac{w_0}{k_B T} < 1$, we can expand the exponential up to first order ($\exp(x) \approx 1 + x$) to obtain

$$a_2 \approx \frac{2\pi}{3} {R_0}^3 - 2\pi {R_0}^S \frac{w_0}{k_B T} \int_{R_0}^\infty \mathrm{d}r \, r^{2-S} \ . \tag{5.46}$$

The integral in eq. (5.46) is now solvable and converges for $S > 3$, which is typically the case. Thus, we may write the second virial coefficient for the potential in eq. (5.44) as

$$a_2 = b' - \frac{a'}{k_B T} \ , \tag{5.47}$$

where we have defined the quantities

$$a' := \frac{2\pi}{S-3} R_0^3 w_0 \ , \qquad b' := \frac{2\pi}{3} R_0^3 \ . \tag{5.48}$$

---

[1] This assumption is related to the high temperature approximation. It is valid when the attractive interaction is weak compared to the kinetic energy of the gas molecules.

Now, we plug the second virial coefficient into the virial expansion (eq. (5.40)), which yields

$$\begin{aligned} \frac{P}{k_B T} &= c + a_2 c^2 = c + \left( b' - \frac{a'}{k_B T} \right) c^2 \\ \Rightarrow \quad P + a'c^2 &= c k_B T (1 + b'c) \ . \end{aligned} \tag{5.49}$$

The next step involves a “dirty” trick: we use the first-order Taylor expansion $\frac{1}{1-x} \approx 1 + x$ backwards for the term $(1 + b'c)$. We thereby assume that $b'c \ll 1$, implying that the gas molecules are not closely packed. This assumption seems unreasonable in principle but will turn out to be physically justified (as explained below). Applying the trick leads to

$$P + a'c^2 = \frac{c k_B T}{1 - b'c} \ , \tag{5.50}$$

and by reinserting the definition $c = N/V$ we obtain the *Van der Waals equation of state*,

$$\boxed{\left( P + a' \frac{N^2}{V^2} \right) \left( V - b'N \right) = N k_B T} \ . \tag{5.51}$$

This is the equation of state for a real gas described by the potential in eq. (5.44). The parameters $a'$ and $b'$ are stated in eq. (5.48). A comparison with the form of the ideal gas law suggests that we may identify an effective pressure $P_{\text{eff}}$ and an effective volume $V_{\text{eff}}$:

$$\left. \begin{aligned} P_{\text{eff}} &:= P + a' \frac{N^2}{V^2} \\ V_{\text{eff}} &:= V - b'N \end{aligned} \right\} \quad \Rightarrow \quad P_{\text{eff}} V_{\text{eff}} = N k_B T \ . \tag{5.52}$$

From the Van der Waals equation of state we may draw the following conclusions.

- In the ideal gas limit, the interactions disappear ($w_0 \to 0$) and the gas particles do not occupy any volume (i.e. $R_0 \to 0$). This implies $a' = b' = 0$ and the Van der Waals equation of state reduces to the ideal gas equation of state, $PV = N k_B T$.
- Note that $b'$ corresponds to half the excluded volume occupied by one gas particle. Thus, the effective volume $V_{\text{eff}} = V - b'N$ is reduced by the volume excluded by the gas particles. When $V \to b'N$, the system volume $V$ approaches the sum of the particle volumes and the gas becomes closely packed. Physically, this means that the pressure must diverge, which is reflected in the Van der Waals equation of state as a consequence of the “dirty trick” we used in the derivation. We may therefore motivate the trick retrospectively by physical intuition.
- The effective pressure $P_{\text{eff}}$ is increased by the attractive interaction between gas particles (because $a' > 0$). As a consequence, the particles move closer together. The effect is proportional to the interaction strength $w_0$ as well as $N^2$, the number of pairs of particles.

To analyze the Van der Waals equation further, we now rearrange eq. (5.51) to obtain the pressure as a function of volume,

$$\boxed{P = \frac{N k_B T}{V - b'N} - a' \frac{N^2}{V^2}} \ . \tag{5.53}$$

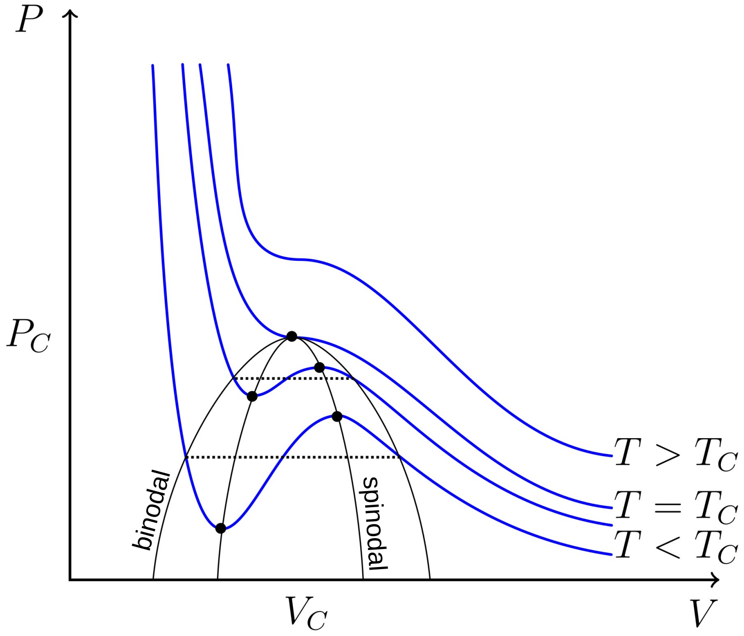


**Figure 5.2:** P-V diagram of the Van-der-Waals equation. The black solid lines show the boundaries of the binodal and spinodal regions, respectively. Horizontal dotted lines illustrate the Maxwell construction.

Figure 5.2 shows eq. (5.53) in a P-V diagram for several temperatures. Below a critical temperature $T_c$, the pressure isotherms exhibit a regime where the pressure increases with increasing volume. This would imply a negative isothermal compressibility $\kappa_T$ (eq. (4.16)),

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T < 0 \quad (!) \ ,$$

which clearly appears unphysical. However, we will see below that a phase separation prevents such unphysical behavior. First of all, let us quantify the region of negative compressibility.

We begin with determining the critical temperature. Above $T_c$, the pressure decreases monotonically; below $T_c$ the pressure behaves non-monotonically. This implies the existence of a saddle point on the critical isotherm where

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \ . \tag{5.54}$$

We call this point the *critical point* $(V_c, P_c, T_c)$. Calculating the first and second derivatives from eq. (5.53) and inserting the results in eq. (5.54) yields the two conditions

$$\frac{k_B T_c}{a'N} = \frac{2(V_c - b'N)^2}{V_c^3} \qquad \text{and} \qquad \frac{k_B T_c}{a'N} = \frac{3(V_c - b'N)^3}{V_c^4} \ . \tag{5.55}$$

It follows that $(V_c - b'N) = \frac{2}{3}V_c$ and consequently $V_c = 3b'N$. Reinserting into one of the conditions (5.55) yields $T_c$, and from this we also obtain $P_c$ using eq. (5.53). Altogether, the critical point is given by

$$T_c = \frac{8}{27}\frac{a'}{k_B b'} \ , \qquad V_c = 3b'N \ , \qquad P_c = \frac{a'}{27b'^2} \ . \tag{5.56}$$

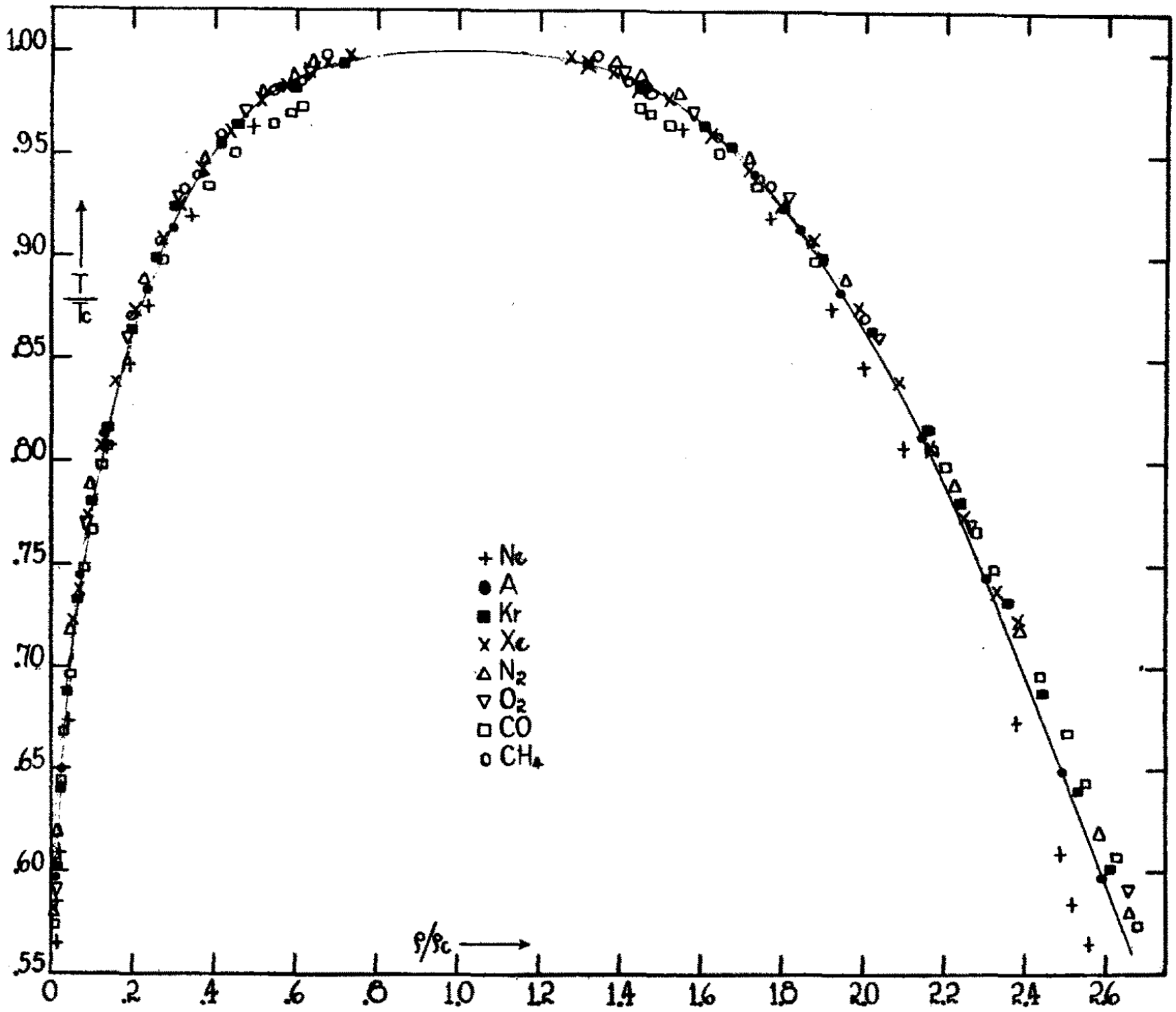


**Figure 5.3: Guggenheim's fit and the law of corresponding states.** The plot shows the reduced temperature $T/T_C$ as a function of the reduced density $\rho/\rho_c \equiv n/n_c = \frac{N/V}{(N/V)_c}$ for eight different substances (see legend). Despite their different properties, all substances follow the same fit (solid curve) rather well. The data thus provides experimental evidence for the law of corresponding states. This figure was originally published in [2].

Now, we define the *reduced* temperature $\mathcal{T}$, reduced pressure $\mathcal{P}$, and reduced volume $\mathcal{V}$ according to

$$\mathcal{T} := \frac{T}{T_c}\ , \quad \mathcal{P} := \frac{P}{P_c}\ , \quad \text{and} \quad \mathcal{V} := \frac{V}{V_c}\ .$$

In terms of these rescaled variables, the Van der Waals equation of state reads

$$\boxed{\mathcal{P} = \frac{8\mathcal{T}}{3\mathcal{V}-1} - \frac{3}{\mathcal{V}^2}}\ . \tag{5.57}$$

Note that this result does not depend on the parameters $a'$ and $b'$ anymore. This means that eq. (5.57) is *universal*; it holds for all substances, independent of their properties. The rescaled equation of state expresses the *law of corresponding states*, which says that near the critical point all substances behave similarly. An experimental confirmation of the law is displayed in figure 5.3.

As mentioned, the critical point is a saddle point; both the first and second derivatives of the pressure with respect to the volume vanish there. For any temperature $T < T_c$, the corresponding isotherm features precisely two extrema (where $(\mathrm{d}P/\mathrm{d}V)_T = 0$). The set of extrema encloses the regime of negative compressibility which we call the *spinodal* region (see fig. 5.2).

Let us now return to the issue raised by the appearance of a negative isothermal compressibility – clearly an unphysical feature of the van der Waals equation of state. The resolution originates from the coexistence of phases. Inspecting fig. 5.3, we notice that at temperatures below $T_c$ the substances each have two distinct reduced densities. In fig. 5.2, the isotherms $T < T_c$ describe the liquid phase left of the coexistence region, while the substance is in the gaseous phase right of the coexistence region. In between lies the so-called *binodal* region where liquid and gas coexist and a single density is not defined. Therefore the isotherms have no physical meaning in this regime.

