Lecture notes

Statistical Mechanics and Thermodynamics

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Abstract

These notes are based on a lecture on statistical mechanics and thermodynamics held in the winter term 2019/2020 at the University of Düsseldorf. While this has been a standard physics course a strong emphasis has been put on following a modern information-theoretic approach and on keeping the exposition as mathematically rigorous as possible. After a self-contained introduction to probability theory, Shannon entropy, and convex analysis, the generalized canonical distribution is derived from Jaynes' maximum-entropy principle and serves as the common root of all thermostatistical ensembles, including a dissipation-fluctuation theorem. The framework is then extended to *quantum* statistical mechanics in terms of density operators, with a discussion of equilibration, thermalization, and indistinguishable particles. Finally, the basic theory of thermodynamics is derived from the framework of classical statistical mechanics. The Legendre transformation (properly phrased is in convex analysis), connects the thermodynamic potentials, from which the Maxwell relations, stability conditions, thermodynamic processes, and the laws of thermodynamics follow. The final chapter applies the theory to model systems, including real gases, ideal quantum gases and Bose-Einstein condensation, and the Ising model as an introduction to phase transitions.

Based on the following literature:

- F. Schlögl, *Probability and Heat – Fundamentals of Thermostatistics* [1]: reference for the generalized canonical distribution and the concepts directly connected to it
- F. Schwabl, *Statistische Physik* [2]
- W. Nolting, *Grundkurs Theoretische Physik 6 – Statistische Physik* [3] (with exercises and solutions)
- G. Kluge and G. Neugebauer, *Grundlagen der Thermodynamik*
- F. Scheck, *Theoretische Physik 5 – Statistische Theorie der Wärme* [4] (covering some geometric aspects)
- T. Fließbach, *Statistische Physik* [5]
- R. Egger, *Statistische Mechanik – Vorlesungsskript* (close to Schwabl [2]), available for download [6]

- References for the mathematical parts of the notes:
  J. Elstrodt, *Maß- und Integrationstheorie* [7];
  R. T. Rockafellar, *Convex Analysis* [8];
  T. M. Cover and J. A. Thomas, *Elements of Information Theory* [9]

Contents

1 Introduction and mathematical preliminaries

1.1 Motivation

Goals of statistical mechanics/physics:

- Justification of thermodynamics
- More precise thermodynamic predictions (e.g. dissipation-fluctuation statements, non-equilibrium, . . .)
- Providing broadly applicable methods (e.g. cosmology, economics)
- Objects of study: many-body systems

Basic idea:

- Description of macroscopic systems that are composed of microscopic particles.
  - Classically, the *microstate* of a many-body system is given by phase-space coordinates $\xi := (q_1, p_1, \ldots, q_N, p_N)^\mathsf{T}$. Typically, $N \sim 6 \cdot 10^{23}$.
- The initial conditions (positions and momenta) of all particles determine all information about the corresponding macroscopic system.

- Knowledge of all initial conditions: unrealistic and unnecessary for the relevant questions
- Idea: capture the lack of knowledge/ignorance about microscopic details using statistical methods (such as averaging)
  - The *macrostate* is determined by a few macroscopic variables relevant for the application (such as energy E, volume V, particle number (density), temperature T, etc.)
- Important example: ideal gas in (quasi-)equilibrium. Physical macroscopic quantities are: energy E, temperature T, volume V, pressure p, particle number N, chemical potential μ

In short: classical statistical mechanics provides probabilistic descriptions of observable physical quantities of many-body systems.

Therefore, the lecture starts with *probability theory* and *information theory*. Information theory leads to Jaynes' principle of maximum entropy. This principle allows one to use the macroscopic knowledge about a system effectively and provides a common thread through large parts of statistical mechanics and thermodynamics.
This mathematical part is followed by the physical part of the lecture; see the table of contents.

Clarification of terms: Statistics is the science of dealing with data, which includes their collection, preparation, analysis, interpretation, and presentation. *Mathematical statistics* is the science of applying probability theory to statistics. *Probability theory* is the science of the mathematical modeling of random events; its central objects are random events, random variables, and stochastic processes. *Stochastics* comprises *probability theory* and *mathematical statistics*.
Statistical physics is the field that applies stochastics to physical (or physically motivated) questions (*stochastic physics* would be a more accurate term). Frequently, *statistical mechanics* is used as a synonym for statistical physics. However, one usually means, more specifically, the physics of many microscopic particles, formalized with the help of stochastics.

1.2 Notation

(i) $\{x_1, x_2, \dots\}$ denotes the *unordered set* and $(x_1, x_2, \dots)$ the *ordered set* of elements $x_1, x_2, \dots$.

(ii) $\emptyset \coloneqq \{\,\}$ denotes the *empty set*.

(iii) The *power set* of a set Ω is the set of all subsets of Ω and is denoted by $\mathcal{P}(\Omega)$.

(iv) For $A, B \subset \Omega$, the symbols $A \cap B$, $A \cup B$, $A \setminus B$ denote the *intersection*, the *union*, and the set-theoretic *difference* of A and B, respectively.

(v) For a natural number n we set

$$[n] \coloneqq \{1, 2, \dots, n\}\,. \tag{1.1}$$

(vi) The derivative of a function $f : \mathbb{R}^n \to \mathbb{R}$ is denoted by df, and we view df as a map $df : \mathbb{R}^n \to \mathrm{L}(\mathbb{R}^n, \mathbb{R})$, where $\mathrm{L}(\mathbb{R}^n, \mathbb{R})$ denotes the vector space of linear maps from $\mathbb{R}^n$ to $\mathbb{R}$; frequently, $\mathrm{L}(\mathbb{R}^n, \mathbb{R})$ is identified with row vectors. The gradient $\nabla f : \mathbb{R}^n \to \mathbb{R}^n$ is the vector dual to df; it is often written as a column vector.

(vii) The coordinate function $\mathbb{R}^n \to \mathbb{R}$, $x \mapsto x_i$ is frequently also denoted by x_i. Since the coordinate function x_i is linear, $\mathrm{d}x_i : \mathbb{R}^n \to \mathrm{L}(\mathbb{R}^n, \mathbb{R})$ is a constant function. More precisely: evaluating $\mathrm{d}x_i$ at $p \in \mathbb{R}^n$ yields

$$\mathrm{d}_p x_i = x_i \,. \tag{1.2}$$

With this, one can write $\mathrm{d}f$ as

$$\mathrm{d}f = \sum_{i=1}^{n} \frac{\partial f}{\partial x_i} \mathrm{d}x_i \,. \tag{1.3}$$

(viii) A function $f : \mathbb{R}^n \to \mathbb{R}$ is called *convex* if

$$f(\lambda x + (1-\lambda)y) \leq \lambda f(x) + (1-\lambda) f(y) \tag{1.4}$$

for all $x, y \in \mathbb{R}^n$ and $\lambda \in [0, 1]$.

Information that was not covered in the lecture is written in gray or has a gray heading.

1.3 Probability theory

Providing a full introduction to probability theory is beyond the scope of this course. Nevertheless, we start with a reminder on the basic concepts.

1.3.1 Events and probability measures

1.3.1.1 Event spaces

- A collection of sets $\Sigma \subset \mathcal{P}(\Omega)$ (power set) over a set Ω is called a *σ-algebra* if
  (i) $\Omega \in \Sigma$,
  (ii) $\Omega \setminus A \in \Sigma$ for all $A \in \Sigma$ (closed under complements), and
  (iii) $\bigcup_{j=1}^{\infty} A_j \in \Sigma$ for all $A_1, A_2 \cdots \in \Sigma$
  (closed under countable unions).
- An *event space* is a tuple (Ω, Σ) where $\Sigma \subseteq \mathcal{P}(\Omega)$ is a σ-algebra.
  Examples:
  - Die: $\Omega = \{1, \ldots, 6\}$ and $\Sigma = \mathcal{P}(\Omega)$
  - Point particle in 1D (real numbers): $\Omega = \mathbb{R}$ and $\Sigma \subsetneq \mathcal{P}(\Omega)$.

    The set Σ is frequently the Borel σ-algebra. The details are not important for this lecture, but let it be noted that $\Sigma = \mathcal{P}(\Omega)$ cannot lead to any consistent notion of probability (Banach-Tarski paradox).
- *Events* are modeled by elements of Σ; e.g. $\{1, 3, 5\}$ is identified with the event "the die shows an odd number".
- Logical operations for $A, B \in \Sigma$ are

$$\begin{aligned} \text{NOT } A &= \Omega \setminus A, \\ A \text{ AND } B &= A \cap B, \\ A \text{ OR } B &= A \cup B, \\ A \text{ XOR } B &= A \Delta B, \end{aligned} \tag{1.5}$$

  where $A \Delta B \coloneqq (A \cup B) \setminus (A \cap B)$ denotes the *symmetric difference*.
- In particular, a *σ-algebra* is closed under these operations.

- Optional exercise: Show the following:
  - $(\mathcal{P}(\Omega), \Delta, \cap)$ is a ring.
  - This ring is also an algebra over the field $\{0, 1\}$ with the operations $0 \cdot A = \emptyset$ and $1 \cdot A = A$.
  - Hence, a σ-algebra $\Sigma \subset \mathcal{P}(\Omega)$ is a subalgebra.
  - Conversely, a subalgebra $\Sigma' \subset \mathcal{P}(\Omega)$ is also a σ-algebra, provided that (i) $\Omega \in \Sigma'$ and (ii) Σ' is closed under countable unions.

1.3.1.2 Probability measures

Two sets $A, B \subset \Omega$ are called *disjoint* if $A \cap B = \emptyset$.

Definition 1.1 ((Probability) measures [A. Kolmogorov 1930s])**.** *A* probability measure *on an event space* (Ω, Σ) *is a map*

$$\mathbb{P} : \Sigma \to \mathbb{R}\,, \tag{1.6}$$

satisfying the following:
(i) $0 \leq \mathbb{P}[A] \leq 1$ *for all* $A \in \Sigma$,
(ii) $\mathbb{P}[\Omega] = 1$, *and*
(iii) $\mathbb{P}$ *is* σ*-additive, i.e.*

$$\mathbb{P}\left[\bigcup_{j=1}^{\infty} A_j\right] = \sum_{j=1}^{\infty} \mathbb{P}[A_j] \tag{1.7}$$

for all pairwise disjoint events $A_1, A_2, \ldots \in \Sigma$.
A measure $\mu : \Sigma \to \mathbb{R}$ *is defined similarly to a probability measure, except that* $\mu \geq 0$ *is required instead of (i) and (ii). The triple* $(\Omega, \Sigma, \mathbb{P})$ *is called a* probability space *and* (Ω, Σ, μ) *a* measure space.

For $\Omega = \mathbb{R}^n$, the function defined by

$$F(t) \coloneqq \mathbb{P}[(-\infty, t_1] \times \cdots \times (-\infty, t_n]] \tag{1.8}$$

is called the *cumulative distribution function* (**CDF!**). If $\mathbb{P}$ has a *probability density function* (**PDF!**; see below), it is given as the derivative of F.

Remark: In practice, little attention is usually paid to the σ-algebra. In the cases relevant to us, it suffices to check all properties of $\mathbb{P}$ on well-behaved sets such as open or closed sets or arbitrary intervals.

It follows from the definition of a measure, e.g., that $A \subset B$ implies $\mathbb{P}[A] \leq \mathbb{P}[B]$ (exercise).

1.3.1.3 Discrete and continuous probability measures

There are two classes of probability measures that are important for us:
(i) A *continuous* (or *absolutely continuous*) probability measure on $\mathbb{R}^n$ is given by a **PDF!** $\rho : \mathbb{R}^n \to [0, \infty)$, i.e., ρ is integrable and

$$\mathbb{P}[A] = \int_A \rho(x)\,\mathrm{d}x \tag{1.9}$$

for all $A \in \Sigma$.
(ii) We call a probability measure on $\mathbb{R}^n$ *discrete* (or *purely atomic*) if there exists a countable set $\Gamma = \{x_1, x_2, \ldots\} \subset \mathbb{R}^n$ such that

$$\mathbb{P}[A] = \sum_{x \in A \cap \Gamma} \mathbb{P}[\{x\}] \tag{1.10}$$

for all events $A \in \Sigma$. Then $\mathbb{P}[\mathbb{R}^n \setminus \Gamma] = 0$.
The function $p : \mathbb{R}^n \to [0,1]$, $x \mapsto p_x \coloneqq \mathbb{P}[\{x\}]$ is also called the probability function or *probability mass function* (**PMF!**).
The measure

$$\delta_x(A) = \begin{cases} 1 & \text{if } x \in A \\ 0 & \text{otherwise} \end{cases} \tag{1.11}$$

is also called the *Dirac measure* (it can be written using the Dirac delta "function"). With this, the discrete measure (1.10) can also be written as a convex combination

$$\mathbb{P} = \sum_{x \in \mathbb{R}^n} p_x \delta_x \,. \tag{1.12}$$

If $p_x \neq 0$ for only finitely many x, one also calls p a *probability vector*. In this case,

$$p_x = \lim_{N \to \infty} \frac{N_x}{N} \,, \tag{1.13}$$

where the event x occurs N_x times among N drawn samples.

1.3.1.4 Conditional probabilities and independent events

For $\mathbb{P}[B] > 0$,

$$\mathbb{P}[A|B] \coloneqq \frac{\mathbb{P}[A \cap B]}{\mathbb{P}[B]} \tag{1.14}$$

defines the *conditional probability* of A given B; here is an XKCD[1] on this. Two events A and B are *(stochastically) independent* if $\mathbb{P}[A \cap B] = \mathbb{P}[A]\,\mathbb{P}[B]$. That is, for $\mathbb{P}[B] > 0$, if $\mathbb{P}[A|B] = \mathbb{P}[A]$.
The definition (1.14) implies the *chain rule* or *product rule*,

$$\mathbb{P}[A \cap B] = \mathbb{P}[A|B]\,\mathbb{P}[B] \,. \tag{1.15}$$

Moreover, *Bayes' theorem*

$$\mathbb{P}[B|A] = \frac{\mathbb{P}[A|B]\mathbb{P}[B]}{\mathbb{P}[A]} \tag{1.16}$$

follows directly for $\mathbb{P}[A] \neq 0 \neq \mathbb{P}[B]$.

1.3.1.5 Composing probability spaces

For two probability spaces $(\Omega_1, \Sigma_1, \mathbb{P}^{(1)})$ and $(\Omega_2, \Sigma_2, \mathbb{P}^{(2)})$ we can form the composite probability space $(\Omega, \Sigma, \mathbb{P})$, where $\Omega \coloneqq \Omega_1 \times \Omega_2$ (Cartesian product) and the *product measure* is defined via

$$\mathbb{P}[A_1 \times A_2] \coloneqq \mathbb{P}^{(1)}[A_1]\,\mathbb{P}^{(2)}[A_2] \,, \tag{1.17}$$

where $A_1 \in \Sigma_1$ and $A_2 \in \Sigma_2$. If $\mathbb{P}^{(1)}$ and $\mathbb{P}^{(2)}$ have **PMF!**s $p^{(1)}$ and $p^{(2)}$, the **PMF!** p of the product measure $\mathbb{P}$ is given by

$$p_{(i,j)} = p^{(1)}_i \, p^{(2)}_j \,. \tag{1.18}$$

If $\mathbb{P}^{(1)}$ and $\mathbb{P}^{(2)}$ have **PDF!**s $\rho^{(1)} : \Omega_1 \to [0,\infty)$ and $\rho^{(2)} : \Omega_2 \to [0,\infty)$, the **PDF!** ρ of the product measure $\mathbb{P}$ is given by

$$\rho(x,y) = \rho^{(1)}(x)\,\rho^{(2)}(y) \,. \tag{1.19}$$

[1] https://xkcd.com/795/

1.3.1.6 Marginal distribution

Given a probability space $(\Omega_1 \times \Omega_2, \Sigma, \mathbb{P})$, we can form the *marginal distribution* on Ω_1. It is given by a probability measure $\mathbb{P}^{(1)}$ on Ω_1 with

$$\mathbb{P}^{(1)}[A] \coloneqq \mathbb{P}[A \times \Omega_2] \tag{1.20}$$

for events $A \subset \Omega_1$. If $\mathbb{P}$ has a **PMF!** p, it is given by probabilities of the form $p_{(i,j)}$ with $i \in \Omega_1$ and $j \in \Omega_2$, and the marginal distribution has the **PMF!** $p^{(1)}$ with

$$p_i^{(1)} \coloneqq \sum_{j \in \Omega_2} p_{(i,j)} \,. \tag{1.21}$$

If $\mathbb{P}$ has a **PDF!** ρ, the marginal distribution has the **PDF!** $\rho^{(1)} : \Omega_1 \to [0, \infty)$ with

$$\rho^{(1)}(x) \coloneqq \int_{\Omega_2} \rho(x, y) \, \mathrm{d}y \,. \tag{1.22}$$

The marginal distribution on Ω_2 is defined similarly.

1.3.1.7 Summary

- Events are modeled by subsets; set operations correspond to logical operations.
- Probability measures assign probabilities to events.
- Discrete and continuous probability measures are important examples.
- Chain rule and stochastically independent events

1.3.2 Random variables

Motivation: We would like to view, e.g., the number shown by a die as a variable that is associated with a probability distribution.
Let $(\Omega, \Sigma, \mathbb{P})$ be a probability space. A real random variable is a map

$$X : \Omega \to \mathbb{R} \tag{1.23}$$

that satisfies certain consistency conditions (it must be measurable). These consistency conditions are automatically satisfied for all functions appearing in this lecture and for all functions one can intuitively imagine. Frequently, all details concerning the σ-algebra are kept quiet, which we also do here. By definition, $\mathbb{P}$ is regarded as the probability distribution of X.