But how do we determine the boundaries of the binodal region in a P-V diagram? What do the isotherms look like within the binodal region? And what are the densities of the two coexisting phases? To answer these questions, we first recall from section 4.10 that the coexisting phases (labeled with subscripts 1 and 2 below) must have equal pressure and temperature. In addition, two phases in equilibrium must have the same chemical potential $\mu$,

$$\mu = g_1(P,T) = g_2(P,T) \ . \tag{5.58}$$

Here $g(P,T) := G(N,P,T)/N$ represents the free enthalpy per particle, where the *free enthalpy* $G$, or Gibbs free energy, is defined by

$$G(N,P,T) := U + PV - TS = \mu N \ . \tag{5.59}$$

The total differential of the free enthalpy per particle is then given in terms of the volume per particle $v = V/N$ and the entropy per particle $s = S/N$ according to

$$\mathrm{d}g = v\mathrm{d}P - s\mathrm{d}T \ . \tag{5.60}$$

Along an isotherm, the temperature is constant, so we have

$$g_1 - g_2 = \int_{g_2}^{g_1} \mathrm{d}g = \int_{P_2}^{P_1} v(P)\,\mathrm{d}P \ . \tag{5.61}$$

The start and end point of this integral have the same pressure $P_1 = P_2$ but different volumes $v_1 \neq v_2$ because the function $v(P)$ is not uniquely defined in the binodal region, as illustrated in fig. 5.4. But we can split the integral into a sum of well-defined parts such that

$$\begin{aligned}\int_{P_2}^{P_1} v\,\mathrm{d}P &= \int_{P_A}^{P_B} v\,\mathrm{d}P + \int_{P_B}^{P_C} v\,\mathrm{d}P + \int_{P_C}^{P_D} v\,\mathrm{d}P + \int_{P_D}^{P_E} v\,\mathrm{d}P \\ &= \text{ Area 1 } - \text{ Area 2 } \ ,\end{aligned} \tag{5.62}$$

where the subscripts and areas refer to fig. 5.4. According to eq. (5.58), the integral must vanish because we require $g_1 - g_2 = 0$. This only happens when the areas 1 and 2 are equally large. We conclude that in the phase coexistence region only one pressure is possible. The value of the *coexistence pressure* $P_{\mathrm{coex}}(P)$ is found by drawing a horizontal

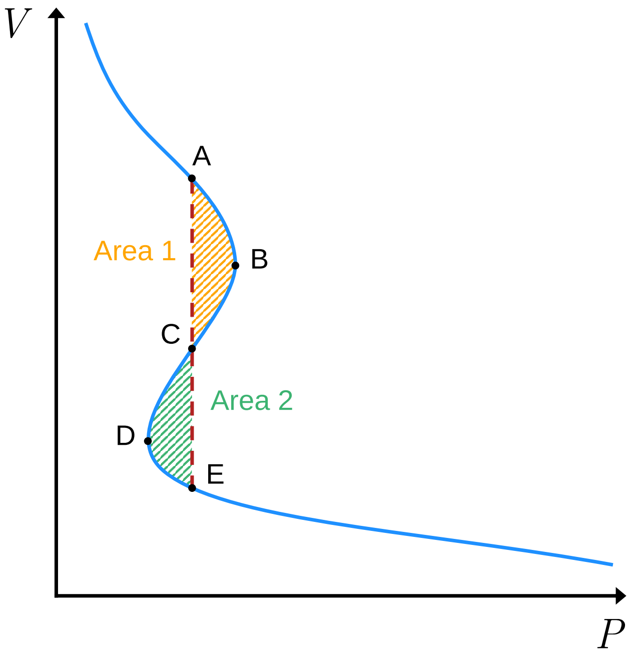


**Figure 5.4: Illustration of the Maxwell construction** in a VP diagram. The two areas $A_1$ and $A_2$ must be equal; only then the integral in eq. (5.62) vanishes.

line in the P-V diagram such that the areas below and above the line become equal. This procedure is known as *Maxwell construction.*

The Maxwell construction tells us how to connect the isotherms between purely liquid and purely gaseous states. In the binodal region, which is defined by the Maxwell construction, the isotherms actually follow the dotted lines shown in fig. 5.2. As the volume changes, the pressure remains constant while the relative amounts of the gas and liquid phases change. Note that at the critical point, liquid and gas coexist at the same pressure *and* volume, implying that their density difference vanishes there.

## 5.4 Transfer matrix method

In some cases, a useful way to tackle the partition function is by exploiting the power of linear algebra. To demonstrate this, we consider the example of a one-dimensional system of interacting spins commonly known as the 1D Ising model.

**1D Ising model.** The Ising model is an idealized system of interacting spins used to describe magnetism. In the one-dimensional (1D) case, it consists of a chain of $N$ sites. Each site $i \in \{1, \dots, N\}$ represents an atomic spin $s_i \in \{+1, -1\}$ that may either take the value $+1$ ("spin up", $\uparrow$) or $-1$ ("spin down", $\downarrow$). Let the boundary conditions be periodic, such that the chain forms a ring and $s_{N+1} \equiv s_1$.

Suppose that the spins interact with their nearest neighbors and with an external magnetic field. In a simple form, the Hamiltonian of the 1D Ising model in the configuration $\{s_i\}$ is then written as

$$\mathcal{H}(\{s_i\}) = -\varepsilon \sum_{\langle i,j\rangle} s_i s_j - h \sum_{j=1}^{N} s_j \ , \tag{5.63}$$

where $\varepsilon$ denotes the interaction strength between two spins $i$ and $j$, while $h$ represents the coupling to an external magnetic field. The notation $\langle i,j\rangle$ indicates a summation over all nearest neighbor pairs, avoiding double counting. Given that a site $i$ has two nearest neighbor sites $i-1$ and $i+1$, which themselves have site $i$ as one of their nearest neighbors, we may simplify eq. (5.63) to

$$\mathcal{H}(\{s_i\}) = -\varepsilon \sum_{j=1}^{N} s_j s_{j+1} - h \sum_{j=1}^{N} s_j \ . \tag{5.64}$$

The system seeks to minimize its free energy $F = \langle \mathcal{H} \rangle - TS$. Assume zero temperature ($T = 0$) and let $\varepsilon > 0$. Then, two aligned neighboring spins (↑↑ or ↓↓) would contribute the interaction energy $-\varepsilon$ to the free energy, whereas a spin pair of opposing orientation (↑↓ or ↓↑) would contribute the energy $+\varepsilon$, leading to a higher total energy. Hence, the Ising model with $\varepsilon > 0$ favors aligned spins (ferromagnetism). In the case $\varepsilon < 0$, adjacent spins tend to anti-align in order to minimize the free energy (anti-ferromagnetism). At finite temperature, the situation is a bit more subtle, as we will discuss below.

The partition function of the 1D Ising model (eq. (5.64)) reads

$$Z = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} \exp\left\{ \beta\varepsilon \sum_{j=1}^{N} s_j s_{j+1} + \beta h \sum_{j=1}^{N} s_j \right\} \ , \tag{5.65}$$

where each summation $\sum_{s_i}$ runs through the two possible spin states $s_i = \pm 1$. Once again, especially for large $N$, this expression is rather clunky. However, we can make use of the fact that sites only interact with their nearest neighbors. Defining $E := \beta\varepsilon$, $H := \beta h$ and using the periodic boundary conditions, we rewrite eq. (5.65) as

$$\begin{aligned}
Z &= \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} \exp\left\{ E \sum_{j} s_j s_{j+1} + \frac{H}{2} \sum_{j} (s_j + s_{j+1}) \right\} \\
&= \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} \prod_{j=1}^{N} \exp\left\{ E s_j s_{j+1} + \frac{H}{2} (s_j + s_{j+1}) \right\} \\
&= \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} \prod_{j} T_{s_j s_{j+1}} \\
&= \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} T_{s_1 s_2} T_{s_2 s_3} \cdots T_{s_N s_1} \ .
\end{aligned} \tag{5.66}$$

We have shown that the exponential factorizes into terms $T_{ss'} := e^{Ess' + \frac{H}{2}(s+s')}$. Each of these terms can take one of four possible values depending on the spin configuration $ss' \in \{$↑↑, ↑↓, ↓↑, ↓↓$\}$, which we may regard as elements of a $2 \times 2$ matrix called the *transfer matrix* $\boldsymbol{T}$,

$$\boldsymbol{T} = (T_{ss'}) = \begin{bmatrix} T_{+1,+1} & T_{+1,-1} \\ T_{-1,+1} & T_{-1,-1} \end{bmatrix} = \begin{bmatrix} e^{E+H} & e^{-E} \\ e^{-E} & e^{E-H} \end{bmatrix} \ . \tag{5.67}$$

The expression for the partition function in eq. (5.66) boils down to a number of matrix multiplications. Note that

$$\sum_{s_2=\pm1} T_{s_1s_2}T_{s_2s_3} = (\boldsymbol{T}^2)_{s_1s_3} \ ,$$

where

$$(T^2)_{s_1s_3} = \begin{bmatrix} (T^2)_{s_1=+1,s_3=+1} & (T^2)_{s_1=+1,s_3=-1} \\ (T^2)_{s_1=-1,s_3=+1} & (T^2)_{s_1=-1,s_3=-1} \end{bmatrix} \ .$$

Furthermore,

$$\sum_{s_3=\pm1} (\boldsymbol{T}^2)_{s_1s_3}T_{s_3s_4} = (\boldsymbol{T}^3)_{s_1s_4} \ .$$

We can continue this iteration until we end up with the simple result

$$Z = \mathrm{tr}(\boldsymbol{T}^N) \ , \tag{5.68}$$

where $\mathrm{tr}(\boldsymbol{T}^N) = \sum_{s_1}(\boldsymbol{T}^N)_{s_1s_1}$ is the *trace* of the transfer matrix to the power of $N$.

Since $\boldsymbol{T}$ is symmetric, it is diagonalizable (for a quick refresher on matrices, see Appendix A.2). In other words, we can find a linear transformation $\boldsymbol{U}$ that turns $\boldsymbol{T}$ into a diagonal matrix $\boldsymbol{\Lambda}$ with eigenvalues $\lambda_1$ and $\lambda_2$ as its diagonal elements. This yields

$$\begin{aligned} Z = \mathrm{tr}(\boldsymbol{T}^N) &= \mathrm{tr}\left((\boldsymbol{U}\boldsymbol{U}^\top\boldsymbol{T})^N\right) = \mathrm{tr}\left((\boldsymbol{U}^\top\boldsymbol{T}\boldsymbol{U})^N\right) \\ &= \mathrm{tr}\left(\boldsymbol{\Lambda}^N\right) = \mathrm{tr}\begin{bmatrix}\lambda_1^N & 0 \\ 0 & \lambda_2^N\end{bmatrix} = \lambda_1^N + \lambda_2^N \\ \Rightarrow \quad Z &= \lambda_1^N + \lambda_2^N \ . \end{aligned} \tag{5.69}$$

Once we know the eigenvalues of the transfer matrix, we obtain an exact solution for partition function of the 1D Ising model, which originally was a complicated sum over many configurations. To find the eigenvalues, we solve the characteristic equation of the eigenvalue problem:[2]

$$\det(\boldsymbol{T} - \lambda\mathbb{I}_2) = 0 \qquad \Rightarrow \qquad \det\begin{vmatrix} e^{E+H} - \lambda & e^{-E} \\ e^{-E} & e^{E-H} - \lambda \end{vmatrix} = 0 \ . \tag{5.70}$$

Computing the determinant gives

$$\begin{aligned} 0 &= \left(e^{E+H} - \lambda\right)\left(e^{E-H} - \lambda\right) - e^{-2E} \\ &= \lambda^2 - \lambda e^E(e^H + e^{-H}) + e^{2E} - e^{-2E} \ , \end{aligned} \tag{5.71}$$

and solving this quadratic equation for $\lambda$ yields

$$\begin{aligned} \lambda_{1,2} &= \frac{e^E(e^H + e^{-H})}{2} \pm \sqrt{\left(\frac{e^E(e^H + e^{-H})}{2}\right)^2 - (e^{2E} - e^{-2E})} \\ &= e^E\left[\cosh H \pm \sqrt{\frac{(e^H + e^{-H})^2}{4} - 1 + e^{-4E}}\right] \\ &= e^E\left[\cosh H \pm \sqrt{\sinh^2 H + e^{-4E}}\right] \ . \end{aligned} \tag{5.72}$$

---

[2] Here $\mathbb{I}_2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ denotes the 2 × 2 unit matrix.

With this, we have obtained an explicit expression for $Z$ and may now calculate thermodynamic properties of the ring of interacting spins. For instance, the Gibbs free energy $G$ follows as

$$G(h,T) = -k_BT \ln Z = -k_BT \ln \left(\lambda_1^N + \lambda_2^N\right) \ . \tag{5.73}$$

After slight rearrangement, the Gibbs free energy per spin, $g(h,T) := G(h,T)/N$ is

$$g(h,T) = -\frac{k_BT}{N} \ln \lambda_1^N - \frac{k_BT}{N} \ln \left(1 + \left(\frac{\lambda_2}{\lambda_1}\right)^N\right) \ . \tag{5.74}$$

In the large system limit ($N \to \infty$), since $\lambda_1 > \lambda_2$, this simplifies to

$$g(h,T) \approx -k_BT \ln \lambda_1 - \underbrace{\frac{k_BT}{N}\left(\frac{\lambda_2}{\lambda_1}\right)^N}_{\to 0 \ (N\to\infty)} \approx -k_BT \ln \lambda_1 \ , \tag{5.75}$$

where we have used $\ln\left(a^b\right) = b \ln a$ and $\ln(1+x) \approx x$ for $||x|| \ll 1$. Inserting eq. (5.72) for $\lambda_1$ now leads to

$$g(h,T) \approx -k_BT \ln \left[\cosh \frac{h}{k_BT} + \sqrt{\sinh^2 \frac{h}{k_BT} + e^{-4\varepsilon/(k_BT)}}\right] - \varepsilon \ . \tag{5.76}$$

We have re-substituted $\varepsilon = Ek_BT$ and $h = Hk_BT$ here in order to use the original parameters of the Ising model (eq. (5.64)).

The magnetization per spin, $m := M/N$ ($M$ denotes total magnetization), follows from the Gibbs free energy per spin by taking a partial derivative:

$$m = -\frac{\partial g}{\partial h} = \frac{\sinh(h/(k_BT)) + \cosh(h/(k_BT))\sinh(h/(k_BT))}{\cosh(h/(k_BT)) + \sqrt{\sinh^2(h/(k_BT)) + e^{-4\varepsilon/(k_BT)}}} \tag{5.77}$$

With a bit of algebra (factorizing the hyperbolic sine and dividing both the numerator and the denominator by the square root term), the expression simplifies to

$$\boxed{m = \frac{\sinh(h/(k_BT))}{\sqrt{\sinh^2(h/(k_BT)) + e^{-4\varepsilon/(k_BT)}}}} \ . \tag{5.78}$$

This result for the *magnetization per spin* in the 1D Ising model is plotted in fig. 5.5 for different temperatures. Notably, this implies $m(h=0) = 0$, i.e. in the absence of an external magnetic field no spontaneous magnetization occurs. The slope of the magnetization curve is given by the susceptibility $\chi := \partial m/\partial h$, which in the zero field limit becomes

$$\lim_{h\to 0} \chi = \lim_{h \to 0} \frac{\partial m}{\partial h} = \frac{e^{2e/(k_BT)}}{k_BT} \ . \tag{5.79}$$

We see that as the temperature approaches absolute zero ($T \to 0$), the susceptibility at zero field diverges, indicating a phase transition[3] at the critical temperature $T_c = 0$.

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[3] Since a critical temperature of absolute zero $T_c = 0$ is purely theoretical, it is often said that the Ising model does not exhibit a phase transition in 1D. At dimensions larger than 1, the Ising model also features finite temperature phase transitions.

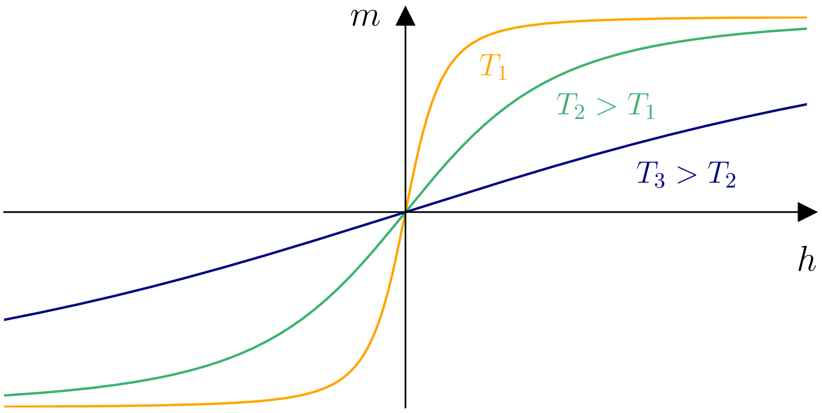


**Figure 5.5: Magnetization $m$ as a function of external magnetic field $h$** for the 1D Ising model (eq. (5.78)) at three different temperatures, $T_1 < T_2 < T_3$. At $h = 0$, the susceptibility (slope of the magnetization curve) diverges as $T \to 0$.

But how can we explain the absence of spontaneous magnetization, or ordering of spins, at finite temperatures? As remarked in the introduction of the Ising model (blue info box, p. 103), spins tend to align in order to minimize the free energy at $T = 0$ and $\varepsilon > 0$.

Consider first a ring of $N$ spins, all pointing upwards (fig. 5.6a). Suppose now that $L < N$ adjacent spins flip their orientation, creating a domain wall at the edges (fig. 5.6b). Compared to the completely ordered configuration, the introduction of the two domain walls leads to an energy change of $\Delta U = 4\varepsilon$, increasing the total energy. However, the domain flip also changes the entropy. Since there are $N$ possible positions for the domain walls of a subdomain of length $L$, the associated entropy change is $\Delta S = k_B \ln N$. Put together, the change in free energy becomes

$$\Delta F = \Delta U - T\Delta S = 4\varepsilon - k_B T \ln N \ . \tag{5.80}$$

The system always strives to minimize the free energy. A domain flip reduces the free energy if $\Delta F < 0$, hence if

$$4\varepsilon < k_B T \ln N \qquad \Leftrightarrow \qquad N > e^{4\varepsilon/(k_B T)} \ .$$

Since we typically deal with large systems ($N \gg 1$), this inequality is easily satisfied (for finite temperature). In that case, introducing a domain wall always pays off energetically, and any ordered configuration will break into a disordered state (Landau-Peierls argument).

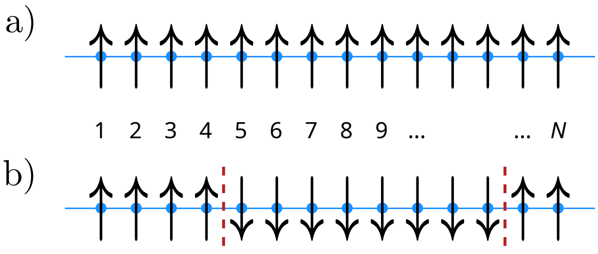


**Figure 5.6:** Domain flip in a 1D ring of $N$ spins, creating two domain walls (red dotted lines).

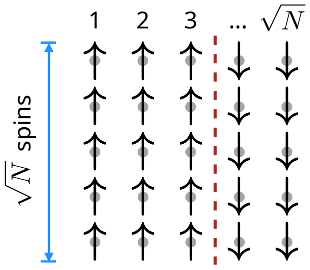


**Figure 5.7:** 2D Ising model with $N$ sites and one domain wall (red dotted line).

In 2D, this argument does not hold anymore. Here the free energy change associated with the creation of a domain wall as depicted in fig. 5.7 (without periodic boundary conditions) is

$$\Delta F = 2\varepsilon\sqrt{N} - k_B T \ln\left(\sqrt{N} - 1\right) \ . \tag{5.81}$$

The condition for persistent order, or magnetization, is thus

$$2\varepsilon\sqrt{N} > k_B T \ln\left(\sqrt{N} - 1\right) \ .$$

Note that now both sides of the inequality depend on $N$. For large $N$, the energy term dominates if the temperature is sufficiently low, such that order is possible in 2D!

## 5.5 Variational principle

Suppose we wish to study a statistical system described by the Hamiltonian $\mathcal{H}$, but this Hamiltonian is so complicated that we must give up all hope for exact calculations. For example, it would be unfeasible to compute the system's free energy,

$$F = -k_B T \ln\left(\int \{\mathrm{d}x\}\, e^{-\beta\mathcal{H}(\{x\})}\right) \ . \tag{5.82}$$

Therefore, we seek an approximate method that yields a best estimate of the true free energy. To do this, we introduce a *trial Hamiltonian* $\mathcal{H}_0$ which is sufficiently simple such that we can solve its partition function. The trial Hamiltonian shall depend on the two variational parameters $a$ and $b$, whose values we may choose arbitrarily for now.

We write the free energy in terms of the trial Hamiltonian by "adding zero" to eq. (5.82):

$$F = -k_B T \ln\left(\int \{\mathrm{d}x\} \exp\left\{-\frac{\mathcal{H}_0(\{x\},a,b)}{k_B T} + \frac{\mathcal{H}_0(\{x\},a,b) - \mathcal{H}(\{x\})}{k_B T}\right\}\right) \ . \tag{5.83}$$

This can be reformulated as

$$\begin{aligned} F &= -k_B T \ln\left(\int \{\mathrm{d}x\}\, e^{-\beta\mathcal{H}_0}\right) - k_B T \ln\left(\frac{\int \mathrm{d}\{x\}\, e^{-\beta\mathcal{H}_0}\, e^{\beta(\mathcal{H}_0 - \mathcal{H})}}{\int \mathrm{d}\{x\}\, e^{-\beta\mathcal{H}_0}}\right) \\ &= F_0 - k_B T \ln\left\langle e^{\beta(\mathcal{H}_0 - \mathcal{H})}\right\rangle_0 \ , \end{aligned} \tag{5.84}$$

where $F_0$ is the free energy corresponding to the trial Hamiltonian and $\langle\cdots\rangle_0$ denotes an expectation value taken with respect to the trial system. We now claim that

$$\left\langle e^{\beta(\mathcal{H}_0 - \mathcal{H})}\right\rangle_0 \geq e^{\langle\beta(\mathcal{H}_0 - \mathcal{H})\rangle_0} \ , \tag{5.85}$$

which follows from the following theorem.

**Theorem.** Given an arbitrary convex function $f(z)$ (i.e. $f''(z) > 0$) and another function $a(x)$ depending on a random variable $x$, the following inequality holds:

$$\langle f(a(x))\rangle \geq f(\langle a\rangle) \ . \tag{5.86}$$

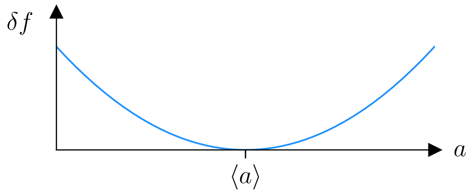


**Figure 5.8:** Qualitative sketch of the function $\delta f(a)$, which is always non-negative and zero at $\langle a\rangle$.

**Proof.** Expanding the function $f(a(x))$ around the expectation value of $a$,

$$\langle a\rangle = \frac{\int \mathrm{d}x\, P(x)a(x)}{\int \mathrm{d}x\, P(x)}\ , \qquad P(x):\ \text{probability distribution of } x\ ,$$

we get

$$f(a(x)) = f(\langle a\rangle) + (a(x)-\langle a\rangle)f'(\langle a\rangle) + \delta f \tag{5.87}$$

such that the residual $\delta f$ is given by

$$\delta f = f(a(x)) - f(\langle a\rangle) - (a(x)-\langle a\rangle)f'(\langle a\rangle)\ . \tag{5.88}$$

The convexity of $f$ implies that $\delta f$ is a positive function (see fig. 5.8). Consequently, we necessarily have $\langle\delta f\rangle \geq 0$. Taking the expectation value of eq. (5.88) yields

$$\begin{aligned} \langle\delta f\rangle &= \langle f(a(x))\rangle - f(\langle a\rangle) - \underbrace{(\langle a\rangle - \langle a\rangle)}_{=0} f'(\langle a\rangle) \\ \Rightarrow \quad & \langle f(a(x))\rangle = f(\langle a\rangle) + \langle\delta f\rangle \\ \Rightarrow \quad & \langle f(a(x))\rangle \geq f(\langle a\rangle) \qquad \text{q.e.d.} \end{aligned} \tag{5.89}$$

This conclude the proof. ■

If we now identify

$$f(z) = e^z \qquad \text{and} \qquad a(x) = \beta\Big(\mathcal{H}_0(\{x\},a,b) - \mathcal{H}(\{x\})\Big)\ ,$$

we have shown eq. (5.85) (note that the exponential function $e^z$ is a convex function everywhere on the domain $\mathbb{R}$).

Continuing with eq. (5.85), we reformulate the inequality according to

$$\begin{aligned} \left\langle e^{\beta(\mathcal{H}_0-\mathcal{H})}\right\rangle_0 &\geq e^{\langle\beta(\mathcal{H}_0-\mathcal{H})\rangle_0} \\ \Leftrightarrow \qquad \ln\left\langle e^{\beta(\mathcal{H}_0-\mathcal{H})}\right\rangle_0 &\geq \langle\beta(\mathcal{H}_0-\mathcal{H})\rangle_0 \\ \Leftrightarrow \qquad -\ln\left\langle e^{\beta(\mathcal{H}_0-\mathcal{H})}\right\rangle_0 &\leq \langle\beta(\mathcal{H}_0-\mathcal{H})\rangle_0\ . \end{aligned} \tag{5.90}$$

Finally, applying the inequality (5.90) to eq. (5.84) yields

$$\boxed{F \leq F_0 + \langle\mathcal{H}-\mathcal{H}_0\rangle_0 =: F_{\mathrm{var}}}\ . \tag{5.91}$$

This result is *Gibbs' variational principle.* It states that the *true* free energy $F$ poses a lower bound to the variational free energy $F_{\mathrm{var}}$. By minimizing the right hand side of eq. (5.91) with respect to the parameters $a$ and $b$, we obtain an optimal approximation of the free energy given the trial Hamiltonian $\mathcal{H}_0$. However, it is important to note that the accuracy of approximation depends on the choice of the trial Hamiltonian.

# 6 Quantum Statistics

Typical thermodynamic systems in the real world – solids, liquid, gases – consist of a large number of very small particles, such as electrons, atoms, and molecules. On the size scales of these particles, quantum effects become important. One crucial insight of quantum mechanics is that quantum objects are intrinsically indistinguishable. This required us to include the factor $1/N!$ in chapters 3 and 4 to avoid over-counting. But the implications of quantum theory reach much further.

This chapter studies gases from a quantum perspective. Essentially, we combine the grand canonical ensemble with the occupation number formalism of quantum mechanics. Quantum statistics is all about counting quantum states, and there are two distinct ways to count: one for particles called fermions, and one for bosons. We study both cases in the context of ideal quantum gases (neglecting interactions). Applications include the free electron gas (Fermi gas) inside a metal, the photon gas (Bose gas) as a model for black body radiation, as well as Bose-Einstein condensation.