In short: a random variable is a function with an associated probability distribution.

Frequently, the measure associated with X is also denoted by $\mathbb{P}_X$. Similarly, the associated **CDF!** is denoted by F_X and the **PDF!**, if it exists, by ρ_X.

The definition of random variables can be generalized directly to vector-valued random variables.

Definition 1.2 (Random vector)**.** *Let $(\Omega, \Sigma, \mathbb{P})$ be a probability space. We also view $\mathbb{R}^N$ as an event space (equipped with the Borel σ-algebra). Then a* random vector (in $\mathbb{R}^N$) *is a map*

$$X : \Omega \to \mathbb{R}^N \,, \tag{1.24}$$

satisfying very mild consistency conditions (it must be measurable). In the case $N = 1$, one calls X a random variable*.*

For the discrete and continuous measures that are important for us (section 1.3.1.3), it is difficult to construct maps that violate the mentioned consistency conditions, i.e., that are not measurable. Therefore, this aspect will not be considered any further. We frequently consider events of the form

$$\{X \in A\} \coloneqq X^{-1}(A) \coloneqq \{\omega \in \Omega : \ X(\omega) \in A\}\,, \tag{1.25}$$

i.e. the event that X takes a value that belongs to an event $A \subset \Omega$. Similarly,

$$\{X \leq x\} \coloneqq \{\omega \in \Omega : \ X_i(\omega) \leq x_i \ \forall i = 1, \ldots, N\}\,, \tag{1.26}$$

$\{X = x\}$, $\{X \notin A\}$, etc. are defined. One usually writes $\mathbb{P}[X \in A] \coloneqq \mathbb{P}[\{X \in A\}]$. Every random vector (1.24) also has a **CDF!**, given by

$$\begin{aligned} F_X : \mathbb{R}^N &\to \mathbb{R} \\ x &\mapsto \mathbb{P}[X \leq x]\,. \end{aligned} \tag{1.27}$$

It coincides with the **CDF!** of the measure associated with X (quick exercise).
We say that a random vector X in $\mathbb{R}^N$ has a **PDF!** if the associated probability measure has a **PDF!** ρ_X. In this case,

$$F_X(x) = \int_{-\infty}^{x_1} \mathrm{d}y_1 \cdots \int_{-\infty}^{x_N} \mathrm{d}y_N \ \rho_X(y)\,. \tag{1.28}$$

It is helpful to note that the **CDF!** (1.27) does not explicitly depend on the event space Ω.

Example 1.3.

- The number X shown by a die is a random variable. If the die is fair, one also speaks of a *uniformly distributed random variable*.
- Every function of the number shown by a die is a random variable. For example, one can define a random variable Y that takes the value 0 if the die shows an even number and 1 otherwise.
- The probability that an odd number was rolled is $\mathbb{P}[X \in \{1, 3, 5\}]$, where X is the number shown.
- In statistical mechanics, random phase-space coordinates of the form $\xi \coloneqq (q_1, p_1, \ldots, q_N, p_N)^\mathsf{T}$ play a central role. These are random vectors in $\mathbb{R}^{6N}$.

1.3.2.1 Independent random variables

The notion of statistical independence can be extended from events to random variables and random vectors.

Definition 1.4 (Independent random vectors)**.** *Two random vectors $X : \Omega \to \mathbb{R}^N$ and $Y : \Omega \to \mathbb{R}^{N'}$ are called* independent *if*

$$\mathbb{P}[X \in A \ \text{ AND } \ Y \in B] = \mathbb{P}[X \in A]\,\mathbb{P}[Y \in B] \tag{1.29}$$

for all events $A \subset \mathbb{R}^N$ and $B \subset \mathbb{R}^{N'}$.

For random variables, it suffices to check independence on intervals of the form $A = (-\infty, a]$ and $B = (-\infty, b]$, i.e., for dependent random variables there are a and b such that the corresponding intervals violate the equation above. A similar statement with multidimensional intervals can be made for random vectors. Hence, random vectors X and Y are independent if their **CDF!**s factorize, i.e.,

$$F_{(X,Y)}(x, y) = F_X(x) F_Y(y) \tag{1.30}$$

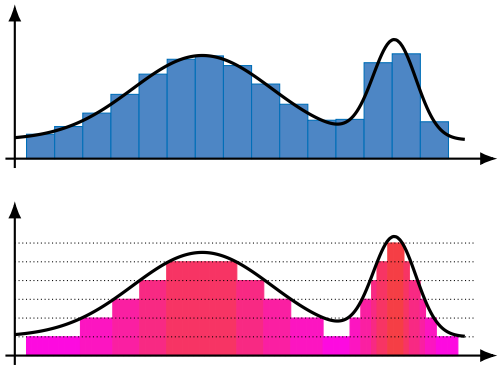

Figure 1.1: For a given function, approximating step functions can be constructed in two ways. (i) An equidistant partition of the x-axis (top) leads to the definition of the Riemann integral. (ii) An equidistant partition of the y-axis (bottom) leads to the definition of the Lebesgue integral. In either case, a measure on the domain is needed for the integration. For non-negative functions the following holds: if both the Riemann integral and the Lebesgue integral exist, they are also equal.

for all x, y. If (X, Y) has a **PDF!** ρ and X and Y are independent, then it factorizes as well,

$$\rho(x, y) = \rho_X(x)\rho_Y(y)\,, \tag{1.31}$$

where ρ_X and ρ_Y are then the respective **PDF!**s of X and Y. An analogous statement holds if (X, Y) has a **PMF!**.

1.3.2.2 Expectation values

On a measure space (Ω, Σ, μ), an integral

$$f \mapsto \int f(\omega)\,\mathrm{d}\mu(\omega) \tag{1.32}$$

is always defined for sufficiently "well-behaved" (i.e. measurable) functions f. A constant function $C : \Omega \to \mathbb{R}$ with $C(\omega) = c$ can be integrated over a set $A \in \Sigma$ very easily:

$$\int_A C(\omega)\,\mathrm{d}\mu(\omega) \coloneqq c\,\mu(A)\,. \tag{1.33}$$

A central property of the integral (1.32) is that it is linear. This makes it clear how step functions are integrated. If f is a sufficiently well-behaved function, it can be approximated by step functions; see fig. 1.1. Its integral can then be computed via increasingly accurate approximations. This leads to the integral for the continuous and discrete probability measures from section 1.3.1.3.

(i) If a random vector X in $\mathbb{R}^N$ is continuously distributed, i.e. has a continuous probability measure, then it also has a **PDF!** ρ.

(ii) If a random vector Y in $\mathbb{R}^N$ is discretely distributed, it has a **PMF!** p.

Definition 1.5 (Expectation value)**.** *Let $X, Y : \mathbb{R}^n \to \mathbb{R}^N$ be random vectors with respective probability measures μ and ν. Let X have a **PDF!** ρ and $Y : \mathbb{R}^n \to \mathbb{R}^N$ a **PMF!** p. Then the* expectation values *of these random vectors are given by*

$$\begin{aligned}
\mathbb{E}[X] &\coloneqq \int X\,\mathrm{d}\mu \equiv \int_{\mathbb{R}^n} X(\omega)\mathrm{d}\mu(\omega) = \int_{\mathbb{R}^n} X(\omega)\,\rho(\omega)\,\mathrm{d}\omega \\
\mathbb{E}[Y] &\coloneqq \int Y\,\mathrm{d}\nu \equiv \int_{\mathbb{R}^n} Y(\omega)\mathrm{d}\nu(\omega) = \sum_{\omega\in\mathbb{R}^n} Y(\omega)\,p_\omega\,,
\end{aligned} \tag{1.34}$$

respectively, provided they exist. Otherwise, the corresponding random vector is called

non-integrable.

Frequently, one also writes $\langle X \rangle \equiv \mathbb{E}[X]$, $\mathbb{E}_{X\sim\mu}[X]$, $\mathbb{E}_{X\sim\rho}[X]$, $\mathbb{E}_{Y\sim p}[Y]$ for the corresponding expectation values.

Now let $f : \mathbb{R}^N \to \mathbb{R}^M$ be a (measurable) function and X a random vector in $\mathbb{R}^N$. Then $f(X)$ is a random vector in $\mathbb{R}^M$ and, correspondingly, may again have an expectation value $\mathbb{E}[f(X)]$.
Optional exercise: Consider the two cases where (i) X has a **PDF!** and (ii) a **PMF!**. Compute the **PDF!**/**PMF!** of $f(X)$ for the special case where f is injective.
Here are important examples of $\mathbb{E}[f(X)]$ (we assume that all occurring expectation values exist):

- The *variance* of a random variable X is $\mathrm{Var}[X] \coloneqq \mathbb{E}[(X - \mathbb{E}[X])^2]$. From it one obtains the *standard deviation* $\sqrt{\mathrm{Var}[X]}$.
- The *covariance* of two random variables X and Y with the same event space Ω is

$$\begin{aligned} \mathrm{Cov}(X, Y) &\coloneqq \mathbb{E}[(X - \mathbb{E}[X])(Y - \mathbb{E}[Y])] \\ &= \mathbb{E}[XY] - \mathbb{E}[X]\,\mathbb{E}[Y]\,. \end{aligned} \tag{1.35}$$

- The *characteristic function* of a random vector X is defined via

$$\varphi_X(q) \coloneqq \mathbb{E}[\exp(\mathrm{i}\,\langle q, X\rangle)]\,, \tag{1.36}$$

  where $\langle \cdot\,, \cdot \rangle$ denotes the canonical inner product on $\mathbb{R}^N$. Frequently, one just writes φ instead of φ_X when it is clear which random vector is meant.

The variance $\mathrm{Var}[X]$ measures how strongly X fluctuates, i.e. how large the expected squared deviation from the mean $\mathbb{E}[X]$ is.

1.3.2.3 Correlations

Two random variables X, Y are called *uncorrelated* if

$$\mathbb{E}[XY] = \mathbb{E}[X]\,\mathbb{E}[Y]\,. \tag{1.37}$$

For example, the following holds:

$$X, Y \;\text{ independent} \quad \Rightarrow \quad \mathbb{E}[f(X)g(Y)] = \mathbb{E}[f(X)]\,\mathbb{E}[g(Y)] \tag{1.38}$$

for all (measurable) functions f and g (quick exercise). However, there are also random variables that are not independent but uncorrelated (exercise sheet). The covariance $\mathrm{Cov}(X, Y)$ is a measure of the correlations between X and Y.

Intuition: Among medical patients, high alcohol consumption is correlated with liver diseases. Note that neither does high alcohol consumption imply the occurrence of a liver disease nor vice versa; here is an XKCD[2] on this fact. Random variables can also be anticorrelated (negative covariance); e.g. regularly doing endurance sports is anticorrelated with the occurrence of cardiovascular diseases.

1.3.2.4 Moments, cumulants

In this section we consider random variables. The k-th moment of a random variable X is $\mathbb{E}[X^k]$. For example, the variance is $\mathrm{Var}[X] = \mathbb{E}[X^2] - \mathbb{E}[X]^2$ (quick exercise), i.e. a polynomial in moments.
From the characteristic function φ of X, all moments m_k can be computed, provided they exist:

$$m_k \coloneqq \mathbb{E}[X^k] = (-\mathrm{i})^k \varphi^{(k)}(0) \qquad (k\text{-th derivative}) \tag{1.39}$$

[2] https://xkcd.com/552/

(quick exercise), i.e. the characteristic function serves as a *moment-generating function*. We now assume that all moments exist. Then

$$\varphi(q) = \sum_{k=0}^{\infty} \frac{(\mathrm{i}q)^k}{k!} m_k. \tag{1.40}$$

We have $\varphi(0) = 1$. Hence, $\ln(\varphi(q))$ can be expanded as a power series around $q = 0$, which we write as

$$\ln \varphi(q) = \sum_{k=1}^{\infty} \frac{(\mathrm{i}q)^k}{k!} \kappa_k \,. \tag{1.41}$$

This expansion is called the *cumulant expansion*, and the expansion coefficients κ_k are called the *cumulants* of X. $\ln \varphi$ is called the *cumulant-generating function* of X, and we have

$$\kappa_k = (-\mathrm{i})^k \left. \frac{\mathrm{d}^k}{\mathrm{d}q^k} \right|_{q=0} \ln \varphi(q) \ . \tag{1.42}$$

By direct differentiation, or by applying the series expansion $\ln(1+x) = \sum_{k=1}^{\infty} (-1)^{k+1} \frac{x^k}{k}$ to $\ln(\varphi)$ and inserting eq. (1.40), one finds the first cumulants (optional exercise)

$$\kappa_1 = m_1 \tag{1.43}$$
$$\kappa_2 = m_2 - m_1^2 = \mu_2 \tag{1.44}$$
$$\kappa_3 = m_3 - 3m_2 m_1 + 2m_1^3 = \mu_3 \tag{1.45}$$
$$\kappa_4 = \mu_4 - 3\mu_2^2 \,, \tag{1.46}$$

where $\mu_k \coloneqq \mathbb{E}[(X - \mathbb{E}[X])^k]$ denotes the k-th *central moment* of X (by convention one sets $\mu \coloneqq \mu_1 \coloneqq m_1$).

1.3.2.5 Normal distribution and central limit theorem

The normal distribution takes a special place among the probability distributions, which can be justified by the **CLT!** (**CLT!**). One writes $X \sim \mathcal{N}(\mu, \sigma^2)$ if X has the **PDF!**

$$\rho(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\Big(-\frac{(x-\mu)^2}{2\sigma^2}\Big) \tag{1.47}$$

and then calls X *normally distributed with expectation value* μ *and variance* σ^2. We denote the corresponding **CDF!** by

$$\Phi_{\mu,\sigma^2}(z) = \int_{-\infty}^{z} \rho(x)\, \mathrm{d}x \,. \tag{1.48}$$

Optional exercise: Check the normalization and that the characteristic function is given by

$$\varphi_{\mu,\sigma^2}(q) = \exp\Big(\mathrm{i}\,\mu\, q - \frac{1}{2}\sigma^2 q^2\Big) \,. \tag{1.49}$$

Hence, the cumulant-generating function is given by

$$\ln \varphi_{\mu,\sigma^2}(q) = \mathrm{i}\,\mu\, q - \frac{1}{2}\sigma^2 q^2 \tag{1.50}$$

and the cumulants (1.42) are obtained as

$$\kappa_1 = \mu \tag{1.51}$$
$$\kappa_2 = \sigma^2 \tag{1.52}$$
$$\kappa_k = 0 \quad \forall k \geq 3 \,. \tag{1.53}$$

Theorem 1.6 (Central limit theorem)**.** *Let $X_1, X_2, \ldots, X_N$ be independent random variables whose first and second moments exist, and set*

$$Z_N = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} X_i \,. \tag{1.54}$$

Then, for every $z \in \mathbb{R}$,

$$\lim_{N\to\infty} \mathbb{P}[Z_N \leq z] = \Phi_{\mu,\sigma^2}(z) \tag{1.55}$$

where

$$\begin{aligned} \mu &= \lim_{N\to\infty} \frac{1}{\sqrt{N}} \sum_{i=1}^{N} \mathbb{E}[X_i] \,, \\ \sigma^2 &= \lim_{N\to\infty} \frac{1}{N} \sum_{i=1}^{N} \mathrm{Var}[X_i] \,. \end{aligned} \tag{1.56}$$

Remarks:

- In particular, the *empirical mean*

$$\overline{X}^N \coloneqq \frac{1}{N} \sum_{i=1}^{N} X_i \tag{1.57}$$

  converges to a Gaussian distribution that is concentrated arbitrarily sharply around the average mean of the X_i.

- The random variables (X_i) may be discretely distributed. The limit (1.55) yields a continuous distribution.

For the following proof, the following observation concerning the characteristic function (1.36) is helpful. For independent random vectors X and Y, we have

$$\begin{aligned} \varphi_{X+Y}(q) &= \mathbb{E}[\exp(\mathrm{i}\langle q, X\rangle)\, \exp(\mathrm{i}\langle q, Y\rangle)] \\ &= \mathbb{E}[\exp(\mathrm{i}\langle q, X\rangle)]\, \mathbb{E}[\exp(\mathrm{i}\langle q, Y\rangle)] \\ &= \varphi_X(q)\, \varphi_Y(q) \,. \end{aligned} \tag{1.58}$$

The definition (1.36) also directly implies that

$$\varphi_{\lambda X}(q) = \varphi_X(\lambda q) \tag{1.59}$$

for all $\lambda \in \mathbb{R}$ and q.
Now let X be a random variable. Then, furthermore,

$$\varphi_{\lambda+X}(q) = \mathrm{e}^{\mathrm{i}\lambda q} \varphi_X(q) \tag{1.60}$$

for all $\lambda \in \mathbb{R}$ and q. If X has a **PDF!** ρ, we can recover it from its characteristic function φ,

$$\rho(x) = \frac{1}{2\pi} \int \mathrm{d}q\, \mathrm{e}^{-\mathrm{i}qx} \varphi(q) \,, \tag{1.61}$$

using the Fourier transform and its inverse.

Proof of theorem 1.6. For our proof we assume that all cumulants $\kappa_k^{(X_i)}$ exist and are uniformly bounded in i.