## 6.1 Retrospective: Development of quantum theory

The origins of quantum theory entail fundamental changes in our understanding of matter, particles and waves. In classical Newtonian physics, a particle has a well-defined position and momentum; its energy can take on continuous values. Conceptually different, waves are characterized by their wavelength and frequency.

Experiments have shown that the classical picture breaks down on very small length scales. In 1887, Hertz observed the *photoelectric effect* which revealed that the kinetic energy of electrons, emitted from a metal by shining light on it with a certain frequency $\nu$, does not depend on the intensity of the electromagnetic radiation. Instead, it depends on the light frequency $\nu$. Einstein concluded in 1905 that light comes in quanta – so-called *photons* – each with energy $E = h\nu$, where $h$ denotes Planck's constant. For sufficiently high frequencies, each photon releases one electron with kinetic energy $E_{\text{kin}} = h\nu - h\nu_0$ from the metal (here $h\nu_0$ represents the work function). Thus, light has particle properties and energy is quantized in quantum mechanics.

In 1927, Davisson and Germer conducted scattering experiments with electrons. They observed a diffraction pattern, confirming the *wave-particle dualism* in the sense that particles have wave properties, too. The *de Broglie wavelength* $\lambda$ of a particle relates to its momentum $p$ according to $\lambda = h/p$.

Based on the wave-particle dualism, we may describe a free particle with energy $E$ and momentum $p$ as a plane wave $\Psi$,

$$\Psi(x,t) \propto e^{i(kx-\omega t)} , \tag{6.1}$$

where $x$ is the space variable, $t$ the time variable, and (with $h = 2\pi\hbar$)

$$k = \frac{2\pi}{\lambda} = 2\pi\frac{p}{h} = \frac{p}{\hbar} \; , \qquad \hbar\omega = h\nu = E \; . \tag{6.2}$$

Instead of having a certain and precise position, the location of the particle is given in terms of a probability distribution $\rho(x,t)$,

$$\rho(x,t) := |\Psi^2(x,t)|^2 = \Psi(x,t)\Psi^*(x,t) \propto e^{i(kx-\omega t)}e^{-i(kx-\omega t)} \propto 1 \; . \tag{6.3}$$

Hence the free particle has a constant probability distribution. In classical mechanics, the energy-momentum relation for a free particle with mass $m$ reads $E = \frac{p^2}{2m}$. Combining this with eqs. (6.1) and (6.2) motivates the *free-particle Schrödinger equation*,

$$\boxed{i\hbar\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}} \; . \tag{6.4}$$

In the presence of an external potential $V(x)$, the energy is classically given by $E = \frac{p^2}{2m} + V(x)$. In quantum mechanics, this translates into the *Hamiltonian* operator $\hat{H}$,

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \; . \tag{6.5}$$

In terms of the Hamiltonian, the fundamental equations of quantum theory are

$$i\hbar\dot{\Psi} = \hat{H}\Psi \qquad \text{Time-independent Schrödinger eq.} \tag{6.6}$$

$$E\Psi = \hat{H}\Psi \qquad \text{Stationary Schrödinger eq.} \tag{6.7}$$

Typically, the stationary Schrödinger equation has many solutions:

$$E_n\Psi_n(x) = \hat{H}\Psi_n(x) \; , \tag{6.8}$$

where $E_n$ and $\Psi_n$ denote the eigenvalues and eigenfunctions of the Hamiltonian, respectively. The energy eigenvalues correspond to the quantized energy levels of the system.

## 6.2 Many-particle wave functions

In Statistical Mechanics, we deal with systems composed of many particles. Consider, for example, a gas of $N$ atoms. The (non-relativistic) Hamiltonian of the gas can be written as

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\left(\vec{\nabla}_i\right)^2}_{\text{kin. energy}} + \underbrace{\sum_{i=1}^{N} u(\vec{r}_i)}_{\text{ext. potential}} + \underbrace{\sum_{i=1}^{N}\sum_{j=i+1}^{N} v(\vec{r}_i - \vec{r}_j)}_{\text{pair interactions}} \; , \tag{6.9}$$

where the labeled terms represent the kinetic energy, interactions with an external potential, and two-body interactions between atoms. The functions $u(\vec{r})$ and $v(\vec{r})$ describe the external potential and the atom-atom pair potential, respectively.

While written down compactly, eq. (6.9) contains complicated expressions; especially the pair interactions are generally too difficult to handle. In principle, however, the *many-body* *wave function* follows from the Hamiltonian as the solution of the stationary Schrödinger equation:

$$\hat{H}\Psi_n(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = E_n \Psi_n(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \ . \tag{6.10}$$

Evidently, $\Psi_n$ is a function of all $N$ particle positions. In quantum mechanics, particles are *indistinguishable*. You cannot tell two quantum objects of the same type (e.g. two electrons) apart – not even by trying to color them, label them, or, as Griffiths puts it [3], hiring private detectives to follow them around.

The fact that we deal with identical particles impacts the symmetry of the many-body wave function. Following Pauli [4], we introduce the *permutation operator* $\hat{P}_{ij}$ which exchanges the positions of particles $i$ and $j$,

$$\hat{P}_{ij}\Psi_n(\vec{r}_1, \ldots, \vec{r}_i, \ldots, \vec{r}_j, \ldots, \vec{r}_N) = \Psi_n(\vec{r}_1, \ldots, \vec{r}_j, \ldots, \vec{r}_i, \ldots, \vec{r}_N) \ . \tag{6.11}$$

We immediately see that applying the permutation operator twice leads back to the original wave function,

$$\hat{P}_{ij}^2 \Psi_n = \hat{P}_{ij}\hat{P}_{ij}\Psi_n = \Psi_n \ . \tag{6.12}$$

Assuming that $\Psi_n$ is an eigenfunction of the permutation operator, i.e. $\hat{P}_{ij}\Psi_n = \lambda\Psi_n$, we infer that the eigenvalue must be $\lambda = \pm 1$:

$$\hat{P}_{ij}\Psi_n = \pm\Psi_n \ . \tag{6.13}$$

The positive eigenvalue means that the many-particle wave function is symmetric with respect to the permutation of particles, while for the negative eigenvalue the wave function becomes anti-symmetric under particle permutations. This indicates two kinds of quantum particles:

| | | | |
|---|---|---|---|
| - Bosons: | $\lambda = +1$, | integer spin, | e.g. photons, phonons, $\mathrm{He}^4$, alkali atoms |
| - Fermions: | $\lambda = -1$, | half-integer spin, | e.g. electrons, protons, $\mathrm{He}^3$, ... |

The concept of bosons and fermions is highly important. But we still do not know what the many-particle wave function looks like. Let us now assume that we may construct the $N$-particle wave function from products of single-particle wave functions, such that

$$\Psi_n(\vec{r}_1, \ldots, \vec{r}_N) = \phi_{\alpha_1}(\vec{r}_1) \cdot \phi_{\alpha_2}(\vec{r}_2) \cdots \phi_{\alpha_N}(\vec{r}_N) \ . \tag{6.14}$$

Here $\{\alpha_n\}$ denotes a set of $N$ quantum numbers that characterize the single-particle wave functions $\phi_{\alpha_n}$. Applying the permutation operator to this product wave function gives

$$\begin{aligned} \hat{P}_{ij}\Psi_{\{\alpha_n\}}(\vec{r}_1, \ldots, \vec{r}_N) &= \hat{P}_{ij}\phi_{\alpha_1}(\vec{r}_1) \cdots \phi_{\alpha_i}(\vec{r}_i) \cdots \phi_{\alpha_j}(\vec{r}_j) \cdots \phi_{\alpha_N}(\vec{r}_N) \\ &= \hat{P}_{ij}\phi_{\alpha_1}(\vec{r}_1) \cdots \phi_{\alpha_i}(\vec{r}_j) \cdots \phi_{\alpha_j}(\vec{r}_i) \cdots \phi_{\alpha_N}(\vec{r}_N) \\ \text{(fermions)} \qquad &\overset{!}{=} -\hat{P}_{ij}\phi_{\alpha_1}(\vec{r}_1) \cdots \phi_{\alpha_i}(\vec{r}_i) \cdots \phi_{\alpha_j}(\vec{r}_j) \cdots \phi_{\alpha_N}(\vec{r}_N) \ . \end{aligned} \tag{6.15}$$

The last line of this equation, which must hold for fermions according to eq. (6.13), implies

$$\phi_{\alpha_i}(\vec{r}_j)\phi_{\alpha_j}(\vec{r}_i) = -\phi_{\alpha_i}(\vec{r}_i)\phi_{\alpha_j}(\vec{r}_j) \ . \tag{6.16}$$

Consider the special case where the particles $i$ and $j$ have the same quantum numbers, i.e. $\alpha_i = \alpha_j = \alpha$. In that situation eq. (6.16) would yield

$$\phi_\alpha(\vec{r}_j)\phi_\alpha(\vec{r}_i) = -\phi_\alpha(\vec{r}_i)\phi_\alpha(\vec{r}_j) \quad \Rightarrow \quad 1 = -1 \ . \tag{6.17}$$

Clearly we cannot solve or satisfy eq. (6.17) in any way. The immediate consequence of this is known as *Pauli's exclusion principle*:

> **Pauli's exclusion principle.** Two identical fermions cannot occupy the same quantum state. It is impossible that they are described by the same set of quantum numbers.

Pauli's principle has wide implications for quantum systems. Let us describe the $N$-particle system in the occupation number picture, where the state of the system is given by specifying how many particles $n_\alpha$ occupy each single-particle state $\alpha$. Naturally, the sum of all occupation numbers must equal the total number of particles,

$$N = \sum_\alpha n_\alpha \ . \tag{6.18}$$

For fermions, not more than one particle can occupy each state, such that the occupation number can take the values $n_\alpha \in \{0, 1\}$. Bosons, on the other hand, must not obey Pauli's exclusion principle; thus any number of particles could occupy the same state and we have $n_\alpha \in \{0, 1, 2, \ldots, N\}$ for bosons.

## 6.3 Bose and Fermi statistics: General results

Consider a quantum system composed of $N$ particles. The system features a set of single-particle energy levels $\varepsilon_i$ which we number by $i = 0, 1, 2, 3, \ldots$, neglecting the possibility of degenerate states. In the occupation number picture, the system state is defined by the occupation numbers $n_i$ of the energy levels. Then, the total number of particles satisfies

$$N = \sum_{i=0}^{\infty} n_i \ .$$

Furthermore, the Hamiltonian of the system is given by the sum of the individual particle energies,

$$H(\{n_i\}) = \sum_{i=0}^{\infty} n_i \varepsilon_i \ . \tag{6.19}$$

In the canonical ensemble, the corresponding partition function $Z$ (see section 3.5) is found by summing over all possible configurations of occupation numbers:

$$Z(N, V, T) = \sum_{\substack{\{n_i\} \\ N \text{ fixed}}} e^{-\beta H(\{n_i\})} \ , \tag{6.20}$$

where $\beta = (k_B T)^{-1}$ denotes the inverse temperature as usual. It will turn out convenient to switch to the grand canonical ensemble. Then, the grand canonical partition function reads

$$\mathcal{Z}(z, V, T) = \sum_{N=0}^{\infty} z^N Z(N, V, T) = \sum_{N=0}^{\infty} z^N \sum_{\substack{\{n_i\} \\ N \text{ fixed}}} e^{-\beta H(\{n_i\})} \ . \tag{6.21}$$

Here $z := e^{\beta\mu}$ is the fugacity which we have already defined in section 5.2. In eq. (6.21) we have two different summations: the first summation sums over all possible particle numbers $N$, and the second summation runs through all possible occupation number configurations at fixed $N$. We can combine these sums into a single sum over all possible distributions of $n_i$ without constraints on $N$. Thus,

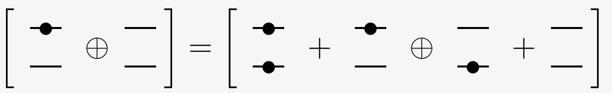
$$\begin{aligned}
\mathcal{Z} &= \sum_{\{n_i\}} z^{\sum_i n_i}\, e^{-\beta\sum_i n_i\varepsilon_i} \\
&= \sum_{n_0}\sum_{n_1}\sum_{n_2}\cdots z^{n_0+n_1+\dots}\, e^{-\beta\varepsilon_0 n_0-\beta\varepsilon_1 n_1-\dots} \\
&= \sum_{n_0}\sum_{n_1}\sum_{n_2}\cdots z^{n_0} z^{n_1} z^{n_2}\cdots e^{-\beta\varepsilon_0 n_0}\, e^{-\beta\varepsilon_1 n_1}\cdots \\
&= \sum_{n_0}\left[z e^{-\beta\varepsilon_0}\right]^{n_0}\sum_{n_1}\left[z e^{-\beta\varepsilon_1}\right]^{n_1}\sum_{n_2}\left[z e^{-\beta\varepsilon_2}\right]^{n_2}\cdots\ .
\end{aligned} \tag{6.22}$$

We see that the grand canonical partition function factorizes completely into sums over the occupation number for each energy level individually. For fermions, the sums would range from 0 to 1 (i.e. $\sum_{n_i=0}^{1}$ for each $i = 0, 1, 2, \dots$). In contrast, bosonic systems would exhibit infinite sums ($\sum_{n_i=0}^{\infty}$).