We use the notation $\varphi[X](q) \coloneqq \varphi_X(q)$ and $\varphi_i \coloneqq \varphi_{X_i}$. Then

$$\begin{aligned} \ln \varphi_Z(q) &= \ln \varphi\Big[\sum_{i=1}^{N} X_i\Big](q/\sqrt{N}) \\ &= \sum_{i=1}^{N} \ln \varphi_i(q/\sqrt{N}) \end{aligned} \tag{1.62}$$

for every q. Now we fix q and use the cumulant expansion (1.41),

$$\begin{aligned} \ln \varphi_Z(q) &= \sum_{i=1}^{N} \sum_{k=1}^{\infty} \frac{(\mathrm{i}q/\sqrt{N})^k}{k!} \kappa_k^{(X_i)} \\ &= \sum_{i=1}^{N} \Big(\mathrm{i}q\mathbb{E}[X_i]/\sqrt{N} - \frac{1}{2} q^2 \operatorname{Var}[X_i]/N \Big) + \mathrm{O}(1/\sqrt{N}) \\ &= \mathrm{i}\mu q - \frac{1}{2} q^2 \sigma^2 + \mathrm{O}(1/\sqrt{N}) \\ &= \ln \varphi_{\mu,\sigma^2}(q) + \mathrm{O}(1/\sqrt{N})\,. \end{aligned} \tag{1.63}$$

This implies

$$\lim_{N\to\infty} \varphi_Z(q) = \varphi_{\mu,\sigma^2}(q) \tag{1.64}$$

for all $q \in \mathbb{R}$. This pointwise convergence of φ_Z implies the pointwise convergence of the **CDF!** of Z (by Lévy's continuity theorem). □

1.4 Information theory

Information theory was founded by Claude Shannon (1948) and deals with the quantification, storage, and transmission of information. In particular, this includes data encoding and compression.
The quantification of information can be illustrated particularly well by means of compression. We assume that we obtain independent samples of a random variable X that can take m different values $x \in \{a_1, a_2, \ldots, a_m\}$. We denote the probabilities of these values by

$$p_i \coloneqq \mathbb{P}[X = a_i]\,, \qquad i = 1, 2, \ldots, m \tag{1.65}$$

and assume that these values (and also the a_i) are explicitly known.
We now consider N independent samples of X, i.e. we consider N independent copies $X_1, \ldots, X_N \sim p$ of X. One also speaks of N **iid!** (**iid!**) random variables.

- How many bits (binary variables) are needed to store a sample of $(X_1, \ldots, X_N)$?

One possibility for storage would be to encode each a_i by the binary representation of i. This encoding scheme requires $\lceil \log_2(m) \rceil\, N$ bits, where $\lceil x \rceil \coloneqq \min\{k \in \mathbb{Z} :\ x \le k\}$ denotes rounding up.
Exercise: Find examples where fewer bits are needed for the encoding.

1.4.1 Shannon entropy

The *Shannon entropy*, or simply *entropy*, turns out to be a meaningful measure of information. It can be viewed as a measure of the "randomness" of a random variable.

Definition 1.7 (Shannon entropy)**.** *Let X be a random vector with **PMF!** p. Then the entropy (to base $b > 0$) of X is defined as*

$$H(X) \coloneqq H(p) \coloneqq -\sum_i p_i \log_b(p_i)\,. \tag{1.66}$$

The base b fixes a unit of information, which is usually clear from the context. In computer science, where information is carried by bits, one typically chooses $b = 2$. In statistical physics, we choose the units such that the entropy is given by

$$S(X) \coloneqq -k_{\mathrm{B}} \sum_i p_i \ln(p_i) \tag{1.67}$$

where k_{B} is the *Boltzmann constant* (discussed later).

Properties:

(i) For a discretely distributed random variable X, we have $H(X) \geq 0$. If X is a "constant" random variable, then $H(X) = 0$, i.e., if $\mathbb{P}[X = x] = 1$ for some x and $\mathbb{P}[X = y] = 0$ for all $y \neq x$.

(ii) Let X be a uniformly distributed and Y an arbitrary random variable on $\{a_1, a_2, \ldots, a_m\}$. Then $H(Y) \leq H(X) = \log_b(m)$.

(iii) The entropy is concave:

$$H(\lambda p + (1-\lambda)q) \geq \lambda H(p) + (1-\lambda)H(q) \tag{1.68}$$

for all $\lambda \in [0,1]$ and probability vectors $p, q \in [0,1]^m$. This property follows from the concavity of the logarithm (short exercise).

(iv) The entropy is additive for independent random vectors X and Y:

$$H((X,Y)) = H(X) + H(Y) \tag{1.69}$$

(easy exercise). More generally, using the non-negativity of the Kullback-Leibler divergence (1.76), one can show that for a **PMF!** p with marginal distributions $p^{(1)}$ and $p^{(2)}$ we always have

$$H(p) \leq H(p^{(1)}) + H(p^{(2)})\,. \tag{1.70}$$

We will prove this property later (lemma 3.5), once we have become acquainted with generalizations of the Shannon entropy and the Kullback-Leibler divergence to quantum states.

Theorem 1.8 (Shannon's source coding theorem (informal) [9, Chap. 5])**.** *N **iid!** discrete random variables, each having entropy $H(X)$, can be compressed into at least $N\,H(X)$ bits with the probability of data loss vanishing in the limit $N \to \infty$.*
If the random variables are compressed into fewer than $N\,H(X)$ bits, the probability of losing data converges to 1.

We can write the entropy as an expectation value. To this end, we turn the probability vector (p_i) itself into a random variable by substituting the random variable X with image $\{i\}$ for the index i, which yields $p_{i=X} = p_X$ (i.e. a random variable with the same event space as X and finitely many values in $[0,1]$). We define the *information content* of i with respect to p as

$$\iota(i) \coloneqq -\log_b(p_i) \tag{1.71}$$

and thereby obtain

$$H(X) = \mathbb{E}[\iota(X)]\,. \tag{1.72}$$

The information content ι indicates how surprising it is to observe a certain value of X: the less likely a value is, the more surprising it is. In this sense, the entropy indicates the average information content of a random variable X that must be stored by the encoding.
The information content can also be derived axiomatically. For this, we demand that

1. ι is continuous,
2. $\iota(j) = f(p_j)$ for some function f, and
3. ι is additive.

To formulate the last point more precisely, let $X, Y \sim p$ be two **iid!** random variables with probability vector $p \in [0,1]^n$. Then the probability vector of (X,Y) is given by $P_{(i,j)} = p_i p_j$ with $i, j \in \{1, \dots, n\}$. Additivity of the information content means

$$\iota((X,Y)) = \iota(X) + \iota(Y)\,. \tag{1.73}$$

In general, this can only hold if

$$f(p_i p_j) = f(p_i) + f(p_j) \tag{1.74}$$

for all i and j and all probability vectors p. That is, we are looking for a nontrivial function $f : [0,1] \to \mathbb{R}$ that satisfies the functional equation

$$f(xy) = f(x) + f(y)\,. \tag{1.75}$$

We also required the information content ι to be continuous. This implies $f(x) = \log_b(x)$ for all $x \in [0,1]$ and a free constant b (without proof).

1.4.2 Kullback-Leibler divergence (supplementary material)

What happens if, in the setting of Shannon coding, one uses a code for a probability distribution p that was optimized for a different probability distribution q? In this case, additional bits become necessary to store the data drawn from p (theorem 1.8). One can show [9, Chapter 2.3] that, in the limit of much data, the number of additionally required bits is exactly $ND(p\|q)$, where N is the number of **iid!** letters drawn from $\{a_1, \dots, a_m\}$ and $D(p\|q)$ is defined as follows.

Definition 1.9 (Relative entropy)**.** *Let p and q be two **PMF!**s on the same event space. The* relative entropy*, also called* Kullback-Leibler divergence*, between p and q is*

$$D(p\|q) \equiv D_{\mathrm{KL}}(p\|q) \coloneqq -\sum_x p_x \ln\Big(\frac{q_x}{p_x}\Big)\,. \tag{1.76}$$

Properties:

(i) For all probability distributions p and q, we have

$$D(p\|q) \geq 0 \tag{1.77}$$

(the proof follows later) and

$$D(p\|p) = 0\,. \tag{1.78}$$

We will exploit the non-negativity later.

(ii) If $p_x > 0$ for some x with $q_x = 0$, then $D(p\|q) = \infty$.

(iii) In general, $D(p\|q) \neq D(q\|p)$.

1.4.3 Differential entropies

We also need a notion of entropy for continuously distributed random variables. To this end, we fix a random variable X with continuous **PDF!** $\rho : \mathbb{R} \to [0, \infty)$. Then we introduce a discretization of $\mathbb{R}$,

$$\mathbb{R} = \bigcup_{i \in \mathbb{Z}} (i\Delta, (i+1)\Delta]\,, \tag{1.79}$$

where $1 \gg \Delta > 0$. To the interval $(i\Delta, (i+1)\Delta]$ we can assign the probability

$$p_{\Delta,i} \coloneqq \mathbb{P}[X \in (i\Delta, (i+1)\Delta]] = \int_{i\Delta}^{(i+1)\Delta} \rho(x)\,\mathrm{d}x \approx \Delta \cdot \rho(i\Delta)\,. \tag{1.80}$$

This leads to the entropy of the discretized distribution

$$\begin{aligned} H_\Delta(\rho) \coloneqq H(p_\Delta) &= -\sum_{i\in\mathbb{Z}} \Delta\,\rho(i\Delta)\ln(\Delta\,\rho(i\Delta)) \\ &= -\sum_{i\in\mathbb{Z}} \Delta\,\rho(i\Delta)\big(\ln(\rho(i\Delta)) + \ln(\Delta)\big) \\ &\approx -\sum_{i\in\mathbb{Z}} \Delta\,\rho(i\Delta)\ln(\rho(i\Delta)) - \ln(\Delta)\,. \end{aligned} \tag{1.81}$$

The term $\ln(\Delta)$ does not depend on the distribution ρ, which is why we can simply drop it. Therefore, we define the (differential) entropy of ρ as

$$H(\rho) \coloneqq -\lim_{\Delta\searrow 0} \sum_{i\in\mathbb{Z}} \Delta\,\rho(i\Delta)\ln(\rho(i\Delta)) = -\int_{\mathbb{R}} \rho(x)\ln(\rho(x))\,\mathrm{d}x\,. \tag{1.82}$$

Generalizing this idea to multidimensional event spaces leads to the following definition of the *(differential) entropy*.

Definition 1.10 (Entropies for continuous distributions)**.** *The* entropy *of a continuously distributed random vector X with* ***PDF!*** $\rho : \mathbb{R}^N \to [0,\infty)$ *is defined as*

$$H(X) \coloneqq H(\rho) \coloneqq -\int_{\mathbb{R}^N} \rho(x)\log(\rho(x))\,\mathrm{d}x\,. \tag{1.83}$$

The relative entropy *between* ***PDF!****s $\rho : \mathbb{R}^N \to [0,\infty)$ and $\sigma : \mathbb{R}^N \to [0,\infty)$ is defined as*

$$D(\rho\|\sigma) \coloneqq -\int_{\mathbb{R}^N} \rho(x)\log\Big(\frac{\sigma(x)}{\rho(x)}\Big)\,\mathrm{d}x\,. \tag{1.84}$$

The differential entropy H inherits all properties of the Shannon entropy, except for (i) and (ii), i.e. the entropy of continuous distributions can take arbitrary values in $\mathbb{R}$ and, in particular, can become negative. This will not bother us, however, since in statistical physics we are interested in entropy differences and entropy changes.

Similarly, the differential relative entropy D inherits all properties of the relative entropy. In particular,

$$D(\rho\|\sigma) \geq 0 \tag{1.85}$$

holds for all **PDF!**s ρ and σ. The reason is that the relative entropy can be approximated by the relative entropies of the discretized distributions: A discretization similar to eq. (1.81) yields

$$\begin{aligned} D_\Delta(\rho\|\sigma) \coloneqq D(p_\Delta\|q_\Delta) &= -\sum_{i\in\mathbb{Z}} \Delta\,\rho(i\Delta)\ln\Big(\frac{\Delta\,\sigma(i\Delta)}{\Delta\,\rho(i\Delta)}\Big) \\ &= -\sum_{i\in\mathbb{Z}} \Delta\,\rho(i\Delta)\ln\Big(\frac{\sigma(i\Delta)}{\rho(i\Delta)}\Big)\,, \end{aligned} \tag{1.86}$$

so that

$$\lim_{\Delta\searrow 0} D_\Delta(\rho\|\sigma) = D(\rho\|\sigma)\,. \tag{1.87}$$

1.5 Convexity and Legendre transformation

Convex analysis deals with convex sets and convex functions. In statistical mechanics, we frequently encounter concave functions, i.e. functions whose negative is convex. Therefore, a few statements from convex analysis are very helpful.

1.5.1 Legendre transformation

A comprehensive explanation of the Legendre transformation with regard to applications in physics can be found in Ref. [10], and the complete mathematical background in the book [8].
The *Legendre transform* (or *Fenchel dual* or *convex conjugate*) f^* of a function $f : \mathbb{R}^n \to \mathbb{R} \cup \{\infty\}$ is defined via

$$f^*(y) \coloneqq \sup_x \{\langle y, x\rangle - f(x)\} \tag{1.88}$$

[8, Section 12]. One can show that f^* is always a convex lower semicontinuous function on $\mathbb{R}^n$ [8, Theorem 12.1]. If f is also convex and lower semicontinuous, then $(f^*)^* = f$ [8, Theorem 12.2].
For statistical physics, it is helpful to define the Legendre transformation for concave functions via

$$\begin{aligned} \tilde{f}(y) &\coloneqq \inf_x \{\langle y, x\rangle - f(x)\} \\ &= -(-f)^*(-y)\,. \end{aligned} \tag{1.89}$$

Then $\tilde{f}$ is always a concave upper semicontinuous function, and if f is concave and upper semicontinuous, then

$$\tilde{\tilde{f}} = f\,. \tag{1.90}$$

Now we assume that f is a concave upper semicontinuous function and that the infimum in eq. (1.89) is attained for a given y. If $\overline{x} = \overline{x}(y)$ is a critical point of the likewise concave function

$$x \mapsto f(x) - \langle y, x\rangle\,, \tag{1.91}$$

it follows that

$$\tilde{f}(y) = \langle y, \overline{x}\rangle - f(\overline{x}) \tag{1.92}$$

(critical points of concave functions are global maxima). The same equation holds for the Legendre transformation in the convex case.
Now we additionally assume that f is continuously differentiable and that ∇f is invertible; i.e. there exists a map $h : \mathbb{R}^n \to \mathbb{R}^n$ such that $y = h \circ \nabla f(y)$. Then $\overline{x} = h(y)$, i.e.

$$\begin{aligned} \tilde{f}(y) &= \langle y, h(y)\rangle - f(h(y)) \\ &= \big\langle y, (\nabla f)^{-1}(y)\big\rangle - f\big((\nabla f)^{-1}(y)\big)\,. \end{aligned} \tag{1.93}$$

1.5.1.1 Homogeneous functions of degree one (supplementary material)

Here we consider an example where the Legendre transform is not computed by means of derivatives. To this end, we define the *indicator function* $\delta_C : \mathbb{R}^n \to \mathbb{R} \cup \{\infty\}$ of a convex set $C \subset \mathbb{R}^n$ via

$$\delta_C(y) \coloneqq \begin{cases} 0 & \text{if } y \in C\,, \\ \infty & \text{otherwise} \end{cases} \tag{1.94}$$

and note that these functions are convex. We call a function $f : \mathbb{R}^n \to \mathbb{R}$ *homogeneous of degree p* if

$$f(\lambda x) = \lambda^p f(x) \qquad \forall \lambda > 0\,. \tag{1.95}$$

The Legendre transform of a concave function $f : \mathbb{R}^n \to \mathbb{R}$ that is homogeneous of degree one (think of a norm) is

$$\begin{aligned} \tilde{f}(y) &= \inf_x \{\langle y, x\rangle - \lambda f(x/\lambda)\} \\ &= \inf_x \{\langle y, \lambda x\rangle - \lambda f(x)\} \\ &= \lambda \tilde{f}(y) \end{aligned} \tag{1.96}$$

for all $\lambda > 0$. Therefore, $\tilde{f}(y) \in \{-\infty, 0\}$ for all y. More precisely,

$$\tilde{f}(y) = -\delta_C(y) \tag{1.97}$$

where

$$C \coloneqq \{y : \ \langle y, x\rangle \geq f(x) \ \forall x\} \tag{1.98}$$

is a closed convex set. Since f is concave, C is convex and $\tilde{f}$ is thus indeed concave again. If f is upper semicontinuous, then $f = \tilde{\tilde{f}} = \tilde{\delta}_C$. This yields

$$f(x) = \tilde{\delta}_C(x) = \inf_{y \in C} \langle y, x\rangle \,. \tag{1.99}$$

The function $-\tilde{\delta}_C = \delta_C^*$ is called the *support function* of C. Further details on support functions can be found in [8, Section 13].
Optional exercise: Show that for an upper semicontinuous concave function f that is homogeneous of degree one, indeed $\tilde{\tilde{f}} = f$.

1.5.2 A construction of convex functions

There is another mathematical fact that will help us when we derive the generalized canonical distribution.

Theorem 1.11 ([8, Theorem 5.7])**.** *Let $A : \mathbb{R}^n \to \mathbb{R}^m$ be linear and $f : \mathbb{R}^n \to \mathbb{R}$ convex. Then the function $f_A : \mathbb{R}^m \to \mathbb{R}$ defined by*

$$f_A(y) \coloneqq \inf\{f(x) : \ Ax = y\} \tag{1.100}$$

is also convex.

Proof. We directly verify the definition of convex functions, eq. (1.4). So let $\lambda \in (0, 1)$ and $y_1, y_2 \in \mathbb{R}^m$. Then

$$\begin{aligned} \lambda f_A(y_1) + (1-\lambda) f_A(y_2) &= \inf\{\lambda f(x_1) : \ Ax_1 = y_1\} + \inf\{(1-\lambda) f(x_2) : \ Ax_2 = y_2\} \\ &= \inf\{\lambda f(x_1) + (1-\lambda) f(x_2) : \ Ax_1 = y_1 \,, \ Ax_2 = y_2\} \\ &\geq \inf\{f(\lambda x_1 + (1-\lambda) x_2) : \ Ax_1 = y_1 \,, \ Ax_2 = y_2\} \\ &= \inf\{f(x_1' + x_2') : \ Ax_1' = \lambda y_1 \,, \ Ax_2' = (1-\lambda) y_2\} \,, \end{aligned} \tag{1.101}$$

where we have set $x_1' \coloneqq \lambda x_1$ and $x_2' \coloneqq (1-\lambda) x_2$. Then

$$\begin{aligned} \lambda f_A(y_1) + (1-\lambda) f_A(y_2) &\geq \inf\{f(x_1' + x_2') : \ A(x_1' + x_2') = \lambda y_1 + (1-\lambda) y_2\} \\ &= f_A(\lambda y_1 + (1-\lambda) y_2) \,. \end{aligned} \tag{1.102}$$

□

1.6 1-Forms

We recall the derivative $\mathrm{d}f : \mathbb{R}^n \to \mathrm{L}(\mathbb{R}^n, \mathbb{R})$ of a differentiable function $f : \mathbb{R}^n \to \mathbb{R}$ from item (vii) of section 1.2. The derivative is an example of so-called 1-*forms*.

A 1-*form* (also called a *Pfaffian form*) on $\mathbb{R}^n$ is a map

$$\omega : \mathbb{R}^n \to \mathrm{L}(\mathbb{R}^n, \mathbb{R})\,. \tag{1.103}$$

We write $\omega_p \in \mathrm{L}(\mathbb{R}^n, \mathbb{R})$ for the corresponding linear form at a point $p \in \mathbb{R}^n$. Similarly, we write $\mathrm{d}_p f \in \mathrm{L}(\mathbb{R}^n, \mathbb{R})$ for $\mathrm{d}f$ evaluated at $p \in \mathbb{R}^n$.
One can always write ω as

$$\omega = \sum_{i=1}^{n} \phi_i \,\mathrm{d}x_i \qquad \text{(basis expansion)} \tag{1.104}$$

where the $\phi_i : \mathbb{R}^n \to \mathbb{R}$ are given by

$$\phi_i(p) = \omega_p(e_i) \tag{1.105}$$

with the i-th canonical basis vectors $e_i \in \mathbb{R}^n$.
1-forms can be integrated along a curve $\gamma : [a, b] \to \mathbb{R}^n$:

$$\int_\gamma \omega \coloneqq \int_a^b \omega_{\gamma(t)}(\dot\gamma(t))\,\mathrm{d}t \qquad \text{(line integral)}. \tag{1.106}$$

Important example: If $F : \mathbb{R}^n \to \mathbb{R}^n$ is a vector field, then

$$\omega^F \coloneqq \langle F, \cdot\,\rangle \tag{1.107}$$

defines a 1-form with $\omega^F_p = \langle F(p), \cdot\,\rangle \in \mathrm{L}(\mathbb{R}^n, \mathbb{R})$. The line integral of ω^F along $\gamma : [a, b] \to \mathbb{R}^n$ is then

$$\int_\gamma \omega^F = \int_a^b \langle F(\gamma(t)), \dot\gamma(t)\rangle\,\mathrm{d}t\,, \tag{1.108}$$

i.e. the perfectly ordinary line integral of a vector field. If one interprets F as a force, the integral (1.108) is also called a *work integral*.
We call a 1-form ω on $\mathbb{R}^n$ *closed* if the following *integrability conditions* are satisfied for the representation (1.104):

$$\frac{\partial \phi_i}{\partial x_j} = \frac{\partial \phi_j}{\partial x_i} \tag{1.109}$$

for all $i, j \in [n]$. We call ω *exact* if there exists a differentiable function f such that

$$\omega = \mathrm{d}f\,. \tag{1.110}$$

One then calls f a *potential* of ω, and for an arbitrary curve $\gamma : [a, b] \to \mathbb{R}^n$ we then have

$$\int_\gamma \omega = f(\gamma(b)) - f(\gamma(a))\,, \tag{1.111}$$

i.e. the work integral is path-independent. This also implies, for every closed path γ, that

$$\oint_\gamma \mathrm{d}f = 0\,. \tag{1.112}$$

Comprehension exercise: Show that exact forms are closed.
Analysis teaches us that the converse also holds:

Theorem 1.12. *Closed* 1*-forms on* $\mathbb{R}^n$ *are exact. General* 1*-forms with path-independent work integral are also exact.*

The first statement of the theorem does not extend to arbitrary domains:

$$\omega = \frac{x\,\mathrm{d}y - y\mathrm{d}x}{x^2 + y^2} \tag{1.113}$$

is a closed but not exact 1-form on $\mathbb{R}^2 \setminus \{0\}$ (exercise).

1.6.1 Integrating factors

Given a 1-form ω on $\mathbb{R}^n$, we call a function $\varphi : \mathbb{R}^n \to \mathbb{R}$ an *integrating factor* for ω if $\varphi\,\omega$ is exact.
In physics, we frequently denote 1-forms that are not exact by $\omega = đf$ or $\omega = \delta f$.
Optional exercise: Find a non-exact 1-form with an integrating factor.

1.6.2 Homogeneous functions

We call a function $f : \mathbb{R}^n \to \mathbb{R}$ *homogeneous of degree* k if

$$f(tx) = t^k f(x) \qquad \forall t > 0\,. \tag{1.114}$$

Theorem 1.13 (Euler's identity)**.** *Let $f : \mathbb{R}^n \setminus \{0\} \to \mathbb{R}$ be a differentiable function that is homogeneous of degree k with $k \geq 1$. Then*

$$kf = \sum_{j=1}^{n} \frac{\partial f}{\partial x_j}\,\mathrm{d}x_j\,. \tag{1.115}$$

Proof. Differentiating eq. (1.114) yields

$$\begin{aligned} kt^{k-1} f(x) &= \sum_{j=1}^{n} \frac{\partial f}{\partial x_j}(tx)\,\frac{\partial (tx_j)}{\partial t} \\ &= \sum_{j=1}^{n} \frac{\partial f}{\partial x_j}(tx)\,x_j\,. \end{aligned} \tag{1.116}$$

Evaluating at $t = 1$ and using the identification (1.2) completes the proof. □

1.7 Spectral calculus

Here we want to briefly explain the spectral calculus for finite-dimensional Hilbert spaces. We call an operator $A \in \mathrm{L}(\mathcal{H})$ *normal* if

$$[A, A^\dagger] = 0\,. \tag{1.117}$$

Important examples of normal operators are self-adjoint ($A^\dagger = A$) and unitary ($A^\dagger = A^{-1}$) operators. Given a basis of $\mathcal{H}$, we call $A \in \mathrm{L}(\mathcal{H})$ *unitarily diagonalizable* if there exists a unitary operator $U \in \mathrm{L}(\mathcal{H})$ such that

$$A = UDU^\dagger\,, \tag{1.118}$$

where $D = \mathrm{diag}(a_1, \ldots, a_{\dim(\mathcal{H})})$ is *diagonal* in that basis. Then A can also be written with respect to an orthonormal basis (ONB) of eigenvectors $\{|a_j\rangle\} \subset \mathcal{H}$ as

$$A = \sum_j a_j |a_j\rangle\langle a_j|\,, \tag{1.119}$$

using the Dirac notation from quantum mechanics.
The following connection is known from linear algebra.

Theorem 1.14 (Unitary diagonalization)**.** *An operator A on a Hilbert space is unitarily diagonalizable if and only if A is normal.*

The *spectral calculus* helps us to apply functions to the spectrum of normal operators and thereby obtain new operators.

Definition 1.15 (Spectral calculus)**.** *Let $f : \mathbb{C} \to \mathbb{C}$ be a function and $A \in \mathrm{L}(\mathcal{H})$ a normal operator of the form (1.118). Then we define $f(A) \in \mathrm{L}(\mathcal{H})$ as*

$$f(A) = U f(D) U^\dagger \,, \tag{1.120}$$

where, in the matrix case, $f(D)$ is obtained from D by applying f to the diagonal of the diagonal matrix D, $(f(D))_{i,j} \coloneqq f(D_{i,j})\delta_{i,j}$.

Remark: The spectral calculus can also be generalized to the case $\dim(\mathcal{H}) = \infty$: If A has a purely discrete spectrum (point spectrum), $f(D)$ is computed, unchanged, via the eigenvalues of A. If A (additionally) has a continuous spectrum, then D is a multiplication operator by a function $x \mapsto a(x)$ (e.g. for the position operator, $a(x) = x$) and $f(D)$ is given by $f \circ a$.

Alternatively to eq. (1.120), one can define $f(A)$ via a power series $f(x) = \sum_j a_j x^j$ as

$$f(A) = \sum_{j=0}^{\infty} a_j A^j \,, \tag{1.121}$$

where $A^0 \coloneqq \mathbb{1}$ and $A^{j+1} \coloneqq A A^j$ define the powers of A.

Exercise: Show that the definition (1.120) agrees with the definition via power series (1.121).

2 Classical statistical mechanics

In this chapter we get to know the various ensembles of statistical mechanics (canonical, grand canonical, microcanonical, ...) and the physical quantities associated with them (energy, temperature, pressure, ...). These are stochastic descriptions of many-body systems in terms of precisely such macroscopic quantities.

In general, one can estimate/characterize probability distributions (i) via observed frequencies (1.13) or (ii) via expectation values, where in statistical physics one typically follows the latter strategy. A macroscopic thermal state is described here by macroscopic quantities, which we describe as averages over microscopic states. However, there are typically far fewer macroscopic quantities than microscopic degrees of freedom, so that they are by far not sufficient to single out *one* probability distribution. This raises the question of whether and how one can systematically find physically meaningful probability distributions that describe many-body systems. A particularly successful approach, which was formalized by E.T. Jaynes, is to use a probability distribution that maximizes the entropy given the macroscopic quantities. This leads to the *generalized canonical distribution*, as we will see in the following section. This distribution generalizes the classical ensembles of statistical mechanics.
From now on, we will denote the entropy of a distribution p by

$$S(p) \coloneqq -k \sum_x p_x \ln(p_x) \,, \tag{2.1}$$

where k is a constant (H traditionally also denotes Hamiltonian functions and the thermodynamic enthalpy).

2.1 The generalized canonical distribution

In its outline, this section follows [1, Chapter 1.3] and is presented in a mathematically largely rigorous way with little additional effort.
We consider a many-body system that is described by an event space Ω. Furthermore, we assume that the relevant macroscopic quantities can be written as expectation values with respect to the probability distribution to be determined and are given as

$$\mathbb{E}[M^{(\nu)}] \equiv \langle M^{(\nu)} \rangle = \mathsf{M}^{(\nu)} \quad \text{with} \quad \nu = 1, 2, \ldots, m\,. \tag{2.2}$$

Here, each $M^{(\nu)}(x)$ describes a physical quantity that is uniquely determined by the coordinate $x \in \Omega$. We write $M_i^{(\nu)}$ instead of $M^{(\nu)}(x)$ in the discrete case. For shorter notation, it can also be helpful to view $M = (M^{(\nu)})_{\nu \in [m]}$ as a random vector.

Examples:

- $\Omega = \mathbb{R}^{6N}$ is the phase space of N particles and $M^{(1)}(x)$ is the energy of a particle with phase-space coordinate x.
- $\Omega = \bigcup_{N=0}^{N_{\max}} \mathbb{R}^{6N}$ is the phase space of a system that contains at most $N_{\max}$ particles and $M^{(2)}(x)$ is the particle number associated with x.

In statistical physics, one is usually not explicitly interested in how exactly the event space is given.

What is still missing is a probability distribution for given

$$\mathsf{M} := (\mathsf{M}^{(\nu)})_{\nu \in [m]}\,. \tag{2.3}$$

Here, we would like to choose a distribution that makes as few assumptions as possible. One also speaks of an *unbiased estimate*. This leads to Jaynes' maximum-entropy principle, which is grounded in the information-theoretic interpretation (Shannon coding, theorem 1.8) of the entropy. Jaynes phrased it as follows [11]: "*[The] maximum entropy distribution may be asserted for the positive reason that it is uniquely determined as the one which is maximally noncommittal with respect to missing information.*"

Jaynes' principle [11]:

Among all states of a physical system that are compatible with the available knowledge about the system, one should choose the one that maximizes the entropy.

More precisely, the state of the system is here the state of our knowledge about the system, which is given by a probability distribution (and later by a density matrix). This point of view is compatible with Bayesian inference [12, 13].

In the case where each of the random variables $M^{(\nu)}$ can take at most n different values, we thus have to solve the following constrained minimization problem (we omit the constraints $p_i \geq 0$, since they will be satisfied automatically):

$$\begin{aligned} \text{minimize} \quad & -S(p) \\ \text{subject to} \quad & \sum_{i=1}^{n} p_i = 1 \\ & \sum_{i=1}^{n} M_i^{(\nu)}\, p_i = \mathsf{M}^{(\nu)} \quad \forall \nu \in [m] \end{aligned} \tag{2.4}$$

This is a minimization problem with a continuous convex function $-S(p)$ under affine-linear constraints. Convex analysis teaches us [8] that here every critical point that can be found via Lagrange multipliers is also a global minimum.

The Lagrangian function associated with eq. (2.4) is given by

$$\Lambda(p,\tilde{\lambda}) = k\sum_{i=1}^{n} p_i \ln(p_i) - \tilde{\lambda}_0\left(1-\sum_{i=1}^{n} p_i\right) - \sum_{\nu=1}^{m}\tilde{\lambda}_\nu\left(\mathsf{M}^{(\nu)} - \sum_{i=1}^{n} M_i^{(\nu)}\, p_i\right), \tag{2.5}$$

where $\tilde{\lambda}_0$ is the Lagrange multiplier for $\sum_i p_i = 1$ and $\tilde{\lambda}_\nu$ is the Lagrange multiplier for the constraint concerning $M^{(\nu)}$. From now on, we will use the Einstein summation convention (ESC) for the summation over $\nu \in [m]$. Then a critical point of eq. (2.4) satisfies

$$k\ln(p_i) + k + \tilde{\lambda}_0 + \tilde{\lambda}_\nu M_i^{(\nu)} = 0 \qquad \forall i \in [n]\,. \tag{2.6}$$

This yields

$$p_i = \exp\bigl(\Psi - \lambda_\nu M_i^{(\nu)}\bigr) \tag{2.7}$$

with $\Psi \coloneqq -\frac{k+\tilde{\lambda}_0}{k}$ and

$$\lambda_\nu \coloneqq \tilde{\lambda}_\nu / k\,. \tag{2.8}$$

An analogous argument can be carried out for the continuous case using the calculus of variations (exercise sheet). In summary, this yields the following.

Generalized canonical distribution

Given the expectation values (2.2), the *generalized canonical distribution* is the distribution that maximizes the entropy (see section 1.4) and is given by

$$p_i = \exp\bigl(\Psi - \lambda_\nu M_i^{(\nu)}\bigr) \qquad \text{(discrete case)}, \tag{2.9}$$

$$\rho(x) = \exp\bigl(\Psi - \lambda_\nu M^{(\nu)}(x)\bigr) \qquad \text{(continuous case)} \tag{2.10}$$

(with ESC), where Ψ is a normalization constant and $(\lambda_\nu)_{\nu\in[m]}$ are real constants that are still to be determined and that are fixed by eq. (2.2).
The entropy of the generalized canonical distribution is denoted by $S(\mathsf{M})$.

Remarks:

- Since Ψ corresponds to the Lagrange multiplier for the normalization, we regard Ψ as a normalization constant. More precisely, the normalization constant

$$\begin{aligned} Z(\lambda) &\coloneqq \sum_i \exp(-\lambda_\nu M_i^{(\nu)}) = \mathrm{e}^{-\Psi(\lambda)} && \text{(discrete case)}, \\ Z(\lambda) &\coloneqq \int \mathrm{d}x\, \exp(-\lambda_\nu M^{(\nu)}(x)) = \mathrm{e}^{-\Psi(\lambda)} && \text{(continuous case)} \end{aligned} \tag{2.11}$$

  is the so-called *partition function*.

- The Lagrange multipliers λ are regarded as functions of the expectation values M. Thereby, the canonical distribution depends implicitly on the expectation values M. We will characterize this dependence more precisely in the following.

- By theorem 1.11, the entropy function $\mathsf{M} \mapsto -S(\mathsf{M})$ is convex.

The entropy of the canonical distribution follows from

$$\begin{aligned} \frac{S(\mathsf{M})}{k} &= \begin{cases} -\sum_i p_i \ln(p_i) & \text{(discrete case)} \\ -\int \rho(x)\ln(\rho(x))\,\mathrm{d}x & \text{(continuous case)} \end{cases} \\ &= \mathbb{E}[-\Psi(\lambda) + \lambda_\nu M^{(\nu)}] \\ &= \lambda_\nu \mathsf{M}^{(\nu)} - \Psi(\lambda) \\ &\equiv \langle \lambda, \mathsf{M}\rangle - \Psi(\lambda) \end{aligned} \tag{2.12}$$

and hence

$$k\Psi(\lambda) = k\langle\lambda, \mathsf{M}\rangle - S(\mathsf{M})\,. \tag{2.13}$$

Moreover, it follows from eq. (2.12) that

$$\frac{\partial S(\mathsf{M})}{\partial \mathsf{M}^{(\nu)}} = k\lambda_\nu\,, \tag{2.14}$$

i.e., M is a stationary point of $\mathsf{M} \mapsto k\langle\lambda, \mathsf{M}\rangle - S(\mathsf{M})$, since thus

$$\frac{\partial}{\partial \mathsf{M}^{(\nu)}}\Big[k\langle\lambda, \mathsf{M}\rangle - S(\mathsf{M})\Big] = k\lambda_\nu - \frac{\partial S(\mathsf{M})}{\partial \mathsf{M}^{(\nu)}} = 0\,. \tag{2.15}$$

By eq. (1.92), therefore,

$$k\Psi(\lambda) = \tilde{S}(k\lambda) \tag{2.16}$$

provided that the infimum in the definition of the Legendre transformation (1.89) is attained. Then Ψ is the Legendre transform of S. Moreover, as the Legendre transform[1] of a concave function, Ψ is concave as well, see section 1.5.1.