*Example 6.1.* **Two-level system of fermions**

To avoid orientation loss in this jungle of summations, let us visualize the sum over all configurations for a simple fermionic system consisting of only two energy levels 0 (ground state) and 1 (excited state):

$$\sum_{\{n_i\}} 1 = \sum_{n_0=0}^{1}\sum_{n_1=0}^{1} 1 = \sum_{n_0=0}^{1}$$



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where the lower and upper line depict the ground and excited state, respectively, while a filled circle represents a fermion. Thus there are four possible configurations to sum over: *1)* $N = 0$, no particles; *2)* $N = 1$, one particle in the ground state; *3)* $N = 1$, one particle in the excited state; *4)* $N = 2$, one particle in each state. It is not possible to have more than two fermions in a two-level system.

We now examine the grand canonical partition function for fermions and bosons separately.

**Fermions.** Beginning with fermions, we find that each product term in the last line of eq. (6.22) simplifies to

$$\sum_{n_i=0}^{1}\left[z e^{-\beta\varepsilon_i}\right]^{n_i} = 1 + z e^{-\beta\varepsilon_i}\ .$$

Therefore, the fermionic grand canonical partition function $\mathcal{Z}_{\text{fermion}}$ is given by the exact formula

$$\mathcal{Z}_{\text{fermion}} = \prod_{i=0}^{\infty}\left(1 + z e^{-\beta\varepsilon_i}\right)\ . \tag{6.23}$$

**Bosons.** In the case of bosons, the sums go to infinity, and the factorized terms in eq. (6.22) become geometric series:

$$\begin{aligned}
\sum_{n_i=0}^{\infty}\left[z e^{-\beta\varepsilon_i}\right]^{n_i} &= 1 + z e^{-\beta\varepsilon_i} + \left(z e^{-\beta\varepsilon_i}\right)^2 + \left(z e^{-\beta\varepsilon_i}\right)^3 + \dots \\
&= \frac{1}{1 - z e^{-\beta\varepsilon_i}}\ ,
\end{aligned} \tag{6.24}$$

where we have used $\sum_{k=0}^{\infty} x^k = \frac{1}{1-x}$ for $|x| < 1$. Thus we also obtain an exact expression for the bosonic grand canonical partition function:

$$\mathcal{Z}_{\text{boson}} = \prod_{i=0}^{\infty} \frac{1}{1 - ze^{-\beta\varepsilon_i}} \ . \tag{6.25}$$

Note that in the limit $ze^{-\beta\varepsilon_i} \to 1$, the bosonic partition function $\mathcal{Z}_{\text{boson}}$ diverges, resulting in a phase transition known as *Bose-Einstein condensation* (see section 6.6).

We can combine the results for fermions (F) and bosons (B) in one compact formula for the grand canonical partition function of a many-particle quantum system:

$$\boxed{\mathcal{Z}_{\text{F/B}} = \prod_{i=0}^{\infty} \left(1 \pm ze^{-\beta\varepsilon_i}\right)^{\pm 1}} \ , \tag{6.26}$$

where the plus sign describes fermions (!) and the minus sign describes bosons. Knowing the partition function, we are able to compute all statistical and thermodynamic quantities of interest. For example, what is the mean occupation number $n_m$ of the energy level $\varepsilon_m$? Starting with the definition of an expectation value, we have

$$\begin{aligned} \langle n_m \rangle &= \frac{\sum\limits_{\{n_i\}} n_m \, z^{\sum_k n_k} \, e^{-\beta \sum_j \varepsilon_j n_j}}{\sum\limits_{\{n_i\}} z^{\sum_k n_k} \, e^{-\beta \sum_j \varepsilon_j n_j}} \\ &= -\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_m} \ln \left( \sum_{\{n_i\}} z^{\sum_k n_k} \, e^{-\beta \sum_j \varepsilon_j n_j} \right), \\ &= -\frac{1}{\beta} \frac{\partial \ln(\mathcal{Z})}{\partial \varepsilon_m} \ . \end{aligned} \tag{6.27}$$

Furthermore, the logarithm of $\mathcal{Z}_{F/B}$ becomes

$$\begin{aligned} \ln\Big(\mathcal{Z}_{\text{F/B}}\Big) &= \ln \left[ \prod_{i=0}^{\infty} \left(1 \pm ze^{-\beta\varepsilon_i}\right)^{\pm 1} \right] \\ &= \pm \sum_{i=1}^{\infty} \ln\left(1 \pm ze^{-\beta\varepsilon_i}\right) \ . \end{aligned} \tag{6.28}$$

Combining eqs. (6.27) and (6.28), we obtain

$$\boxed{\langle n_m \rangle_{\text{F/B}} = \frac{ze^{-\beta\varepsilon_m}}{1 \pm ze^{-\beta\varepsilon_m}} = \frac{1}{\frac{e^{\beta\varepsilon_m}}{z} \pm 1}} \ . \tag{6.29}$$

With the plus sign, eq. (6.29) defines the *Fermi-Dirac distribution* which describes fermion statistics. With the minus sign, the formula becomes the *Bose-Einstein distribution* for bosons.

The mean total particle number $N$ of the system follows immediately:

$$N = \sum_m \langle n_m \rangle = \sum_m \left( \frac{e^{\beta\varepsilon_m}}{z} \pm 1 \right)^{-1} \ . \tag{6.30}$$

Similarly, we find that the mean total energy $U$ is[1]

$$\begin{aligned} U = \langle H \rangle &= \left\langle \sum_m \varepsilon_m n_m \right\rangle \\ &= \sum_m \varepsilon_m \langle n_m \rangle \\ &= \sum_m \frac{\varepsilon_m}{\frac{e^{\beta\varepsilon_m}}{z} \pm 1} \ . \end{aligned} \tag{6.31}$$

Finally, using our results from section 3.9, we obtain the grand canonical equation of state for a quantum gas,

$$\boxed{\frac{PV}{k_B T} = \ln\left(\mathcal{Z}_{\mathrm{F/B}}\right) = \pm \sum_i \ln\left(1 \pm z e^{-\beta\varepsilon_i}\right)} \ . \tag{6.32}$$

Note that the results for $N$, $U$, and the equation of state entail the set of single-particle levels $\{\varepsilon_i\}$. Once these energy levels are known – they are easily written down for ideal, non-interacting systems –, we may conveniently compute thermodynamic properties of a specific system. In conclusion, uniting the occupation number formalism with the grand canonical ensemble allows us to solve quantum statistics – at least in principle. We will discuss specific problems in the following sections.

## 6.4 Free ideal fermions

Let us now focus on fermions, i.e. quantum particles with half-integer spin such as electrons. Since they must obey Pauli's exclusion principle, a system of many non-interacting fermions (*Fermi gas*) will behave very different from a classical ideal gas.

**Ideal Fermi gas.** The particles in a Fermi gas follow the *Fermi-Dirac distribution* (eq. (6.29)),

$$\boxed{\langle n_m \rangle = \frac{1}{\frac{e^{\beta\varepsilon_m}}{z} + 1}} \ . \tag{6.33}$$

Thus the state of the system is defined by the mean distribution of occupation numbers $\langle n_m \rangle$ across the system's single-particle energy levels. We may write the wave function of an individual free fermion as a plane wave,

$$\phi_{\vec{p}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{\frac{i\vec{p}\cdot\vec{r}}{\hbar}} \ , \tag{6.34}$$

---

[1] We may also calculate $U$ from the partition function,

$$U = -\frac{\partial}{\partial\beta} \ln\left(\mathcal{Z}_{\mathrm{F/B}}\right) \ ,$$

if we ignore that the fugacity $z$ depends on $\beta$ and treat $z$ as an independent variable instead.

where the quantum number is given by the momentum $\vec{p}$ and $V$ denotes the volume. We easily check that this solution is normalized (omitting the vector arrow on the subscripts):

$$\begin{aligned} |\phi_p|^2 = \phi_p \phi_p^* &= \frac{1}{V} e^{\frac{i\vec{p}\cdot\vec{r}}{\hbar}} e^{-\frac{i\vec{p}\cdot\vec{r}}{\hbar}} \\ \Rightarrow \quad \int_V \mathrm{d}^3 r \, |\phi_p|^2 &= 1 \; , \end{aligned} \tag{6.35}$$

as required. Furthermore, applying the kinetic energy operator to eq. (6.34) yields

$$-\frac{\hbar^2}{2m} \vec{\nabla}^2 \phi_p(\vec{r}) = \frac{p^2}{2m} \phi_p(\vec{r}) \; . \tag{6.36}$$

Thus we find that the plane waves are eigenfunctions of the kinetic energy operator; the corresponding eigenvalue is the kinetic energy.

Let us now imagine a cubic box with edge length $L$ and volume $V = L^3$. By putting the fermions in this box and imposing periodic boundary conditions at the box edges, we assume that the plane waves are periodic over the box length $L$. Choosing a coordinate system such that the edges lie parallel to the $x$, $y$, or $z$ direction, we consequently require (along the $x$ direction)

$$\phi_p(\vec{r} + \hat{e}_x L) = \phi_p(\vec{r}) \; , \tag{6.37}$$

where $\hat{e}_x$ denotes the unit vector pointing in the $x$ direction. Analogous periodicity conditions hold along $\hat{e}_y$ and $\hat{e}_z$. To satisfy these conditions, the momentum $\vec{p}$ must obey[2]

$$\vec{p} = \frac{2\pi\hbar}{L} \vec{n} \; , \qquad \text{where} \quad \vec{n} = \begin{pmatrix} 0, 1, 2, \ldots \\ 0, 1, 2, \ldots \\ 0, 1, 2, \ldots \end{pmatrix} \; . \tag{6.38}$$

By the notation for $\vec{n}$ we mean that $\vec{n}$ may be any vector with integer components. Thus the momenta constitute a discrete set of quantum numbers. In geometric terms, the momentum quantum numbers form a cubic lattice in 3D space with lattice constant, or discretization constant, $2\pi\hbar/L = h/L$. Note that $h/L \to 0$ as $L \to \infty$, i.e. the momenta become continuous when the box expands infinitely. In this continuum limit, we may switch from a discrete sum over momenta to an integral over momenta:

$$\left(\frac{h}{L}\right)^3 \sum_{\vec{p}} \;\; \underset{\frac{h}{L}\to 0}{\overset{\text{discretize}}{\longleftrightarrow}} \;\; \int \mathrm{d}^3 p \qquad \Rightarrow \qquad \boxed{\sum_{\vec{p}} \leftrightarrow \frac{V}{h^3} \int \mathrm{d}^3 p} \; . \tag{6.39}$$

This transition to a momentum integral allows us to count states in momentum space.

---

[2] As a check, we reinsert eq. (6.38) into the exponent of $\phi_p$ to find

$$\frac{i\vec{p}\cdot\vec{r}}{\hbar} = i\frac{2\pi\hbar}{L}\frac{\vec{n}\cdot(\vec{r} + \hat{e}_x L)}{\hbar} = \frac{i2\pi\vec{n}\cdot\vec{r}}{L} + i2\pi n_x \; .$$

The last term on the RHS is a multiple of $i2\pi$ which does not affect the wave function. Therefore, $\phi_p$ is indeed periodic over $L$.

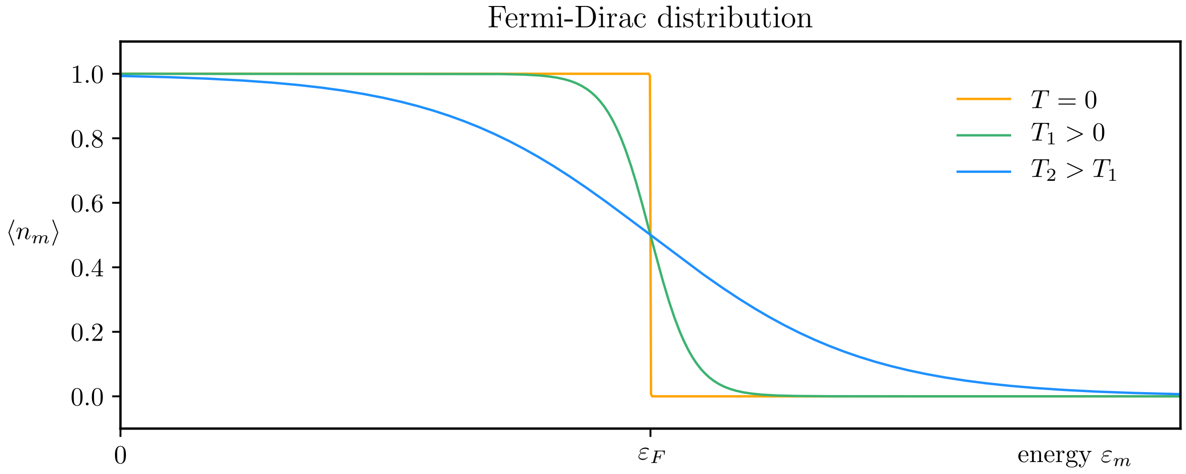

**Figure 6.1:** Fermi-Dirac distribution for three different temperatures. At zero temperature, the Fermi distribution resembles a step function. With increasing temperature, the Fermi edge smears out more and more. For $\varepsilon_m = \varepsilon_F$ the distribution yields $\langle n_m \rangle = 1/2$.