From the normalization condition (2.11) it follows furthermore that

$$\Psi(\lambda) = -\ln \sum_i \exp\bigl(-\lambda_\nu M_i^{(\nu)}\bigr) \tag{2.17}$$

and hence

$$\begin{aligned}\frac{\partial \Psi(\lambda)}{\partial \lambda_\nu} &= -\frac{\sum_i (-M_i^{(\nu)}) \exp\bigl(-\lambda_\nu M_i^{(\nu)}\bigr)}{\sum_i \exp\bigl(-\lambda_\nu M_i^{(\nu)}\bigr)} \\ &= \mathbb{E}[M^{(\nu)}] = \mathsf{M}^{(\nu)}\,.\end{aligned} \tag{2.18}$$

From this it follows that

$$k\tilde{\Psi}(\mathsf{M}) = S(\mathsf{M})\,, \tag{2.19}$$

which confirms eq. (1.90). The Lagrange duality between S and Ψ can also be deduced directly from $S(\mathsf{M}) + k\Psi(\lambda) = k\langle\lambda, \mathsf{M}\rangle$. Our derivation, however, is somewhat more explicit.
We note that, moreover,

$$-\frac{\partial \ln(Z)}{\partial \lambda_\nu} = \mathsf{M}^{(\nu)}\,, \tag{2.20}$$

i.e., the logarithmic derivatives of the partition function yield the expectation values $\mathsf{M}^{(\nu)}$.

To conclude this section, let us mention that eq. (2.14) is often also written as follows (regarding the notation, see also item (vii) in section 1.2).

Generalized Gibbs fundamental equation

$$\mathrm{d}S = k\lambda_\nu\, \mathrm{d}\mathsf{M}^{(\nu)} \qquad \text{(with ESC).} \tag{2.21}$$

Similarly helpful is the equation

$$\mathrm{d}\ln(Z) = -\mathsf{M}^{(\nu)}\mathrm{d}\lambda_\nu \qquad \text{(with ESC).} \tag{2.22}$$

2.1.1 Example: Canonical distribution

The phase space of N *distinguishable* particles located in a region $R \subset \mathbb{R}^3$ is

$$\Gamma_u = R^N \times \mathbb{R}^{3N} \tag{2.23}$$

[1] with the sign convention of the Legendre transformation that is customary in statistical physics, so that concave functions are mapped to concave functions

with associated phase-space coordinates

$$\xi = (q_1, \ldots, q_{3N}, p_1, \ldots, p_{3N})^{\mathsf{T}} . \tag{2.24}$$

We assume that the particles are described by a Hamiltonian function of the form

$$H(\xi) = \frac{p^2}{2m} + V(q) , \tag{2.25}$$

where m is the mass of the individual particles and $p^2 \coloneqq \sum_{i=1}^{3N} p_i^2$.
Now we regard the phase-space function H as the only random variable,

$$M^{(1)}(\xi) = H(\xi) , \tag{2.26}$$

and assume that it has the energy expectation value

$$\mathbb{E}[H] = U . \tag{2.27}$$

We denote the associated Lagrange parameter by

$$\beta \equiv \lambda_1 . \tag{2.28}$$

Then the generalized canonical distribution is given by the **PDF!**

$$\rho(\xi) = \frac{1}{Z_u} \, \mathrm{e}^{-\beta H(\xi)} , \tag{2.29}$$

where the partition function Z_u in the usual units is given by

$$Z_u = \int_{\mathbb{R}^{6N}} \frac{\mathrm{d}^{3N} q \, \mathrm{d}^{3N} p}{h^{3N}} \, \mathrm{e}^{-\beta H(\xi)} , \tag{2.30}$$

where the restriction $q \in R^N$ is taken into account via the potential $V(q)$ and h denotes Planck's constant.
If the particles are indistinguishable, we have to regard two phase-space coordinates ξ_1, ξ_2 as equivalent, i.e., $\xi_1 \sim \xi_2$ if ξ_1 arises from a permutation of the N particles of ξ_2. Since there are $N!$ such permutations, we choose the partition function of N indistinguishable particles as

$$Z = \frac{Z_u}{N!} = \int_{\mathbb{R}^{6N}} \mathrm{d}\xi \, \mathrm{e}^{-\beta H(\xi)} , \tag{2.31}$$

with the phase-space volume element

$$\mathrm{d}\xi \coloneqq \frac{\mathrm{d}^{3N} q \, \mathrm{d}^{3N} p}{h^{3N} \, N!} , \tag{2.32}$$

where we will justify the factor $N!$ more thoroughly by means of quantum mechanics. The corresponding distribution is the *canonical distribution* (also called the *Boltzmann distribution*) and is given by

$$\rho(\xi) = \frac{1}{Z} \, \mathrm{e}^{-\beta H(\xi)} . \tag{2.33}$$

We define the *temperature* T via

$$\frac{\partial S}{\partial U} =: \frac{1}{T} , \tag{2.34}$$

which is justified by using physically meaningful explicit Hamiltonian functions and later by the phenomenology of thermodynamics (chapter 4). With eq. (2.14) we then

have

$$\frac{\partial S}{\partial U} = k\beta = \frac{1}{T} \tag{2.35}$$

and thus

$$\beta = \frac{1}{kT}\,, \tag{2.36}$$

where we choose $k = k_\mathrm{B}$ as the constant fixing the units.

2.1.2 Example: Grand canonical distribution

The grand canonical distribution is an extension of the canonical distribution in which the particle number $N = M^{(2)}$ is also regarded as a random variable. This leads to the following modifications:

- phase space $\Gamma = \bigcup_{n=0}^{\infty} \mathbb{R}^{6n}$ with the notation $\xi_n \in \mathbb{R}^{6n}$
- $M^{(2)} = N$ is the particle number as a phase-space function, so that $N(\xi_n) = n$. Usually, the random variable N and the natural number n are here both denoted by N.
- $\lambda_2 =: -\beta\mu$ (convention), where μ is called the *chemical potential*
- The partition function is denoted by $\mathcal{Z}$ and is given by

$$\mathcal{Z} = \mathrm{e}^{-\Psi} = \sum_{n=0}^{\infty} \int_{\mathbb{R}^{6n}} \mathrm{d}\xi_n \, \mathrm{e}^{-\beta(H(\xi_n)-\mu N(\xi_n))} \tag{2.37}$$

  with $\mathrm{d}\xi_n = \frac{\mathrm{d}^{3n}q\,\mathrm{d}^{3n}p}{h^{3n}n!}$.

- The *grand canonical distribution* is then given by

$$\rho(\xi) = \frac{1}{\mathcal{Z}} \mathrm{e}^{-\beta(H(\xi)-\mu N(\xi))}\,. \tag{2.38}$$

- With the *marginal distribution*

$$p_n \coloneqq \frac{1}{\mathcal{Z}} \int_{\mathbb{R}^{6n}} \mathrm{d}\xi_n \mathrm{e}^{-\beta(H(\xi_n)-\mu n)} \tag{2.39}$$

  of N we have, e.g.,

$$\mathbb{E}[N] = \sum_{n=0}^{\infty} n p_n\,. \tag{2.40}$$

2.1.2.1 Ideal gas

An *ideal gas* is defined by the Hamiltonian function

$$H(\xi) = \frac{p^2}{2m} + V_\mathrm{wall}(q)\,, \tag{2.41}$$

where the potential $V_\mathrm{wall}(q)$ models a hard wall enclosing a connected compact region R of volume V, i.e.,

$$V_\mathrm{wall}(q) = \begin{cases} 0 & \text{if } q \in R\,, \\ \infty & \text{otherwise.} \end{cases} \tag{2.42}$$

The ideal gas corresponds to the idealization of point-like particles that nevertheless collide hard.

Exercise: Compute the grand canonical distribution and partition function for an ideal gas.

2.1.3 A dissipation-fluctuation theorem

Theorem 2.1 (Dissipation-fluctuation theorem)**.** *The random variables $M^{(\nu)}$ of the generalized canonical distribution satisfy*

$$\mathrm{Cov}(M^{(\nu)}, M^{(\alpha)}) = -\frac{\partial^2 \Psi(\lambda)}{\partial \lambda_\nu \partial \lambda_\alpha} = -\frac{\partial \mathsf{M}^{(\nu)}}{\partial \lambda_\alpha} \,. \tag{2.43}$$

Remarks:

- $\mathrm{Cov}(M^{(\nu)}, M^{(\alpha)})$ measures the fluctuations of $M^{(\nu)}$ and $M^{(\alpha)}$ around the expectation values. The theorem tells us that they coincide with the changes of the expectation values, also called susceptibilities.
- The matrix defined by $\mathrm{Cov}(M^{(\nu)}, M^{(\alpha)})$ is also called the covariance matrix and is always positive semidefinite (short exercise). This confirms that Ψ is concave (short exercise).

Proof. The cumulant-generating function (see section 1.3.2.4) can be generalized to our random vectors M and is then given by

$$\ln \varphi(q) = \ln \mathbb{E}[\mathrm{e}^{\mathrm{i}\langle q, M\rangle}] \,. \tag{2.44}$$

By calculations with the corresponding series expansions, one can show that

$$\begin{aligned} -\frac{\partial^2 \ln \varphi(q)}{\partial q_\nu \partial q_\alpha}\bigg|_{q=0} &= \mathbb{E}[M^{(\nu)} M^{(\alpha)}] - \mathbb{E}[M^{(\nu)}]\,\mathbb{E}[M^{(\alpha)}] \\ &= \mathrm{Cov}(M^{(\nu)}, M^{(\alpha)}) \,, \end{aligned} \tag{2.45}$$

which can be verified by directly differentiating $\ln(\varphi)$ (exercise sheet).
The cumulant-generating function of the canonical distribution is

$$\begin{aligned} \ln \varphi(q) &= \ln \sum_i p_i \exp(\mathrm{i}\langle q, M_i\rangle) \\ &= \ln \sum_i \exp(\Psi(\lambda) - \langle \lambda - \mathrm{i}q, M_i\rangle) \\ &= \Psi(\lambda) + \ln \sum_i \exp(-\langle \lambda - \mathrm{i}q, M_i\rangle) \\ &= \Psi(\lambda) - \Psi(\lambda - \mathrm{i}q) \,, \end{aligned} \tag{2.46}$$

where we have used eq. (2.11) in the last step. An analogous calculation yields the same identity for the continuous case. Hence,

$$\begin{aligned} \mathrm{Cov}(M^{(\nu)}, M^{(\alpha)}) &= \frac{\partial^2 \Psi(\lambda - \mathrm{i}q)}{\partial q_\nu \partial q_\alpha}\bigg|_{q=0} \\ &= -\frac{\partial^2 \Psi(\lambda)}{\partial \lambda_\nu \partial \lambda_\alpha} \end{aligned} \tag{2.47}$$

and eq. (2.18) completes the proof. □

2.2 Justification of equilibrium thermodynamics

We will apply Jaynes' maximum-entropy principle to physical many-body systems, which will provide us with generalized canonical distributions (section 2.1). Here, we consider situations where the random variables $M^{(\nu)}$ are chosen to be phase-space functions that correspond to macroscopic quantities. This will lead us to equilibrium thermodynamics (chapter 4).

First, however, we pose the following question.

Fundamental question of statistical physics

When is a system actually described correctly by the generalized canonical distribution?

This question is as old as thermodynamics itself; its details, in particular with regard to quantum mechanics, still occupy scientists today [14–16]. A main focus lies on systems that are in thermal equilibrium. Here, we will only briefly present the most well-known arguments with which such an equilibrium is justified and with which one argues that the generalized canonical distribution then provides a correct description. At the same time, we will justify equilibrium thermodynamics.
As already indicated in sections 2.1.1 and 2.1.2, we apply Jaynes' principle to Hamiltonian many-body systems with phase space Γ and Hamiltonian function $H : \Gamma \to \mathbb{R}$ as follows. We denote the "macroscopically relevant" observables (classically given by phase-space functions) by $M^{(1)}, \dots, M^{(m)} : \Gamma \to \mathbb{R}$. We assume that their expectation values

$$\mathbb{E}[M^{(\nu)}] = \mathsf{M}^{(\nu)} \qquad \nu \in [m] \tag{2.48}$$

are given and arrive, via Jaynes' principle, at the generalized canonical distribution

$$\rho(\xi) = \mathrm{e}^{\Psi(\lambda) - \langle \lambda, M(\xi) \rangle} \tag{2.49}$$

with Lagrange multipliers $\lambda = \lambda(\mathsf{M})$ and partition function

$$Z(\lambda) = \mathrm{e}^{-\Psi(\lambda)} = \int \mathrm{d}\xi \, \mathrm{e}^{-\langle \lambda, M(\xi) \rangle} \,, \tag{2.50}$$

see section 2.1.
The goal is to describe the macroscopic equilibrium thermodynamics of the many-body system by eq. (2.49). Therefore, we make the following assumption.

Conserved-quantities assumption

The observables $M^{(\nu)} : \Gamma \to \mathbb{R}$ are conserved quantities, i.e.,

$$\frac{\mathrm{d}M(\xi(t))}{\mathrm{d}t} = 0 \,, \tag{2.51}$$

where $t \mapsto \xi(t)$ is determined by initial conditions.

It suffices for this assumption to be satisfied approximately, i.e., that the macroscopic expectation values M change much more slowly than the time the system needs to *relax to macroscopic equilibrium*. We will discuss this process in a bit more detail in section 2.2.2. Before that, we will motivate better that the distribution (2.49) makes sense in the context of many-body systems and, in particular, is *stationary*.

2.2.1 Liouville's theorem

We consider a Hamiltonian system with canonical position and momentum coordinates

$$\xi = (q_1, \dots q_N, p_1, \dots, p_N) \,. \tag{2.52}$$

Then the dynamics is given by the canonical equations

$$\dot{q}_k = \frac{\partial H}{\partial p_k} \,, \qquad \dot{p}_k = -\frac{\partial H}{\partial q_k} \,. \tag{2.53}$$

Now we assume that the phase-space coordinates ξ are distributed according to a

PDF! $\rho(\xi)$. Then $\rho(\xi)\dot{\xi}$ can be interpreted as a current density and ρ as a density in phase space. Indeed, these quantities satisfy the continuity equation

$$\dot{\rho} + \operatorname{div}(\rho\,\dot{\xi}) = 0\,, \tag{2.54}$$

which can be shown by the usual argument.
With

$$\begin{aligned} \operatorname{div}(\rho\,\dot{\xi}) &= \langle \operatorname{grad}(\rho), \dot{\xi}\rangle + \rho \operatorname{div}(\dot{\xi}) \\ &= \langle \operatorname{grad}(\rho), \dot{\xi}\rangle \\ &= \sum_{k=1}^{N} \left(\frac{\partial \rho}{\partial q_k}\dot{q}_k + \frac{\partial \rho}{\partial p_k}\dot{p}_k \right) \end{aligned} \tag{2.55}$$

we then obtain the total time derivative of the **PDF!** as

$$\begin{aligned} \frac{d\rho}{dt} &= \frac{\partial \rho}{\partial t} + \sum_{k=1}^{N} \left(\frac{\partial \rho}{\partial q_k}\dot{q}_k + \frac{\partial \rho}{\partial p_k}\dot{p}_k \right) \\ &= \dot{\rho} + \operatorname{div}(\rho\,\dot{\xi})\,. \end{aligned} \tag{2.56}$$

Together with the continuity equation (2.54), we obtain the following result.

Theorem 2.2 (Liouville's theorem)**.** *Let $\rho : \Gamma \to [0,\infty)$ be a **PDF!** on the phase space Γ of a conservative Hamiltonian system. Then*

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = 0\,. \tag{2.57}$$

Remarks:

- The theorem states that **PDF!**s on phase space do not change under the dynamics. Such a distribution is also called *stationary*.
- The theorem holds in general and not only for our distribution (2.49).
- Phase-space cells can nevertheless deform dramatically over time, as long as their volume remains the same. The probability density thus behaves similarly to the density of a moving incompressible fluid.

2.2.2 Equilibrium distributions and thermodynamic variables

We consider a microscopic system that is characterized by a time evolution $\xi(t)$ in phase space. Moreover, we assume that the accessible macroscopic observables, i.e., phase-space functions, are given by $M = (M^{(1)}, \ldots, M^{(m)})^{\mathsf{T}}$. Then macroscopic observations are given by the time average

$$\overline{M} = \frac{1}{\tau}\int_0^\tau \mathrm{d}t\, M(\xi(t))\,, \tag{2.58}$$

where τ is the duration of the observation. If the latter is much larger than the time scale of microscopic changes, then the time average (2.58) is expected to be constant, i.e., independent of the time window $[0,\tau]$ as long as it is large enough. In this case, one says that M has *equilibrated*.
An *equilibrium distribution* is a distribution ρ such that the following *ergodicity assumption* is satisfied:

$$\overline{M} = \int \mathrm{d}\xi\, M(\xi)\,\rho(\xi)\,. \tag{2.59}$$

In this case, (M,ρ) is also called an *ensemble*.

There are two lines of argument for establishing the ergodicity assumption (2.59):

(i) An application of Jaynes' principle to phase space yields: **Accessible phase-space regions of equal volume are equally probable.** This implies eq. (2.59). Note that Liouville's theorem is essential for this argument, since phase-space volumes must not change in time.