**Fermi energy.** Let us return to the Fermi distribution (eq. (6.33)). To get a picture of what we are discussing, suppose that the box of volume $V$ represents a metal, and the fermions are free electrons whirring around in the metal. The Fermi distribution depends on the fugacity $z$, which we do not know. However, recall that we defined the fugacity in terms of the chemical potential $\mu$. The chemical potential of electrons in a metal is known as the *Fermi energy* $\varepsilon_F$. In these terms we redefine the fugacity,

$$z := e^{\beta\mu} = e^{\beta\varepsilon_F} \ . \tag{6.40}$$

Using this definition, the Fermi distribution is now written as

$$\boxed{\langle n_m \rangle = \frac{1}{e^{\beta(\varepsilon_m - \varepsilon_F)} + 1}} \ . \tag{6.41}$$

Since each energy level $m$ corresponds to a certain energy and thereby to a certain momentum, the expectation values $\langle n_m \rangle = \langle n_\varepsilon \rangle = \langle n_p \rangle$ all mean the same. Figure 6.1 shows a plot of the Fermi distribution for different temperatures.

What is the meaning of the Fermi energy, and how do we calculate it? First, we consider zero temperature ($T = 0$). In that case the Fermi distribution looks like a step function; each state is occupied up to the energy $\varepsilon = \varepsilon_F$ and no states are occupied above $\varepsilon_F$. Note that since we deal with fermions, Pauli's exclusion principle applies, and even at zero temperature it is impossible that all electrons occupy the lowest energy level. Instead, starting at the lowest energy, the electrons "fill up" higher and higher states. The energy of the highest electron determines the Fermi energy.

Our task is to count all occupied states, i.e. the total number of electrons. Since electrons have non-zero spin, we must consider the degeneracy of energy levels. The *multiplicity* of states $g$ is given by $g = 2s + 1$, where $s$ denotes spin. Since $s = 1/2$ for electrons, we have $g = 2$, meaning there are two states per electron energy (spin up and spin down). Using the continuum limit relation for switching between sums and integrals (see eq. (6.39)), the total number of electrons in the metal is given by

$$N = g \sum_{p_m < p_F} 1 = g \frac{V}{h^3} \int_{|\vec{p}| < p_F} \mathrm{d}^3 p = g \frac{V}{h^3} \int_0^{p_F} \mathrm{d}p \, 4\pi p^2 \ , \tag{6.42}$$

where the Fermi momentum $p_F$ is defined by

$$\varepsilon_F = \frac{p_F^2}{2m} \tag{6.43}$$

according to the (non-relativistic) energy dispersion relation for free electrons. Performing the integral, we obtain the particle number in terms of the Fermi momentum,

$$N = g\frac{V}{h^3}\frac{4\pi}{3}p_F^3 \ , \tag{6.44}$$

where $g = 2$. Rearranging this result for $p_F$ and inserting it into eq. (6.43) yields the *Fermi energy at zero temperature*,

$$\boxed{E_F = \frac{h^2}{2m}\left(\frac{N}{V}\frac{3}{4\pi g}\right)^{\frac{2}{3}}} \ . \tag{6.45}$$

Keep in mind that our calculation holds for free electrons. In a metal, this is a good approximation for valence electrons. Typically the metal contains one valence electron per atom.

*Example 6.2.* **Electrons are hot!**

What is the Fermi energy of a typical metal? Let us plug some numbers into eq. (6.45):

| | | |
|---|---|---|
| electron mass | $m_e$ | $= 9.1 \times 10^{-31}\,\mathrm{kg}$ |
| Planck's constant | $h$ | $= 6.6 \times 10^{-34}\,\mathrm{J\,s}$ |
| particle concentration | $\frac{N}{V}$ | $\approx \frac{1}{(0.5 \times 10^{-9}\,\mathrm{m})^3} \approx 10^{28}\,\mathrm{m}^{-3}$ |

With $g = 2$, this yields

$$E_F \approx \frac{6.6^2}{18.2} \cdot 10^{-37} \cdot \left(\frac{3}{8\pi} \cdot 10^{28}\right)^{2/3} \mathrm{J} \approx 2.7 \times 10^{-19}\,\mathrm{J}.$$

This energy corresponds to about 1.7 eV. We may compare the Fermi energy to the thermal energy of a classical particle, which is roughly $k_BT$ (see section 3.6.1). At room temperature ($T = 300\,\mathrm{K}$), we have

$$k_BT \approx 4 \times 10^{-21}\,\mathrm{J} \quad (\text{at } T = 300\,\mathrm{K}) \qquad \Rightarrow \qquad E_F \approx 60\,k_BT \ .$$

Thus $E_F$ is about 60 times higher than the thermal energy of a classical particle at room temperature. Defining the *Fermi temperature* $T_F := E_F/k_B$, we find that

$$T_F \approx 18\,000\,\mathrm{K} \ .$$

In other words, electrons are extremely "hot" compared to classical particles.

At the Fermi edge, the electrons have the Fermi momentum $p_F$. From this we may compute their de Broglie wavelength $\lambda$ as

$$\lambda = \frac{h}{p_F} = \frac{h}{\sqrt{2m_eE_F}} \approx 10^{-9}\,\mathrm{m} = 1\,\mathrm{nm}.$$

A wavelength of 1 nm exceeds typical electron distances, which manifests that electrons are true quantum particles.

The relationship between $k_BT$ and the Fermi energy also tells us something about the shape of the Fermi distribution at a finite temperature $T$. The Fermi edge, i.e. the transition region between occupied and unoccupied states, approximately extends to $\varepsilon_F \pm k_BT$. In rescaled units, the borders of the Fermi edge are around $\varepsilon_\pm/\varepsilon_F = 1 \pm k_BT/\varepsilon_F$, which becomes roughly $1 \pm 1/60$ for a metal at $T = 300\,\mathrm{K}$. Thus the width of the Fermi edge is only about $1/60$ of the Fermi energy and the Fermi distribution looks very sharp, or "step-like", for metals at room temperature.

## 6.5 Free ideal bosons and black-body radiation

After discussing fermions, let us now move on to bosons, i.e. particles with integer spin such as photons, phonons or alkali atoms. Bosons behave fundamentally different from fermions because several bosons can be in the same state at the same time. In the ground state of the system (at $T = 0$), all bosons occupy the lowest energy level, which Pauli's exclusion principle prohibits for fermions. Generally, bosons follow the *Bose-Einstein distribution* (see eq. (6.29)),

$$\boxed{\langle n_m \rangle = \frac{1}{\frac{e^{\beta\varepsilon_m}}{z} - 1}} \; . \tag{6.46}$$

**Relativistic energy-momentum relation.** To deal with photons traveling at the speed of light, we cannot neglect relativistic effects anymore. Einstein's famous formula stating the equivalence of mass and energy reads

$$E = mc^2 = \gamma m_0 c^2 \; , \quad \text{where } \gamma = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \; . \tag{6.47}$$

Here $E$ is the relativistic energy, $c$ is the speed of light, and $v$ denotes the velocity of the particle. Note the difference between the rest mass $m_0$ and the relativistic mass $m$. Squaring and rearranging yields

$$\begin{aligned} E^2 \left(1 - \frac{v^2}{c^2}\right) &= m_0^2 c^4 \\ \Rightarrow \quad E^2 &= m_0^2 c^4 + E^2 \frac{v^2}{c^2} = m_0^2 c^4 + m^2 v^2 c^2 \; . \end{aligned} \tag{6.48}$$

Identifying the relativistic momentum $p = mv$, we obtain the relativistic *energy-momentum relation*:

$$\boxed{E = \sqrt{m_0^2 c^4 + p^2 c^2}} \; . \tag{6.49}$$

We see that this equation reduces to $E = m_0 c^2$ if the particle is at rest ($p = 0$). For massless particles such as photons ($m_0 = 0$), we find $E = pc$. Let us discuss two limits of eq. (6.49):

- Non-relativistic limit, $v \ll c$.
  Rewriting the energy-momentum relation as $E = m_0c^2\sqrt{1+p^2/(m_0^2c^2)}$, we may expand it as a Taylor series in $p^2/(m_0^2c^2)$ up to first order to obtain
  $$E = m_0c^2 + \frac{1}{2}\frac{p^2}{m_0} + \mathcal{O}\left(\frac{p^4}{m_0^4c^4}\right) . \tag{6.50}$$
  Note that the second term corresponds to the classical (Newtonian) kinetic energy.
- Ultra-relativistic limit, $v \to c$.
  For velocities $v$ close to the speed of light, the $(pc)^2$ term dominates, and we write the energy-momentum relation as
  $$E = pc\sqrt{1+\frac{m_0^2c^2}{p^2}} ,$$
  which converges to $E = pc$ as $m_0/m = \gamma^{-1} \to 0$.

**Ideal photon gas.** We now focus on free bosons with zero rest mass, which characterizes a photon gas. In this case the ultra-relativistic limit applies. Furthermore, the chemical potential for a photon vanishes, $\mu = 0$. This implies that the fugacity is $z = e^{\beta\mu} = 1$. With $E = pc$ and using eq. (6.29), the mean number of photons with momentum $p$ (at finite temperature) is given by

$$\langle n_p \rangle = \frac{g}{e^{\beta pc} - 1} . \tag{6.51}$$

Here the multiplicity is $g = 2$ for photons because of the two polarization directions.

Suppose the photon gas is confined in a rigid opaque cavity at a constant temperature $T$. We call the idealization of this cavity a *black body.* At equilibrium, the emission and absorption of electromagnetic radiation at the cavity walls are in a steady state, and the energy states of the photon gas inside correspond to the levels of a harmonic oscillator,[3]

$$E_\omega = \hbar\omega\left(n + \frac{1}{2}\right) = pc\left(n + \frac{1}{2}\right) , \tag{6.52}$$

where the last equality holds since $E_{\text{photon}} = \hbar\omega = pc$. The occupation number $n$ follows the Bose-Einstein distribution.

We now ask, what is the energy spectrum of the photon gas? The total energy is given by

$$\begin{aligned} U &= \sum_p \varepsilon_p \langle n_p \rangle \\ &= g\frac{V}{h^3}\int \mathrm{d}^3p\,\frac{|p|c}{e^{\beta pc} - 1} \\ &= g\frac{V}{h^3}\int_0^\infty \mathrm{d}p\,4\pi p^2\frac{pc}{e^{\beta pc} - 1} , \end{aligned} \tag{6.53}$$

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[3] The vacuum energy $E_{\text{vac}} = \frac{1}{2}\hbar\omega$ is irrelevant here.

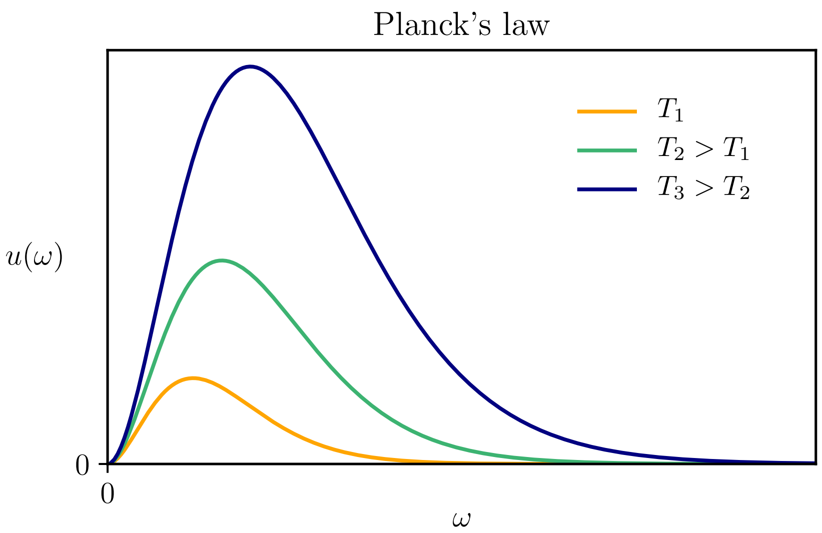

**Figure 6.2: Planck's law.** Black body spectrum for three different temperatures.

where we have applied our knowledge about how to switch from a sum to an integral in the continuum limit (see eq. (6.39)). Using $E = \hbar\omega = pc \Rightarrow p = \frac{\hbar}{c}\omega$, we substitute the momentum integral by a frequency integral to obtain

$$\frac{U}{V} = \frac{8\pi\hbar^4}{h^3c^3}\int_0^\infty \mathrm{d}\omega\, \frac{\omega^3}{e^{\beta\hbar\omega}-1} \equiv \int_0^\infty \mathrm{d}\omega\, u(\omega)\ , \tag{6.54}$$

where we have inserted $g = 2$. Here the function $u(\omega)$ is the *spectral energy density*,

$$\boxed{u(\omega) = \frac{\hbar}{\pi^2c^3}\frac{\omega^3}{e^{\frac{\hbar\omega}{k_BT}}-1}}\ . \tag{6.55}$$

Eq. (6.55) is known as *Planck's law*; it describes the characteristic spectrum of black body radiation at temperature $T$. Figure 6.2 shows a plot of the spectrum for different temperatures.