If the expectation values $\mathbb{E}[M^{(\nu)}]$ are known, Jaynes' principle yields the corresponding generalized canonical distribution.

(ii) An argument that is much older than information theory is based on the following *ergodic hypothesis*. Its origin goes back to Boltzmann (1898).

In a conservative system, the energy $H(\xi)$ is a conserved quantity, i.e., every energy shell defined by $H(\xi) = E$ is preserved under the dynamics.

The *ergodic hypothesis* states: **Given sufficiently long time, every cell on the energy shell is traversed**, where a *cell* is a region of positive volume or, in this case, of positive hypersurface area.

Liouville's theorem implies that the time the system spends in cells of equal size is the same. This implies eq. (2.59), however, only for $\tau \to \infty$ and for certain *non-integrable systems*[2] (in the sense of analytical mechanics), which was proven mathematically by Birkhoff and von Neumann in the 1930s. Here, certain further properties related to *strong mixing* play a role.

For an observer who knows only the energy value E but has no other knowledge about $\xi(0)$, the distribution of states is given by the *microcanonical distribution* $\delta_{H(\xi)-E}$. All ensembles can also be derived from this distribution; we will, however, derive them directly via the generalized canonical distribution.

In most interesting situations, the observables $M^{(\nu)}$ are not truly in equilibrium but merely change much more slowly than the time scale on which the microscopic equilibration takes place. If such a separation of the relevant time scales (observation time vs. microscopic changes) is present, one also speaks of a *quasi-equilibrium*. Similarly, slowly changing phase-space functions are also called quasi-conserved quantities. Examples are energy, volume, and particle number, which change slowly compared to the microscopic dynamics. In equilibrium thermodynamics, one generally assumes that the quasi-conserved quantities change so slowly that the system can be described throughout by the corresponding equilibrium state (generalized canonical distribution). In general, a system with conserved quantities $M^{(\nu)}$ is called *thermodynamic* if it can be described by the generalized canonical distribution. The associated variables $\mathsf{M}^{(\nu)}$ and λ_ν are called *thermodynamic variables*.

2.2.3 Time and irreversibility

A dynamics $\xi(t)$ is called *reversible* if its time reversal is again a physically possible process, i.e., if $\xi(-t)$ does not contradict fundamental physical laws. Important examples of irreversible processes are heat conduction, diffusion, and the mixing of fluids.
Microscopic Hamiltonian dynamics is reversible if no further restrictions are imposed, whereas macroscopic dynamics (e.g., equilibration) is in general irreversible.
A function on a physical system is called a *state function* if it depends only on the current state of the system and not on its history.
The existence of irreversible processes is implied by the following statement: *For every isolated thermodynamic system there exists a state function that cannot decrease with time.* Following the suggestion of R. Clausius (∼1860), this quantity is called *entropy*. We note that Jaynes' principle already implies the irreversibility of the systems described by a generalized canonical distribution:

[2] A conservative Hamiltonian system with N degrees of freedom is called *integrable* if it has N independent conserved quantities (e.g., as for coupled harmonic oscillators).

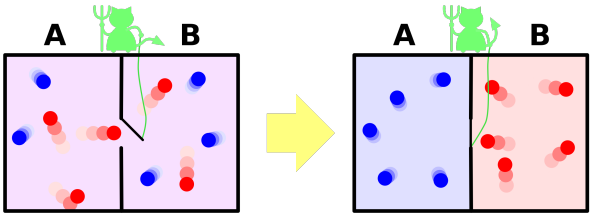

Figure 2.1: Maxwell's demon can "see" the particles of the different types and can thus reduce the mixing entropy of two gases by means of a trapdoor.

Second law of thermodynamics

The entropy S of a completely isolated system cannot decrease with time.

The second law rules out the existence of perpetual motion machines (of the second kind). For example, for two isolated systems at different temperatures, no heat can pass from the colder to the warmer system, as we will see. Hence, for instance, a ship propulsion that extracts heat from the ocean and uses it directly to drive the ship's engine is impossible.
As another example, in a thought experiment, a so-called Maxwell demon (1871) could exploit information about a system in order to reduce the mixing entropy, see fig. 2.1. Much later, however, it was shown that the demon's trapdoor mechanism either needs a "drive" and thus generates entropy in the form of heat, or has to swing in both directions, in which case no separation of the gases is possible.
As a fundamental advance concerning the connection between information theory and thermodynamics, Landauer showed the following: non-reversible processing of information (erasure of bits) generates thermodynamic entropy, which manifests itself as heat.

2.2.4 Extensive and intensive quantities

Many-body systems can be composed, i.e., if we have a system Γ_{I} and a second system Γ_{II}, the composite system is $\Gamma_{\mathrm{I}} \times \Gamma_{\mathrm{II}}$ (Cartesian product). Something similar holds for phase-space functions: if M_{I} and M_{II} are phase-space functions on the two individual systems, then $M_{\mathrm{I}} + M_{\mathrm{II}}$ is a phase-space function on the composite system $\Gamma_{\mathrm{I}} \times \Gamma_{\mathrm{II}}$.

Definition 2.3 (Extensive quantities)**.** *We call a thermodynamic variable* M extensive *if it is additive under composition of systems, i.e.,*

$$\mathsf{M}_{\mathrm{I+II}} = \mathsf{M}_{\mathrm{I}} + \mathsf{M}_{\mathrm{II}}\,, \tag{2.60}$$

where $\mathsf{M}_{\mathrm{I+II}}$ *is the corresponding quantity of the composite system and* M_{I} *and* M_{II} *are the corresponding quantities of the individual systems.*

Examples of extensive variables are the entropy S, particle number N, volume V, internal energy U, magnetization M, and electric charge Q.
Strictly speaking, the energy is not an extensive quantity in relevant situations, since the Hamiltonian function of a composite system contains an additional interaction energy. However, this interaction energy is usually much smaller than the total energy. Therefore, we also regard the energy as an extensive quantity, which is usually approximately correct.

Definition 2.4 (Intensive quantities)**.** *We call a thermodynamic variable* λ intensive *if it remains the same under composition of two systems that are in equilibrium with*

each other, i.e.,

$$\lambda_{\mathrm{I+II}} = \lambda_{\mathrm{I}} = \lambda_{\mathrm{II}}\,, \tag{2.61}$$

where $\lambda_{\mathrm{I+II}}$ is the corresponding quantity of the composite system and λ_{I} and λ_{II} are the corresponding quantities of the individual systems.

Examples of intensive variables are the chemical potential μ, pressure p, temperature T, magnetic field B, and electric field. Strictly speaking, the temperature is not an intensive quantity for interacting particles. However, if the interactions decay sufficiently fast with distance, the temperature behaves intensively on sufficiently large length scales. Such a statement can also be proven for quantum systems [17].
In general, the following holds: **if the phase-space functions $M : \Gamma \to \mathbb{R}^m$ are extensive, then the associated Lagrange multipliers λ are intensive**, since in the case (2.60) the corresponding canonical distributions satisfy

$$\rho(\xi_{\mathrm{I}}, \xi_{\mathrm{II}}) = \rho_{\mathrm{I}}(\xi_{\mathrm{I}})\, \rho_{\mathrm{II}}(\xi_{\mathrm{II}})\,, \tag{2.62}$$

which follows from property (iv) (section 1.4.1) of the entropy and Jaynes' principle (comprehension exercise). Therefore, λ_ν is then also called the *intensive quantity conjugate to $M^{(\nu)}$*.
Moreover, the entropy then satisfies

$$S(\alpha \mathsf{M}) = \alpha S(\mathsf{M}) \tag{2.63}$$

for all $\alpha \geq 0$ (small α can obviously be problematic, e.g., for the particle number, which is, however, not important since we are interested in "large" systems). A function satisfying property (2.63) is also called a *homogeneous function of first degree*.

Remark for attentive readers: It follows that the Legendre transform of the entropy is given by

$$\tilde{S}(k\lambda) = \begin{cases} 0 & \text{if } k\langle \lambda, \mathsf{M}\rangle \geq S(\mathsf{M}) \qquad \forall \mathsf{M}\,, \\ -\infty & \text{otherwise,} \end{cases} \tag{2.64}$$

cf. eq. (2.16) and section 1.5.1.1. The inverse transformation nevertheless yields S again. In this case, however, $\tilde{S}(k\lambda)$ does not yield the normalization function Ψ. In thermodynamics, we will apply the Legendre transformation only to some of the variables of $S(\mathsf{M})$, where it can again be computed via stationary points.

The intensive quantities uniquely determine the equilibrium state given by the generalized canonical distribution. Thus, "being in equilibrium with each other" defines an equivalence relation:

Zeroth law of thermodynamics

If two systems are each in equilibrium with a third system, then they are also in equilibrium with each other.

From this law one can conclude that a physical system cannot be cooled to absolute zero.

2.2.5 The thermodynamic limit

We consider two extensive conserved quantities $M^{(\nu)}$ and $M^{(\nu')}$ of a thermodynamic system with associated conjugate intensive variables λ_ν and $\lambda_{\nu'}$. We now enlarge the system by a factor $\alpha > 1$ and denote the quantities corresponding to $M^{(\nu)}$ and $M^{(\nu')}$ by $M_\alpha^{(\nu)}$ and $M_\alpha^{(\nu')}$. We note that the intensive variables associated with $M_\alpha^{(\nu)}$ and $M_\alpha^{(\nu')}$ do not depend on α and therefore denote them by λ_ν and $\lambda_{\nu'}$. By the definition of extensivity, we have

$$\mathsf{M}_\alpha^{(\nu)} = \alpha \mathsf{M}^{(\nu)} \tag{2.65}$$

and similarly for ν'. Hence,

$$\frac{\partial \mathsf{M}_\alpha^{(\nu)}}{\partial \lambda_{\nu'}} = \alpha \frac{\partial \mathsf{M}^{(\nu)}}{\partial \lambda_{\nu'}} \tag{2.66}$$

and similarly with ν and ν' interchanged. By the dissipation-fluctuation theorem (theorem 2.1), the relative fluctuations of the extensive variables are thus given by

$$\frac{\mathrm{Cov}(M_\alpha^{(\nu)}, M_\alpha^{(\nu')})}{\mathsf{M}_\alpha^{(\nu)} \mathsf{M}_\alpha^{(\nu')}} = -\frac{1}{\alpha} \frac{1}{\mathsf{M}^{(\nu)} \mathsf{M}^{(\nu')}} \frac{\partial \mathsf{M}^{(\nu)}}{\partial \lambda_{\nu'}} \overset{\alpha \to \infty}{\to} 0\,, \tag{2.67}$$

i.e., **the relative fluctuations vanish in the limit of large system sizes**.

Example: The relative energy fluctuations

$$\frac{\Delta U}{U} = \sqrt{\frac{\mathrm{Var}[H]}{U^2}} = \sqrt{\frac{\mathrm{Cov}(H,H)}{U^2}} \tag{2.68}$$

vanish for large systems (H is the Hamiltonian function).

Remark: In the case of non-interacting systems, the **CLT!** (theorem 1.6) can also be used to show that $\mathrm{Var}[M_\alpha^{(\nu)}]/\mathsf{M}^{(\nu)\,2}$ goes to zero like $1/\alpha$ for $\alpha \to \infty$.
In particular, it follows that as soon as a system is correctly described by different generalized canonical distributions (say, canonical and grand canonical), these distributions must be equivalent.

2.3 The classical ensembles

In this section, we choose extensive physical quantities as the random variables $M^{(\nu)}$ of the generalized canonical distribution (section 2.1). Thereby, the Lagrange multipliers λ_ν become intensive physical quantities. We want to identify them here and describe physical situations where the special distributions find applications.
The energy H occurs in each of the classical ensembles as an extensive quantity. It is therefore helpful to rewrite the generalized canonical distribution (section 2.1) as

$$\rho(\xi) = \frac{1}{Z} \mathrm{e}^{-\beta H(\xi) - \lambda_j M^{(j)}} \qquad \text{(ESC)}, \tag{2.69}$$

where the Latin letters (here j) indicate that the summation does not include the energy variable. The quantity

$$\Phi := -\frac{\ln(Z)}{\beta} = -kT \ln(Z) \tag{2.70}$$

is also called the *potential*; we will see that a complete set of thermodynamic variables can be computed from the potential by means of derivatives. One calls $(\beta, \lambda_j/\beta)$ the *natural variables* of Ψ, of the potential Φ, and of the partition function Z. Using the potential Φ, the generalized canonical distribution can also be written as

$$\rho(\xi) = \mathrm{e}^{\beta(\Phi - H(\xi) - \lambda_j/\beta\, M^{(j)})}\,. \tag{2.71}$$

In section 2.1.1 we encountered the *internal energy* as

$$\mathbb{E}[H] = U \tag{2.72}$$

and identified the *inverse temperature* as the associated intensive variable

$$\beta = \lambda_1 = \frac{1}{kT}\,. \tag{2.73}$$

The entropy is then given by

$$S(U, \mathsf{M}) = \frac{1}{T}\, U + k\lambda_j \mathsf{M}^{(j)} - k\Psi\,. \tag{2.74}$$

We can then rewrite the Gibbs fundamental equation (2.21) as

$$\mathrm{d}U = T\,\mathrm{d}S - \frac{\lambda_j}{\beta}\,\mathrm{d}\mathsf{M}^{(j)} \qquad \text{(ESC)}. \tag{2.75}$$

We call $\mathsf{M}^{(\nu)}$ the *natural variables* of S and $(S, \mathsf{M}^{(j)})$ the natural variables of the internal energy U.

Often, the dependence of a function on β (e.g., of the partition function) is rewritten as a dependence on $T = \frac{1}{k\beta}$. Here, it is helpful to note that

$$\frac{\partial f(\beta)}{\partial \beta} = \frac{\partial f(T)}{\partial T}\frac{\partial T}{\partial \beta} = -\frac{1}{k\beta^2}\,\frac{\partial f(T)}{\partial T} \tag{2.76}$$

for a function f that depends on the inverse temperature β.

The constraints

$$\mathbb{E}[M^{(\nu)}] = \mathsf{M}^{(\nu)} \tag{2.77}$$

are also called *macro-constraints*. Usually, the distribution also depends on additional parameters; e.g., the canonical distribution depends implicitly on the particle number and the volume (see the next section). Regarding the choice of such parameters, one also speaks of *micro-constraints*. Often, these parameters are listed as additional variables of the partition function, e.g., in the form

$$Z = Z(\beta, \lambda; \text{micro-constraints})\,. \tag{2.78}$$

The same applies to Ψ and to the potential Φ.
Now we come to the classical distributions of statistical mechanics, which can be found in every textbook and are also explained in detail on Wikipedia.

2.3.1 The canonical ensemble

The *canonical ensemble* (ρ, H) models situations where the system is coupled to a heat bath (also called a heat reservoir) of temperature T and is in equilibrium with it. A *heat bath* is a system of fixed temperature that does not change due to the coupling to the system under consideration. The temperature of the heat bath is fixed but arbitrary, i.e., it can also be very cold. In that case, one sometimes also speaks of a cold bath.
We have already discussed the canonical distribution in section 2.1.1. In the canonical ensemble, the volume V and the particle number N are fixed parameters. N is fixed by the phase space $\Gamma = \mathbb{R}^{6N}$, and the potential term in the Hamiltonian function is infinitely large outside the volume. Alternatively, one can choose the phase space as $\Gamma = R^N \times \mathbb{R}^{3N}$, where $R \subset \mathbb{R}^3$ with $\mathrm{vol}(R) = V$. Thus, the only remaining macro-constraint is the one of the energy, $\mathbb{E}[H] = U$. The conjugate intensive variable is the inverse temperature

$$\beta = \frac{1}{k}\,\frac{\partial S}{\partial U}. \tag{2.79}$$

Hence, we can regard the partition function Z (and also Ψ and F below) as a function of (β, V, N). Therefore, we also write $Z = Z(\beta) = Z(\beta; V, N)$.
The entropy of the canonical ensemble is

$$S(U) = k(\beta U - \Psi) = \frac{U}{T} + k\ln(Z)\,, \tag{2.80}$$

where we have used eq. (2.11). Hence, we can express the internal energy as

$$U(S) = TS + \frac{\Psi(\beta)}{\beta}\,. \tag{2.81}$$

Moreover,

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}U \quad \Leftrightarrow \quad T\,\mathrm{d}S = \mathrm{d}U\,. \tag{2.82}$$

Therefore,

$$\frac{\partial U}{\partial S} = T\,. \tag{2.83}$$

The *(Helmholtz) free energy* is defined as

$$F(T;V,N) \coloneqq U - TS = -kT\ln Z(T;V,N) \tag{2.84}$$

and, by eq. (2.83), can be identified as the negative Legendre transform (section 1.5.1) of U; at the same time, it is the potential of the canonical distribution. The free energy F is the maximal work that can be extracted from the system at constant temperature and constant volume (by quantities that were implicitly assumed to be constant here). Writing out the Legendre transformation tells us that

$$F(T) = \min_S\{U(S) - TS\}\,. \tag{2.85}$$

One can show in general that the canonical distribution minimizes the free energy (among all phase-space distributions). Using the free energy, the canonical distribution (2.33) can also be written as

$$\rho(\xi) = \mathrm{e}^{\beta(F-H(\xi))}\,. \tag{2.86}$$

2.3.1.1 Example: Partition function of an ideal gas

For an ideal gas of N particles of mass m in a volume V, the partition function is

$$Z = \frac{V^N}{N!h^{3N}}\prod_{i=1}^{3N}\int \mathrm{d}p_i\,\exp\Big(-\beta\frac{p_i^2}{2m}\Big)\,, \tag{2.87}$$

which can be evaluated to

$$Z = \frac{(V/\lambda^3)^N}{N!}\,, \tag{2.88}$$

with the *thermal wavelength*

$$\lambda \coloneqq \frac{h}{\sqrt{2\pi mkT}} \tag{2.89}$$

(Exercise 4.3).

Exercise: Show the *caloric equation of state*

$$U = \frac{3}{2}NkT \tag{2.90}$$

and prove the *Sackur-Tetrode equation*

$$\begin{aligned}\frac{S}{kN} &\approx \ln\left[\frac{V}{N\lambda^3}\right] + \frac{5}{2}\\ &= \ln\left[\frac{V}{N}\Big(\frac{4\pi m}{3h^2}\frac{U}{N}\Big)^{3/2}\right] + \frac{5}{2}\end{aligned} \tag{2.91}$$

using the Stirling approximation $\ln(N!) = N\ln(N) - N + \mathrm{O}(\ln N)$.

2.3.2 The Gibbs ensemble

We will see how to model situations where the system is coupled both to a heat bath and to a pressure-controlling environment (impermeable piston) and is in equilibrium with them.
To this end, in addition to the energy $M^{(1)} = H$, we consider the volume V as a random variable $M^{(2)}$, so that $\mathbb{E}[M^{(2)}] = V$. Typically, this random variable is (quasi-)constant, i.e., sharply distributed. Phenomenology teaches us that the work differential is given by

$$\delta W = -p \, \mathrm{d}V \,, \tag{2.92}$$

where p is the pressure (force per area). We recall that such 1-forms can be integrated along curves, see eq. (1.108), which defines the work via the above work differential.

Exercise: Illustrate this law by means of a gas whose pressure is controlled by a piston. Argue using the distance by which the piston is moved.
This motivates the general definition of the *pressure* as

$$p \coloneqq -\mathbb{E}\Big[\frac{\partial H}{\partial V}\Big] = -\frac{\partial U}{\partial V} \,. \tag{2.93}$$

From the Gibbs fundamental equation (2.75) we therefore read off

$$p = \frac{\lambda_2}{\beta} \,, \tag{2.94}$$

so that

$$\mathrm{d}U = T \, \mathrm{d}S - p \, \mathrm{d}V \,. \tag{2.95}$$

The internal energy is thus composed as

$$\mathrm{d}U = \delta Q + \delta W \,, \tag{2.96}$$

where $\delta W = -p \, \mathrm{d}V$ defines the *work* and

$$\delta Q \coloneqq T \, \mathrm{d}S \tag{2.97}$$

the *heat*. Note that the work and heat differentials are in general not exact, which will still play an important role. However, $1/T$ is an integrating factor for the heat δQ.
The *Gibbs distribution* is then given by

$$\rho(\xi) = \frac{1}{Z_G} \, \mathrm{e}^{-\beta(H(\xi)+pV)} \,. \tag{2.98}$$

The ensemble (ρ, H, V) is also referred to as the *pressure ensemble* or likewise as the *canonical ensemble*.
From eq. (2.95), or also from

$$S(U,V) = \frac{1}{T} \, U + \frac{p}{T} \, V - k\Psi(\beta, \beta p) \tag{2.99}$$

(cf. eq. (2.74)), it follows that

$$\Big(\frac{\partial S}{\partial U}\Big)_V = \frac{1}{T} \,, \qquad \Big(\frac{\partial S}{\partial V}\Big)_U = \frac{p}{T} \,, \tag{2.100}$$

where the subscripts V and U each denote the variable that is "held constant" in the partial derivative. Moreover, we obtain

$$U(S,V) = TS - pV + \frac{\Psi(T,p)}{\beta} \,, \tag{2.101}$$

where we now regard Ψ as a function of (T, p). With $T = \left(\frac{\partial U}{\partial S}\right)_V$ and $p = -\left(\frac{\partial U}{\partial V}\right)_S$ we obtain the *Gibbs energy*

$$G(T, p; N) := U - TS + pV = -kT \ln Z_G(T, p; N) \tag{2.102}$$

as the Legendre transform of $U(S, V)$. Alternatively, one can also regard $G(T, p)$ as the Legendre transform with respect to the variable V of the Helmholtz free energy $F(T)$, which is defined here exactly as before.
The Gibbs energy is the potential of the Gibbs distribution. It is the maximal reversible work that can be extracted from the system at constant temperature and constant pressure (by quantities that were implicitly assumed to be constant here, such as, e.g., electromagnetic forces).
Using the Gibbs energy G, the Gibbs distribution (2.98) can also be written as

$$\rho(\xi) = \mathrm{e}^{\beta(G - H(\xi) - pV)}\,. \tag{2.103}$$

2.3.2.1 Example: Ideal gas

Exercise 6.3: Show that $pV = \mathsf{N}kT$ holds for an ideal gas.

2.3.3 The grand canonical ensemble

Grand canonical ensembles describe systems that are coupled to a heat bath with possible particle exchange and are in thermal and chemical equilibrium with it. To this end, the grand canonical distribution from section 2.1.2 can be generalized to several particle species. The extensive quantities are given as

$$U = \mathbb{E}[H] \qquad \text{(internal energy)} \tag{2.104}$$

$$\mathsf{N}^{(j)} = \mathbb{E}[N^{(j)}] \qquad \text{(particle number of species } j\text{)} \tag{2.105}$$

$$\lambda_j = -\beta\mu_j \qquad (\mu_j\text{: associated chemical potential}). \tag{2.106}$$

Typically, one considers systems whose Hamiltonian function confines the particles to a region of volume V. However, the volume is regarded as a fixed parameter and not as an extensive variable of the entropy S. This yields

$$\begin{aligned}
\rho(\xi) &= \frac{1}{\mathcal{Z}}\,\mathrm{e}^{-\beta(H(\xi) - \mu_j N^{(j)}(\xi))} \\
&= \mathrm{e}^{\beta(\Phi - H(\xi) + \mu_j N^{(j)}(\xi))} && (\textbf{PDF!}\text{, with ESC}), && (2.107)\\
\mathcal{Z}(T, \mu; V) &= \mathrm{e}^{-\Psi(T,\mu;V)} \\
&= \sum_{\mathbf{n}} \int \mathrm{d}\xi_{\mathbf{n}}\,\mathrm{e}^{-\beta(H - \mu_j n^j)} && (\text{partition function}), && (2.108)\\
S(U, \mathsf{N}; V) &= \frac{U}{T} - \frac{\mu_j}{T}\,\mathsf{N}^{(j)} - k\Psi(T, \mu; V) && (\text{entropy}), && (2.109)\\
U(S, \mathsf{N}; V) &= TS + \mu_j \mathsf{N}^{(j)} + \frac{\Psi(T, \mu; V)}{\beta} && (\text{internal energy}), && (2.110)\\
\mathrm{d}U &= T\,\mathrm{d}S + \mu_j\,\mathrm{d}\mathsf{N}^{(j)} && (\text{Gibbs f. eq. at const. } V), && (2.111)\\
\Phi(T, \mu; V) &= kT\Psi(T, \mu; V) \\
&= -kT \ln(\mathcal{Z}(T, \mu; V)) && (\text{grand canonical potential}). && (2.112)
\end{aligned}$$

The grand canonical potential is the Legendre transform of $U(S, \mathsf{N})$.

Remark: For non-interacting particles, $(U, \mathsf{N}, V) \mapsto S(U, \mathsf{N}; V)$ is a homogeneous function of first degree. Hence, its Legendre transform $\tilde{S}$ takes only values in $\{0, -\infty\}$ (section 1.5.1.1) and is thus of only limited use in thermodynamics. For this reason, it is advisable to regard V as a fixed parameter.

2.3.3.1 Example concerning the chemical potential

We consider N particles in two coupled reservoirs with chemical potentials $\mu_1 \neq \mu_2$ at constant volume V and constant internal energy U. We denote the number of particles in the respective reservoirs by $N^{(1)}$ and $N^{(2)}$. Then, by eq. (2.111),

$$0 = \mathrm{d}U = T\,\mathrm{d}S + \mu_1 \mathrm{d}\mathsf{N}^{(1)} + \mu_2 \mathrm{d}\mathsf{N}^{(2)} \tag{2.113}$$

and, with constant total particle number $\mathsf{N} := \mathsf{N}^{(1)} + \mathsf{N}^{(2)}$, it follows from $\mathrm{d}S \geq 0$ that

$$\begin{aligned} 0 &\geq \mu_1 \mathrm{d}\mathsf{N}^{(1)} + \mu_2 \mathrm{d}\mathsf{N}^{(2)} \\ &= \mu_1 \mathrm{d}\mathsf{N}^{(1)} + \mu_2 (\mathrm{d}\mathsf{N} - \mathrm{d}\mathsf{N}^{(1)}) \\ &= -(\mu_2 - \mu_1)\,\mathrm{d}\mathsf{N}^{(1)}\,, \end{aligned} \tag{2.114}$$

i.e.,

$$(\mu_2 - \mu_1)\,\mathrm{d}\mathsf{N}^{(1)} \geq 0\,. \tag{2.115}$$

It follows that, out of chemical equilibrium, the particle number $\mathsf{N}^{(1)}$ of the first reservoir increases exactly when $\mu_1 < \mu_2$, i.e., when it has the smaller chemical potential. In other words, the particles move from the higher to the lower chemical potential.

Exercise: Argue by means of the canonical ensemble that when two heat baths with temperatures $T_1 \neq T_2$ are brought into contact, heat always flows from the warmer to the colder bath.

2.3.3.2 Example: Partition function of the ideal gas

For a single particle species, the grand canonical partition function can be written as

$$\mathcal{Z}(\beta, \mu; V) = \sum_{n=0}^{\infty} Z(\beta; V, n)\, \mathrm{e}^{\beta\mu n}\,, \tag{2.116}$$

where $Z(\beta; V, n)$ is the partition function of the ideal gas in the canonical ensemble (2.88) with n particles (micro-constraint). This yields

$$\mathcal{Z} = \exp(zV/\lambda^3) \tag{2.117}$$

with the thermal wavelength λ from eq. (2.89) and the *fugacity*

$$z := \mathrm{e}^{\beta\mu}\,. \tag{2.118}$$

With this, one can compute

$$U = \frac{3}{2}\mathsf{N}kT\,, \tag{2.119}$$

$$\mathsf{N} = \frac{Vz}{\lambda^3} \tag{2.120}$$

(Exercise 5.2). Moreover, it follows that

$$\begin{aligned} S(U, \mathsf{N}; V) &= \frac{U}{T} - \frac{\mu}{T}\mathsf{N} - k\Psi \\ &= k\beta U - k\beta\mu\mathsf{N} + k\,\frac{Vz}{\lambda^3}\,. \end{aligned} \tag{2.121}$$

2.3.4 The magnetic-field ensemble

The *magnetization* $\mathbf{M}$ as an extensive variable has $\lambda_{\mathbf{M}} = -\beta\mathbf{B}$ as its conjugate intensive variable, where $\mathbf{B}$ denotes the magnetic field. A change of the magnetization in the magnetic field $\mathbf{B}$ is associated with work, which can be formalized by the scalar product $\delta W = \mathbf{B} \cdot \mathrm{d}\mathbf{M}$. From this, one can conclude that $\lambda_{\mathbf{M}} = -\beta\mathbf{B}$ is the intensive variable conjugate to the magnetization $\mathbf{M}$.
The further details can be derived analogously to those of the Gibbs ensemble. The resulting potential is the *Gibbs energy*

$$G(T, \mathbf{B}; V, N) = U - TS - \mathbf{B} \cdot \mathbf{M} = -kT \ln(Z)\,, \tag{2.122}$$

which is the Legendre transform of $U(S, \mathbf{M})$.

2.3.5 The microcanonical ensemble

The phase space of the microcanonical ensemble is, as for the canonical ensemble, that of N indistinguishable particles in a region R of volume V. However, here the energy is assumed to be known exactly. Thus, the phase-space coordinates are restricted to the energy shell

$$\{H(\xi) = U\} \coloneqq \{\xi \in R^N \times \mathbb{R}^{3N} \mid H(\xi) = U\}\,. \tag{2.123}$$

Since nothing else is assumed to be known, Jaynes' principle yields the uniform distribution on the energy shell $\{H(\xi) = U\}$, the *microcanonical distribution*

$$\begin{aligned} \rho_{\mathrm{MK}}(\xi) &= \frac{1}{D(U)}\, \delta_{\{H(\xi)=U\}}(\xi) && \text{(Dirac measure)} \\ &= \frac{1}{D(U)}\, \delta(U - H(\xi)) && \text{(delta-distribution notation);} \end{aligned} \tag{2.124}$$

the normalization factor

$$D(U) = \int \mathrm{d}\xi\, \delta(U - H(\xi)) \tag{2.125}$$

is also called the *density of states*.
The phase-space volume enclosed by the energy shell $\{H(\xi) = U\}$ is

$$\Omega(U) = \int \mathrm{d}\xi\, \Theta(U - H(\xi)) \tag{2.126}$$

with the Heaviside function

$$\Theta(x) \coloneqq \begin{cases} 0 & \text{if } x < 0\,, \\ 1 & \text{otherwise.} \end{cases} \tag{2.127}$$

Hence,

$$D(U) = \frac{\mathrm{d}\Omega(U)}{\mathrm{d}U}\,. \tag{2.128}$$

Example: For an ideal gas in a volume V with Hamiltonian function

$$H(\xi) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + V_{\mathrm{wall}}(q) \tag{2.129}$$

one can compute that

$$\Omega(U) = \frac{V^N (2\pi m U)^{3N/2}}{h^{3N} N!\, (3N/2)!} \qquad \text{(ideal gas).} \tag{2.130}$$

Finally, let us remark that the microcanonical ensemble is the "traditional" starting point for the derivation of the canonical ensemble and of the Gibbs ensemble. In particular, the entropy can be defined as follows.

Thermodynamic definition of the entropy

The entropy of a system with phase-space volume $\Omega(E)$ is

$$S = k \ln(\Omega) \,. \tag{2.131}$$

Exercise 4.1: Show that, to good approximation, this definition yields the same value of the entropy as the Shannon entropy of the discretized microcanonical distribution.

2.3.6 Review and ensemble overview

- Probability theory: general mathematical theory, e.g., of **PDF!**s and random variables
- Jaynes' principle provides a general method to estimate a probability distribution from known expectation values of given random variables. This yields the generalized canonical distribution.
- In statistical mechanics, the various ensembles (see below) play a central role. They are special cases of the generalized canonical distribution. Simple physical considerations (such as $\delta W = -p \, \mathrm{d}V$) and phenomenological thermodynamics lead to the physical interpretation of these ensembles.

Ensemble $(\rho, M^{(\nu)})$	Micro-constr. parameters	Macro-constr. $M^{(\nu)}$	Intensive var. λ_ν	Partition fct. $Z = \mathrm{e}^{-\Psi}$	Potential $\Phi = kT\Psi$
Canonical	(V, N)	$\mathbb{E}[H] = U$	β	$Z(\beta; V, N)$	$F(T; V, N)$
Gibbs	N	$\mathbb{E}[H] = U$, $\mathbb{E}[V] = \mathsf{V} =: V$	$(\beta, \beta p)$	$Z(\beta, p; N)$	$G(T, p; N)$
Grand canonical	V	$\mathbb{E}[H] = U$, $\mathbb{E}[\mathbf{N}] = \mathsf{N}$	$(\beta, -\beta\mu)$	$\mathcal{Z}(\beta, \mu; V)$	$\Phi(\beta, \mu; V)$
Magnetic field	V, N	$\mathbb{E}[H] = U$, $\mathbb{E}[\mathbf{M}] = \mathsf{M}$	$(\beta, -\beta\mathbf{B})$	$Z(\beta, \mathbf{B}; V, N)$	$G(\beta, \mathbf{B}; V, N)$
Microcanonical	(U, V, N)	none	none	substitute: $\Omega(U)$	$-kT \ln(\Omega) = -TS(U, V, N)$

3 Quantum statistics

We recall that in classical statistical mechanics, probabilities arose only due to ignorance about microscopic degrees of freedom. However, there are no fundamental physical laws that forbid a deterministic description of classical many-body systems. Experiments with quantum systems, in contrast, are intrinsically probabilistic for various reasons. Hence, a fully probabilistic description appears particularly plausible here.

For a complete probabilistic description of quantum systems it is necessary to be able to combine "classical probabilities" with probabilities that arise purely from the quantum character. The latter originate from the superposition principle for quantum states, which, in general, cannot be measured sharply.
An important property of classical probabilities is that they can be *mixed*, i.e., for probability measures $(\mathbb{P}^{(j)})_{j\in[n]}$ and a probability vector $p \in [0,1]^n$,

$$\sum_{j=1}^{n} p_j \mathbb{P}^{(j)} \qquad \text{(convex combination)} \tag{3.1}$$

is again a probability measure. This classical mixing of probabilities also has an operational meaning: one draws from the distribution $\mathbb{P}^{(j)}$ with probability p_j.
An analogous classical mixing of quantum states is not possible on the level of state vectors (i.e., wave functions), since suitably normalized linear combinations of state vectors yield superpositions of quantum states. Therefore, we will embed state vectors (up to global phases) into the set of operators, where mixing operations generalizing eq. (3.1) are then possible alongside superpositions. This leads to the definition of density operators. We will also see that classical probability distributions can likewise be written as density operators.

3.1 Basics of quantum mechanics

Review the absolute basics of quantum mechanics:

- Hilbert space $\mathcal{H}$. Important examples are $\mathcal{H} = \mathbb{C}^d$ and

$$\mathcal{H} = \mathcal{L}^2(\mathbb{R}^n) = \left\{ \psi : \mathbb{R}^n \to \mathbb{C} \;\middle|\; \|\psi\|^2 := \int |\psi|^2 < \infty \right\}. \tag{3.2}$$

  Throughout this chapter, $\mathcal{H}$ and $\mathcal{H}_i$ with $i \in \mathbb{Z}_+$ are Hilbert spaces.