Let us discuss the frequency limits of Planck's formula:

- Low frequencies, $\beta\hbar\omega \ll 1$.
  The limit of low frequencies corresponds to the classical limit ($\hbar \to 0$). We may approximate $\exp(\beta\hbar\omega) - 1 \approx \beta\hbar\omega$, which leads to the *Rayleigh-Jeans formula*,

  $$u(\omega) = k_BT\frac{\omega^2}{\pi^2c^3}\ . \tag{6.56}$$

- High frequencies, $\beta\hbar\omega \gg 1$.
  As $\omega \to \infty$, the 1 in the denominator of eq. (6.55) becomes negligible compared to the exponential, and we obtain *Wien's first law*,

  $$u(\omega) = \frac{\hbar}{\pi^2c^3}\frac{\omega^3}{e^{\beta\hbar\omega}}\ . \tag{6.57}$$

Furthermore, it is interesting to calculate the maximum $\omega^*$ of the black body spectrum:

$$
\begin{aligned}
0 &= \left.\frac{\partial u(\omega)}{\partial \omega}\right|_{\omega=\omega^*} \\
&= \left.\left[\frac{3}{\omega}u(\omega) - \frac{\hbar}{k_B T}\frac{e^{\frac{\hbar\omega}{k_B T}}}{e^{\frac{\hbar\omega}{k_B T}} - 1}u(\omega)\right]\right|_{\omega=\omega^*} \qquad (6.58)\\
\Rightarrow \qquad 3 &= \frac{\hbar\omega^*}{k_B T}\frac{1}{1 - e^{-\frac{\hbar\omega^*}{k_B T}}} \; .
\end{aligned}
$$

Solving the last equality yields

$$\beta\hbar\omega^* \approx 2.8 \; . \tag{6.59}$$

This result, known as *Wien's second law* or *Wien's displacement law*, states that

$$\boxed{\omega^* \approx 2.8\frac{k_B T}{\hbar}} \quad \text{or} \quad \boxed{\nu^* \approx 2.8\frac{k_B T}{h}} \; . \tag{6.60}$$

Hence the frequency of maximal irradiance depends linearly on temperature.

*Example 6.3.* **Wien's displacement law**

Wien's displacement law appears in everyday life. You may have observed, for example, that a heated wire (e.g. light bulb) first starts to glow in a reddish color, then turns orange, and eventually emits more yellow light as it gets hotter. At an effective temperature of around 6000 K, our sun emits its highest energy density at roughly $\lambda^* = 650\,\text{nm}$, which corresponds to a bright yellow. Camp fires, on the other hand, serve better as heat sources than as light sources because their peak irradiance lies in the infrared range.

What is the temperature dependence of the total energy density $U/V$? To answer this, we rescale the frequency to $\tilde{\omega} := \beta\hbar\omega$. This yields

$$\frac{U}{V} = \frac{\hbar}{\pi^2 c^3}\frac{1}{\hbar^4\beta^4}\int_0^\infty \mathrm{d}\tilde{\omega}\, \frac{\tilde{\omega}^3}{e^{\tilde{\omega}} - 1} \; . \tag{6.61}$$

The rescaled integral has a temperature-independent solution, $\pi^4/15$, and we find

$$\boxed{\frac{U}{V} = \frac{(k_B T)^4}{c^3\hbar^3}\frac{\pi^2}{15} \propto T^4} \; . \tag{6.62}$$

This is the *Stefan-Boltzmann law*, which states that the total energy density scales with the fourth power of the temperature.

Finally, we want to see how the energy density relates to the pressure in a photon gas. In chapter 3, we derived the grand-canonical equation of state,

$$\ln \mathcal{Z} = \frac{PV}{k_B T} = \beta PV \; . \tag{6.63}$$

Moreover, we know that the total energy follows from the grand canonical partition function (for fixed fugacity $z$) according to

$$U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} \; , \tag{6.64}$$

while at the same time $U$ is given by eq. (6.62). From this we infer

$$\begin{aligned} U &= -\frac{\partial \ln \mathcal{Z}}{\partial \beta} = \frac{V\pi^2}{15\beta^4 c^3 \hbar^3} \\ \Rightarrow \quad \ln \mathcal{Z} &= \frac{1}{3}\cdot\frac{V\pi^2}{15\beta^3 c^3\hbar^3} \overset{!}{=} \beta P V \\ \Rightarrow \quad PV &= \frac{1}{3}\cdot\underbrace{\frac{V\pi^2}{15\beta^4 c^3\hbar^3}}_{=U} = \frac{1}{3}U \ . \end{aligned} \tag{6.65}$$

Our results for the classical ideal gas were $PV = Nk_BT$ and (for a mono-atomic ideal gas) $U = \frac{3}{2}Nk_BT$. In comparison:

| | | |
|---|---|---|
| Classical ideal gas: | $U = 3PV$ | $U \propto T$ (equipartition theorem) |
| Ultra-relativistic boson gas: | $U = \frac{3}{2}PV$ | $U \propto T^4$ (Stefan-Boltzmann law) |

In other words, the classical ideal gas and the photon gas have similar relations between energy density and pressure but very different temperature dependencies. Note that the pressure of the photon gas follows from eq. (6.65):

$$P = \frac{\pi^2 (k_BT)^4}{45c^3\hbar^3} \ . \tag{6.66}$$

*Example 6.4.* **Photon gas at atmospheric pressure**

At which temperature does the photon gas have a pressure comparable to the atmospheric pressure of about $10^5$ Pa = 1 bar? Solving eq. (6.66) reveals:

$$T(P = 10^5\,\text{Pa}) \approx 10^5\,\text{K}.$$

This concludes our study of photons – ultra-relativistic massless bosons with vanishing chemical potential. The following section conversely deals with massive bosons and varying chemical potential in order to discuss a peculiar quantum phase transition observed for bosons at very low temperatures.

## 6.6 Bose-Einstein condensation

When deriving the bosonic grand canonical partition function (eq. (6.25)), we noticed a singularity when $ze^{-\beta\varepsilon_i} \to 1$, i.e. when the fugacity $z = e^{\beta\mu}$ approaches the Boltzmann weight $e^{-\beta\varepsilon_i}$ of any of the energy levels $i = 0, 1, 2, \ldots$. This requires a closer look.

Consider a system of massive, non-relativistic atoms, e.g. atoms trapped in a volume $V$. The fugacity $z \neq 1$ may vary in order to yield and conserve a certain number of atoms $N$,

$$N = \sum_i \langle n_i \rangle = \sum_i \frac{1}{\frac{e^{\beta\varepsilon_i}}{z} - 1} = \sum_i \frac{1}{e^{\beta(\varepsilon_i - \mu)} - 1} \ . \tag{6.67}$$

Note that this expression exhibits the same divergence as the partition function. Physically, we argue that $\mu < \varepsilon_i$ for all $i$ because otherwise we would have energy levels with negative mean occupation numbers. Thus, as $\mu$ increases, the singularity will first appear for the ground state $i = 0$ with energy $\varepsilon_0$. In a non-relativistic treatment, the energy levels relate to the corresponding (discrete) particle momenta according to

$$\varepsilon_i \equiv \varepsilon_p = \frac{p^2}{2m} \ ,$$

where $m$ denotes an atom's mass. Then, the lowest energy level $\varepsilon_0$ corresponds to the single-particle state $p = 0$ where atoms stop moving; they "condense" to a zero-momentum state.

We seek to find out under which circumstances a significant fraction of atoms occupies the ground state. The trick is to split the sum over all energy levels into its contribution from the $p = 0$ state and a term comprising everything else. Inserting the energy-momentum relation and replacing the sum over states $i$ by a sum over discrete momenta, we write

$$\begin{aligned} N &= \sum_{\vec{p}} \frac{1}{e^{\beta \frac{p^2}{2m}} z^{-1} - 1} \\ &= \underbrace{\frac{1}{z^{-1} - 1}}_{N_0} + \underbrace{\sum_{\vec{p} \neq 0} \frac{1}{e^{\frac{\beta p^2}{2m}} z^{-1} - 1}}_{N_{\text{rest}}} \ . \end{aligned} \tag{6.68}$$

Here $N_0 := \left(z^{-1} - 1\right)^{-1}$ denotes the the number of particles in the ground state with $p = 0$ while $N_{\text{rest}}$ represents the number of all particles not in the ground state, such that $N = N_0 + N_{\text{rest}}$. Assuming a large volume, we may convert from the sum to an integral following the procedure from eq. (6.39). This leads to

$$N = N_0 + \frac{V}{h^3} \int_0^\infty \mathrm{d}p \, 4\pi p^2 \, \frac{1}{e^{\frac{\beta p^2}{2m}} z^{-1} - 1} \ . \tag{6.69}$$

Note that the integral only includes the $p \neq 0$ states since the integrand vanishes for $p = 0$. Dividing by volume and rescaling the momentum to $\tilde{p}^2 := \frac{\beta}{2m} p^2$, we get

$$\begin{aligned} \frac{N}{V} &= \frac{N_0}{V} + \frac{4\pi}{h^3} \int_0^\infty \mathrm{d}p \, \frac{p^2}{e^{\frac{\beta p^2}{2m}} z^{-1} - 1} \\ &= \frac{N_0}{V} + \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{4}{\sqrt{\pi}} \int_0^\infty \mathrm{d}\tilde{p} \, \frac{\tilde{p}^2}{e^{\tilde{p}^2} z^{-1} - 1} \\ &= \frac{N_0}{V} + \frac{1}{\lambda_t^3} \, g_{3/2}(z) \ , \end{aligned} \tag{6.70}$$

where $\lambda_t$ denotes the thermal wavelength (eq. 3.93). Here we have introduced the special function $g_{3/2}$,

$$g_{3/2}(z) = \frac{4}{\sqrt{\pi}} \int_0^\infty \mathrm{d}\tilde{p} \, \tilde{p}^2 \frac{z e^{-\tilde{p}^2}}{1 - z e^{-\tilde{p}^2}} \ . \tag{6.71}$$

It turns out that we may rewrite $g_{3/2}$ as an infinite sum. Using the relation

$$\sum_{\ell=1}^{\infty} \left( a e^{-b} \right)^{\ell} = \frac{a e^{-b}}{1 - a e^{-b}}$$

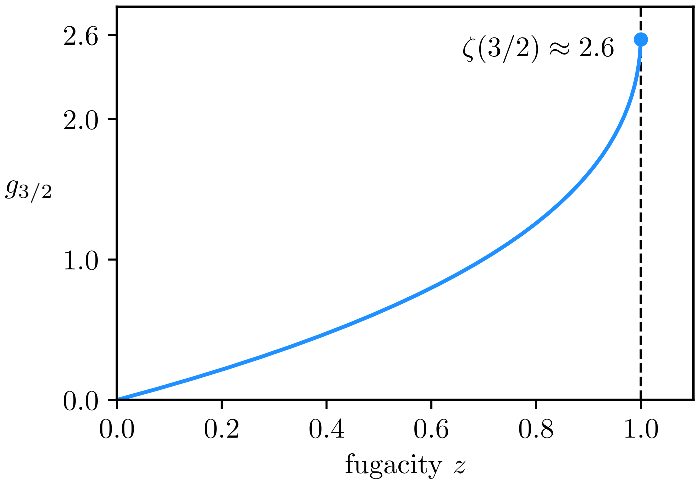

**Figure 6.3:** Plot of the special function $g_{3/2}(z)$ in the domain $0 \leq z \leq 1$. This range corresponds to chemical potentials $\mu < 0$. The upper bound of $g_{3/2}$ is given by the value of the Riemann-Zeta function $\zeta(3/2)$.

we obtain

$$\begin{aligned} g_{3/2}(z) &= \frac{4}{\sqrt{\pi}} \int_0^\infty \mathrm{d}\tilde{p}\, \tilde{p}^2 \sum_{\ell=1}^\infty \left( z e^{-\tilde{p}^2} \right)^\ell \\ &= \sum_{\ell=1}^\infty z^\ell \frac{4}{\sqrt{\pi}} \int \mathrm{d}\tilde{p}\, \tilde{p}^2 e^{-\ell \tilde{p}^2} \\ &= \sum_{\ell=1}^\infty \frac{z^\ell}{\ell^{3/2}} \underbrace{\frac{4}{\sqrt{\pi}} \int \mathrm{d}\tilde{\tilde{p}}\, \tilde{\tilde{p}}^2 e^{-\tilde{\tilde{p}}^2}}_{=1} \ . \end{aligned} \tag{6.72}$$

In the final step we have substituted $\tilde{\tilde{p}}^2 = \ell \tilde{p}^2$. In short, we may define the function $g_{3/2}$ as

$$\boxed{g_{3/2}(z) = \sum_{\ell=1}^\infty \frac{z^\ell}{\ell^{3/2}}} \ . \tag{6.73}$$

The series diverges for $z > 1$, i.e. for positive chemical potentials $\mu > 0$. At $z = 1$, however, it converges to a finite value given by the Riemann-Zeta function $\zeta$,

$$g_{3/2}(z = 1) = \sum_{\ell=1}^\infty \frac{1}{\ell^{3/2}} = \zeta\left(\frac{3}{2}\right) \approx 2.6 \ .$$

In the range $0 \leq z \leq 1$, the function $g_{3/2}$ is finite everywhere and monotonically increasing with $z$ (see figure 6.3 for a plot). Therefore, we obtain the upper bound

$$g_{3/2}(z) \leq \zeta(3/2) \ .$$

Note that the slope of $g_{3/2}(z)$ at $z = 1$ is infinite.

To recapitulate, the particle number density $n := N/V$ of the Bose gas of atoms is given by

$$n = n_0 + \frac{1}{\lambda_t^3} g_{3/2}(z) \ , \tag{6.74}$$

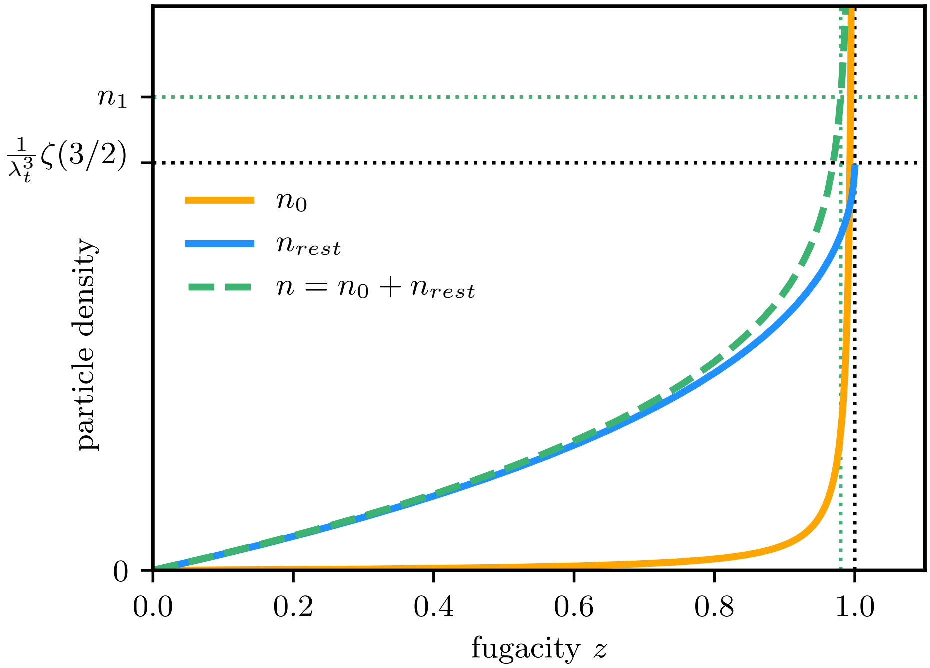

**Figure 6.4: Bose-Einstein condensation.** Particle number densities of atoms in the ground state ($n_0$), not in the ground state ($n_{\text{rest}}$), and combined ($n$), as a function of fugacity. For low fugacities almost no atoms occupy the $p = 0$ state (orange curve). Contrarily, at a total particle density $n_1 > n_c = \frac{1}{\lambda_t^3}\zeta(3/2)$, the fugacity is $z \approx 1$ and a considerable fraction of atoms condenses to the zero-momentum ground state, as indicated by the finite value of $n_0 > 0$. Thus a Bose-Einstein condensate forms. (The volume is chosen to conveniently display the different curves in the plot. As $V \to \infty$, the orange curve becomes infinitely steep.)

where $n_0 := N_0/V$ denotes the concentration of particles in the ground state. Suppose we conduct an experiment where the density $n$ remains constant and we control the temperature. Moreover, the system is large, such that $N \to \infty$ and $V \to \infty$ (while keeping $N/V$ fixed). At sufficiently high temperature $T$, we have

$$n < \frac{1}{\lambda_t^3}\zeta(3/2) = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \zeta(3/2) \ . \tag{6.75}$$

This means that the state of the system is realized with a fugacity significantly smaller than one, $z < 1$. Since we assume a large volume, we see that in this case almost no particles occupy the ground state:

$$n_0 = \frac{N_0}{V} = \frac{1}{V\left(z^{-1}-1\right)} \to 0 \qquad (V \to \infty \text{ and } z < 1) \ . \tag{6.76}$$

However, if the particle number density $n$ surpasses the critical point defined by

$$n_c = \frac{1}{\lambda_t^3(T_c)}\zeta(3/2) \ , \tag{6.77}$$

the fugacity approaches $z \approx 1$ and a finite fraction of atoms occupies the $p = 0$ state. Figure 6.4 illustrates the transition. For the critical temperature $T_c$ determined by eq. (6.77), we find

$$\boxed{T_c = \frac{h^2}{2\pi m k_B}\left(\frac{n_c}{\zeta(3/2)}\right)^{2/3}} \ . \tag{6.78}$$

Below this critical temperature, a so-called *Bose-Einstein condensate* forms. The number density of particles in the ground state is then given by

$$n_0 = n - \frac{V}{\lambda_t^3} g_{3/2}(z) \approx n - \frac{V}{\lambda_t^3}\zeta(3/2) \ .$$

All particles in the Bose-Einstein condensate have zero momentum and are in precisely the same quantum state. In other words, we may describe all atoms in the ground state by *one* wave function. Some physicists describe Bose-Einstein condensation as a condensation in momentum space: the Bose gas separates into two phases, one with finite momentum and one standing still, but no spatial separation occurs as in classical phase separations.

*Example 6.5.* **Experimental observation of BEC**

Although Bose-Einstein condensation has been predicted by theory about a hundred years ago (Einstein 1924), it took some time to observe the phenomenon experimentally. The key limitation arises from the need for extremely low temperatures while maintaining a relatively high particle number density.

In 1995, Cornell, Wieman, and Ketterle conducted experiments with alkali atoms at a density of around $n \approx 10^{14}\,\mathrm{cm}^{-3}$. Inserting this into eq. (6.78) yields

$$T_c \approx 2\,\mu\mathrm{K},$$

which is just two millionths of a Kelvin away from absolute zero! To reach such low temperatures, researchers have employed a combination of

- laser-light cooling to slow down atomic beams, and
- cooling through evaporation.

The figure below shows the formation of a Bose-Einstein condensate observed in 1996 for a gas of Natrium atoms [5]. The 3D plots illustrate the velocity distribution of Na atoms before, during, and after Bose-Einstein condensation. At temperatures above $2\,\mu$K (left), the velocity distribution resembles the classical Maxwell Boltzmann distribution. Lowering the temperature (center), a second component containing "cold" and dense particles emerges. When cooling down even further (right), the non-condensed fraction diminishes and only the condensate remains.

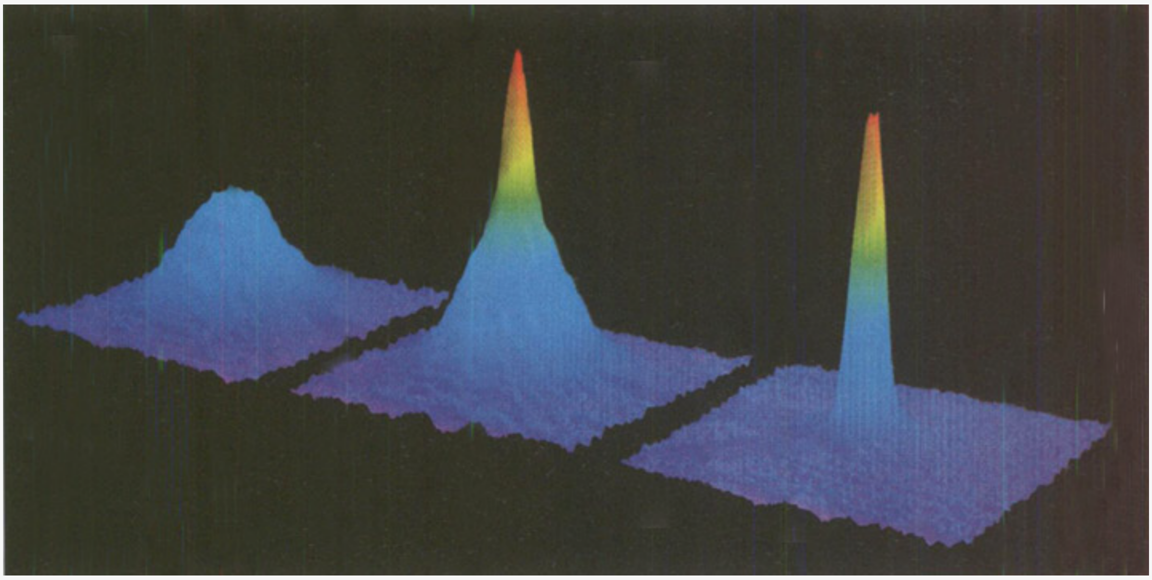

Figure reproduced from [5].

# Appendix

## A.1 Proof of Gaussian integral

When calculating the hyper-surface of a $D$-dimensional sphere (see blue box on p. 55), we stated the integral

$$I = \int_{-\infty}^{\infty} \mathrm{d}x_1 \int_{-\infty}^{\infty} \mathrm{d}x_2 \cdots \int_{-\infty}^{\infty} \mathrm{d}x_D \; e^{-x_1^2 - x_2^2 - \cdots - x_D^2} = \left[ \int_{-\infty}^{\infty} \mathrm{d}x \, e^{-x^2} \right]^D = \pi^{D/2} \; . \tag{A.1}$$

To prove this, we must show

$$J = \int_{-\infty}^{\infty} \mathrm{d}x \, e^{-x^2} = \pi^{1/2} = \sqrt{\pi} \; . \tag{A.2}$$

The integral $J$ is known as *Gaussian integral.*[4] It can be calculated in many ways. Here we demonstrate a common proof introduced by Poisson that makes use of polar coordinates. First, consider the double integral $J^2$,

$$\begin{aligned} J^2 &= J \left( \int_{-\infty}^{\infty} e^{-x^2} \, \mathrm{d}x \right) = \int_{-\infty}^{\infty} J e^{-x^2} \, \mathrm{d}x \\ &= \int_{-\infty}^{\infty} \left( \int_{-\infty}^{\infty} e^{-y^2} \, \mathrm{d}y \right) e^{-x^2} \, \mathrm{d}x = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(x^2+y^2)} \, \mathrm{d}x \, \mathrm{d}y \; . \end{aligned} \tag{A.3}$$

We may consider the variables $x$ and $y$ as Cartesian coordinates spanning a two-dimensional plane. Then $J^2$ becomes an area integral over this plane. Any position $(x, y)$ is also uniquely described by the polar coordinates $(r, \phi)$, where $x = r \cos \phi$ and $y = r \sin \phi$ such that $r^2 = x^2 + y^2$. The area element transforms according to $\mathrm{d}x \, \mathrm{d}y = r \, \mathrm{d}r \, \mathrm{d}\phi$. Thus, we have

$$\begin{aligned} J^2 &= \int_0^{2\pi} \int_0^{\infty} e^{-r^2} r \, \mathrm{d}r \, \mathrm{d}\phi \\ &= 2\pi \int_0^{\infty} r e^{-r^2} \, \mathrm{d}r \\ &= 2\pi \int_0^{\infty} \left( -\frac{1}{2} \right) \frac{\mathrm{d}}{\mathrm{d}r} e^{-r^2} \, \mathrm{d}r \\ &= 2\pi \left[ -\frac{1}{2} e^{-r^2} \right]_0^{\infty} \\ &= 2\pi \left( 0 - \left( -\frac{1}{2} \right) \right) \\ &= \pi \; . \end{aligned} \tag{A.4}$$

Since $e^{-x^2}$ is a positive function for all $x \in \mathbb{R}$, the integral $J$ is also positive. Therefore, the result $J^2 = \pi$ implies

$$J = \sqrt{\pi} \qquad \text{q.e.d.} \; ,$$

which concludes the proof. ■

---

[4] Note that the exponential $e^{-x^2}$ in the Gaussian integral resembles the form of the normal, or Gaussian, distribution (with mean 0 and variance 1/2).

## A.2 Real square matrices in a nutshell

Let $\boldsymbol{A}$ be a square $n \times n$ matrix,

$$\boldsymbol{A} = (A_{ij}) = \begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} & \cdots & A_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ A_{n1} & A_{n2} & \cdots & A_{nn} \end{pmatrix} . \tag{A.5}$$

- The *transpose* of $\boldsymbol{A} = (A_{ij})$ is $\boldsymbol{A}^\top = (A_{ji})$.
- $\boldsymbol{A}^\top = \boldsymbol{A} \Leftrightarrow$ The matrix $\boldsymbol{A}$ is *symmetric.*
- If $\boldsymbol{A}$ is symmetric, then it it diagonalizable.
- The matrix $\boldsymbol{A}$ leaves its *eigenvectors* $\vec{x}_j$ invariant up to a scalar factor, the corresponding *eigenvalue* $\lambda_j$ $(j = 1, \ldots, n)$:

  $$\boldsymbol{A}\vec{x}_j = \lambda_j \vec{x}_j \quad \Leftrightarrow \quad (\boldsymbol{A} - \lambda_j \mathbb{I}_n) \cdot \vec{x}_j = 0 \quad \Leftrightarrow \quad \det(\boldsymbol{A} - \lambda_j \mathbb{I}_n) = 0 \ ,$$

  where the last equation is the *characteristic equation* and $\mathbb{I}_n$ is the $n \times n$ unit matrix.
- If the eigenvalues $\lambda_j$ are pairwise different, then the eigenvectors $\vec{x}_j$ are orthogonal to each other. If we further let the eigenvectors be normalized, we can construct an *orthonormal matrix* $\boldsymbol{U} = (\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_n)$, where the $j$-th column consists of the eigenvector $\vec{x}_j$. For an orthonormal matrix $\boldsymbol{U}^\top \boldsymbol{U} = \mathbb{I}_n$.
- The matrix $\boldsymbol{U}$ transforms the matrix $\boldsymbol{A}$ into a *diagonal matrix* of its eigenvalues such that

  $$\boldsymbol{U}^\top \boldsymbol{A} \boldsymbol{U} = \vec{\lambda} \mathbb{I}_n \ ,$$

  with the column vector $\vec{\lambda} = (\lambda_1, \lambda_2, \ldots, \lambda_n)^\top$.
- The *trace* of the matrix $\boldsymbol{A}$ is defined as $\mathrm{tr}(\boldsymbol{A}) = \sum_j A_{jj}$. It possesses the following properties:
  - $*$ $\mathrm{tr}(\boldsymbol{AB}) = \mathrm{tr}(\boldsymbol{BA})$
  - $*$ $\mathrm{tr}(\boldsymbol{A}) = \mathrm{tr}(\mathbb{I}_n \cdot \boldsymbol{A}) = \mathrm{tr}(\boldsymbol{U}^\top \boldsymbol{U} \boldsymbol{A}) = \mathrm{tr}(\boldsymbol{U}^\top \boldsymbol{A} \boldsymbol{U}) = \mathrm{tr}(\vec{\lambda} \mathbb{I}_n) = \sum_j \lambda_j$.

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