- State vectors: $|\psi\rangle \in \mathcal{H}$ with $\||\psi\rangle\| = 1$
- We denote the space of linear operators on $\mathcal{H}$ by $\mathrm{L}(\mathcal{H})$ and the rank of an operator $\hat{A} \in \mathrm{L}(\mathcal{H})$ by $\mathrm{rank}(\hat{A})$.
- *Observables* are Hermitian/self-adjoint linear operators $\hat{A} : \mathcal{H} \to \mathcal{H}$ (potentially with a restricted domain $\mathrm{dom}(\hat{A}) \subset \mathcal{H}$). The set of observables on $\mathcal{H}$ is denoted by $\mathrm{Herm}(\mathcal{H}) := \{\hat{A} \in \mathrm{L}(\mathcal{H}) : \ \hat{A} = \hat{A}^\dagger\}$.
- Expectation values (pure states): $\langle\psi\,|\,\hat{A}\,|\psi\rangle$

3.1.1 Density operators

The *trace* of an operator $\hat{A} \in \mathrm{L}(\mathcal{H})$ is defined as

$$\mathrm{Tr}[\hat{A}] := \sum_{j=1}^{\dim(\mathcal{H})} \langle j\,|\,\hat{A}\,|j\rangle\,, \tag{3.3}$$

where $\{|j\rangle\} \subset \mathcal{H}$ is an orthonormal basis. It has the following properties:

- $\mathrm{Tr}[\hat{A}\hat{B}] = \mathrm{Tr}[\hat{B}\hat{A}]$ for all $\hat{A}, \hat{B} \in \mathrm{L}(\mathcal{H})$
- It is unitarily invariant, i.e., $\mathrm{Tr}[\hat{U}\hat{A}\hat{U}^\dagger] = \mathrm{Tr}[\hat{A}]$ for all unitary operators $\hat{U} \in \mathrm{L}(\mathcal{H})$, and hence independent of the choice of basis.
- $\mathrm{Tr}[\hat{A} \otimes \hat{B}] = \mathrm{Tr}[\hat{A}]\,\mathrm{Tr}[\hat{B}]$ for all $\hat{A} \in \mathrm{L}(\mathcal{H})$ and $\hat{B} \in \mathrm{L}(\mathcal{H}')$

We call a self-adjoint operator $\hat{A} \in \mathrm{Herm}(\mathcal{H})$ *positive semidefinite* if

$$\langle\psi\,|\hat{A}|\psi\rangle \geq 0 \quad \forall|\psi\rangle \in \mathcal{H}\,. \tag{3.4}$$

For this we also write

$$\hat{A} \succeq 0\,. \tag{3.5}$$

Definition 3.1 (Density operator)**.** *A* density operator *is a self-adjoint operator $\hat{\rho}$ that is positive semidefinite and (trace-)*normalized*, i.e.,* $\mathrm{Tr}[\hat{\rho}] = 1$*. The set of density operators on a Hilbert space $\mathcal{H}$ is*

$$\mathcal{S}(\mathcal{H}) \coloneqq \{\hat{\rho} \in \mathrm{Herm}(\mathcal{H}) \mid \hat{\rho} \succeq 0,\ \mathrm{Tr}[\hat{\rho}] = 1\}\,. \tag{3.6}$$

A matrix representation of a density operator in $\mathcal{S}(\mathbb{C}^d)$ is also called a density matrix*. A density operator is also called a* quantum state *or, in short, a* state*.*

Central examples:

- Let $|\psi\rangle \in \mathcal{H}$ be a state vector. Then

  $$\hat{\rho} = |\psi\rangle\langle\psi| \tag{3.7}$$

  is a density operator.

- Let (p_j) be a **PMF!** and $\{|\psi_j\rangle\} \subset \mathcal{H}$ a set of state vectors in a Hilbert space $\mathcal{H}$. Then $(p_j, |\psi_j\rangle)_j$ is also called an *ensemble* of state vectors. The ensemble average

  $$\hat{\rho} = \sum_j p_j|\psi_j\rangle\langle\psi_j| \tag{3.8}$$

  is a density operator.

With eq. (3.7), quantum states given by state vectors can be represented as density operators. With eq. (3.8) and an orthonormal basis $\{|\psi_j\rangle\}$, classical discrete probability distributions can be represented as diagonal density matrices.
We call $\hat{\rho} \in \mathcal{S}(\mathcal{H})$ a *pure state* if $\hat{\rho}$ is of the form (3.7), i.e., $\mathrm{rank}(\hat{\rho}) = 1$.

Remark on the case $\dim(\mathcal{H}) = \infty$*:* Density operators fall into the category of *trace-class operators*, which are special *compact operators* and hence have a pure point spectrum. In this way, one can describe **PDF!**s that, under quantization, lead to states with only discrete measurement values.

Exercises:

- Show that an operator $\hat{\rho} \in \mathrm{L}(\mathbb{C}^d)$ is a density operator if and only if $\hat{\rho}$ is of the form (3.8).
- Find two different ensembles of state vectors that represent the same state $\hat{\rho}$ via eq. (3.8).
- Show that $\hat{\rho} \in \mathrm{L}(\mathbb{C}^d)$ is a pure state if and only if $\mathrm{Tr}[\hat{\rho}^2] = 1$.
- Show that the set of density operators $\mathcal{S}(\mathcal{H})$ is a convex set.

Now let $\hat{A} \in \mathrm{Herm}(\mathcal{H})$ be an observable and $\hat{\rho} \in \mathcal{S}(\mathcal{H})$ a state. Then the *expectation value* of $\hat{A}$ in the state $\hat{\rho}$ is defined as

$$\langle\hat{A}\rangle_{\hat{\rho}} \coloneqq \mathrm{Tr}[\hat{A}\hat{\rho}]\,. \tag{3.9}$$

For pure states of the form (3.7) it follows that

$$\langle\hat{A}\rangle_{\hat{\rho}} = \langle\psi\,|\hat{A}|\psi\rangle \tag{3.10}$$

and for ensembles of the form (3.8) we have

$$\langle \hat{A} \rangle_{\hat{\rho}} = \sum_j p_j \langle \psi_j \,|\, \hat{A} | \psi_j \rangle \,, \tag{3.11}$$

which corresponds to a classical expectation value of the random variable $j \mapsto \langle \psi_j \,|\, \hat{A} | \psi_j \rangle$. Hence, density operators indeed generalize both classical probability distributions and quantum states given by state vectors.

Exercise: For $\mathcal{H} = \mathbb{C}^2$ we consider the *maximally mixed state*

$$\hat{\rho}_1 := \tfrac{1}{2}\big(|0\rangle\langle 0| + |1\rangle\langle 1|\big) \tag{3.12}$$

and the superposition state

$$\hat{\rho}_2 := \tfrac{1}{2}\big(|0\rangle + |1\rangle\big)\big(\langle 0| + \langle 1|\big) \,, \tag{3.13}$$

where $(|0\rangle, |1\rangle) \subset \mathbb{C}^2$ is the canonical basis. Find an observable that distinguishes $\hat{\rho}_1$ and $\hat{\rho}_2$.

3.1.2 Time evolution

Now we want to see that the description of quantum states by density operators is compatible with the time evolution given by the Schrödinger equation

$$\mathrm{i}\hbar \frac{\mathrm{d}}{\mathrm{d}t} |\psi(t)\rangle = H |\psi(t)\rangle \,. \tag{3.14}$$

As usual, H denotes the Hamiltonian here. For $\hat{\rho}(t) = |\psi(t)\rangle\langle\psi(t)|$ (case (3.7)), the Schrödinger equation implies the *von Neumann equation*

$$\mathrm{i}\hbar\, \dot{\hat{\rho}} = [\hat{H}, \hat{\rho}] \tag{3.15}$$

(quick *exercise*), where $[\hat{A}, \hat{B}] := \hat{A}\hat{B} - \hat{B}\hat{A}$ defines the *commutator*. Since this differential equation (3.15) is linear in $\hat{\rho}$ and every quantum state $\hat{\rho}$ can be written as a linear combination (3.8) of pure quantum states, it also holds for all quantum states. For a time-independent Hamiltonian H, the Schrödinger equation is solved by

$$|\psi(t)\rangle = \hat{U}(t) |\psi(t=0)\rangle \tag{3.16}$$

with the *time evolution operator*

$$\hat{U}(t) := \mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar} \,; \tag{3.17}$$

the exponential of an operator is defined via the spectral calculus (section 1.7). Similarly, the von Neumann equation is solved by

$$\hat{\rho}(t) = \hat{U}(t)\hat{\rho}(t=0)\hat{U}(t)^\dagger \,. \tag{3.18}$$

With this, the expectation value of an observable $\hat{A} \in \mathrm{Herm}(\mathcal{H})$ can be written as

$$\begin{aligned} \langle \hat{A} \rangle_{\hat{\rho}(t)} &= \mathrm{Tr}[\hat{U}(t)\hat{\rho}(t=0)\hat{U}(t)^\dagger \hat{A}] \\ &= \mathrm{Tr}[\hat{\rho}(t=0)\hat{A}(t)] \end{aligned} \tag{3.19}$$

with

$$\hat{A}(t) = \hat{U}(t)^\dagger \hat{A} \hat{U}(t) \qquad \text{(Heisenberg picture)} \,. \tag{3.20}$$

3.1.3 Composite systems

Composite systems are both many-body systems and single particles with several degrees of freedom, such as motional, rotational, vibrational, and spin degrees of freedom. In both cases, each degree of freedom i is associated with a Hilbert space $\mathcal{H}_i$, and the Hilbert space of all degrees of freedom is given as the *tensor product*

$$\mathcal{H} = \bigotimes_{i=1}^{N} \mathcal{H}_i \,. \tag{3.21}$$

Now we briefly summarize the required details on the tensor product. For the sake of clarity, we consider the case $N = 2$.
The *inner product* of two *product vectors* $|\phi_1\rangle \otimes |\phi_2\rangle,\ |\psi_1\rangle \otimes |\psi_2\rangle \in \mathcal{H}_1 \otimes \mathcal{H}_2$ is defined via

$$\big(\langle\phi_1| \otimes \langle\phi_2|\big)\big(|\psi_1\rangle \otimes |\psi_2\rangle\big) \coloneqq \langle\phi_1|\psi_1\rangle\,\langle\phi_2|\psi_2\rangle \,. \tag{3.22}$$

The inner product of two arbitrary vectors is defined accordingly as its sesquilinear extension. It can be computed with respect to orthonormal bases $\{|i\rangle_1\} \subset \mathcal{H}_1$ and $\{|j\rangle_2\} \subset \mathcal{H}_2$. Here we have the *product basis*

$$|i,j\rangle \coloneqq |i\rangle|j\rangle \coloneqq |i\rangle_1 \otimes |j\rangle_2 \,, \tag{3.23}$$

which is an orthonormal basis of $\mathcal{H}_1 \otimes \mathcal{H}_2$. For a vector $|\psi\rangle \in \mathcal{H}_1 \otimes \mathcal{H}_2$, the basis expansion is thus

$$|\psi\rangle = \sum_{i,j} \psi_{i,j}\,|i,j\rangle \tag{3.24}$$

with expansion coefficients

$$\psi_{i,j} = \langle i,j|\psi\rangle \,. \tag{3.25}$$

The inner product of two vectors $|\phi\rangle, |\psi\rangle \in \mathcal{H}_1 \otimes \mathcal{H}_2$ with expansion coefficients $\{\phi_{i,j}\}$ and $\{\psi_{i,j}\}$ is

$$\langle\phi|\psi\rangle = \sum_{i,j} \phi^*_{i,j}\psi_{i,j} \,, \tag{3.26}$$

where $z^* = \mathrm{Re}(z) - \mathrm{i}\,\mathrm{Im}(z)$ denotes the complex conjugate of a number $z \in \mathbb{C}$.
A *product operator* $\hat{A}_1 \otimes \hat{A}_2 \in \mathrm{L}(\mathcal{H}_1 \otimes \mathcal{H}_2) \cong \mathrm{L}(\mathcal{H}_1) \otimes \mathrm{L}(\mathcal{H}_2)$ can be defined as the linear extension of

$$(\hat{A}_1 \otimes \hat{A}_2)|\psi_1\rangle \otimes |\psi_2\rangle \coloneqq (\hat{A}_1|\psi_1\rangle) \otimes (\hat{A}_2|\psi_2\rangle) \,. \tag{3.27}$$

Local observables

An observable on system 1 is an observable of the form

$$\hat{A} = \hat{A}_1 \otimes \mathbb{1} \,. \tag{3.28}$$

This provides the natural extension of observables to larger systems.

Product states

Product states are of the form

$$\hat{\rho} = \hat{\rho}_1 \otimes \hat{\rho}_2 \,. \tag{3.29}$$

They describe independent state preparations on two systems.

Short exercises: Show that

- $(\hat{A}_1 \otimes \hat{A}_2)(\hat{B}_1 \otimes \hat{B}_2) = (\hat{A}_1\hat{B}_1) \otimes (\hat{A}_2\hat{B}_2)$
- $\hat{\rho}_1 \otimes \hat{\rho}_2$ is a density operator if $\hat{\rho}_1$ and $\hat{\rho}_2$ are density operators.
- Find a density operator in $\mathcal{S}(\mathbb{C}^2 \otimes \mathbb{C}^2)$ that is not of the product form $\hat{\rho}_1 \otimes \hat{\rho}_2$.

3.1.4 Reduced states/marginals

Now we consider states in $\mathcal{S}(\mathcal{H}_1 \otimes \mathcal{H}_2)$.

Partial trace

The *partial trace* $\mathrm{Tr}_2 : \mathrm{L}(\mathcal{H}_1 \otimes \mathcal{H}_2) \to \mathrm{L}(\mathcal{H}_1)$ is the linear map defined by

$$\mathrm{Tr}_2[\hat{X}_1 \otimes \hat{X}_2] = \hat{X}_1 \,\mathrm{Tr}[\hat{X}_2]\,. \tag{3.30}$$

The *reduced state* (or the *marginal*) of $\hat{\rho} \in \mathcal{S}(\mathcal{H}_1 \otimes \mathcal{H}_2)$ on $\mathcal{H}_1$ is $\mathrm{Tr}_2[\hat{\rho}] \in \mathcal{S}(\mathcal{H}_1)$. The partial trace Tr_1 and the reduced state on $\mathcal{H}_2$ are defined analogously.

It holds that

$$\mathrm{Tr}\big[\hat{\rho}(\hat{A}_1 \otimes \mathbb{1})\big] = \mathrm{Tr}\big[\mathrm{Tr}_2[\hat{\rho}]\hat{A}_1\big]\,, \tag{3.31}$$

i.e., the reduced state $\mathrm{Tr}_2[\hat{\rho}]$ can describe all *local expectation values* on system 1.

Short exercises:

- Show that the reduced state is indeed a density operator.
- Prove eq. (3.31).
- Let $\hat{\rho} \in \mathcal{S}(\mathbb{C}^{d_1} \otimes \mathbb{C}^{d_2})$ be a diagonal density operator. Show that $\mathrm{Tr}_2[\hat{\rho}]$ is also a diagonal density operator. Furthermore, let p and $p^{(1)}$ be the probability vectors given by the respective diagonals. Explain why $p^{(1)}$ can be regarded as a marginal distribution of p (cf. section 1.3.1.6).

3.2 Information measures for quantum states

The Shannon entropy has a natural generalization to quantum states, which is called the von Neumann entropy. Entropy measures play an important role in quantum information theory [18].
As before, we set $0\ln(0) := 0$.

Definition 3.2 (Von Neumann entropy)**.** *The* von Neumann entropy *of a density operator $\hat{\rho}$ is*

$$S(\hat{\rho}) := -k\,\mathrm{Tr}[\hat{\rho}\ln(\hat{\rho})]\,, \tag{3.32}$$

where the unit constant k is chosen according to the context.

Properties:

(i) The entropy of a density operator $\hat{\rho}$ with spectral decomposition $\hat{\rho} = \sum_i \lambda_i |\lambda_i\rangle\langle\lambda_i|$ is

$$S(\hat{\rho}) = -k\sum_i \lambda_i \ln(\lambda_i) = S(\lambda)\,, \tag{3.33}$$

where the vector of eigenvalues λ of a density operator is always a **PMF!**.

(ii) For all $\hat{\rho} \in \mathcal{S}(\mathcal{H})$ we have

$$0 \le S(\hat{\rho}) \le k\ln(\dim(\mathcal{H}))\,, \tag{3.34}$$

which we briefly prove below. For pure states $\hat{\rho} = |\psi\rangle\langle\psi|$ we have

$$S(|\psi\rangle\langle\psi|) = 0 \tag{3.35}$$

and for the *maximally mixed state* $\hat{\rho} = \frac{\mathbb{1}}{\dim(\mathcal{H})}$

$$S(\mathbb{1}/\dim(\mathcal{H})) = k \ln(\dim(\mathcal{H}))\,. \tag{3.36}$$

These bounds are inherited from the corresponding bounds for the Shannon entropy (section 1.4.1).

(iii) The entropy is *additive on product states*,

$$S(\hat{\rho} \otimes \hat{\sigma}) = S(\hat{\rho}) + S(\hat{\sigma}) \tag{3.37}$$

for all $\hat{\rho} \in \mathcal{S}(\mathcal{H}_1)$ and $\hat{\sigma} \in \mathcal{S}(\mathcal{H}_2)$ (short exercise) and, in general, *subadditive*,

$$S(\hat{\rho}) \leq S(\mathrm{Tr}_2[\hat{\rho}]) + S(\mathrm{Tr}_1[\hat{\rho}]) \tag{3.38}$$

for all $\hat{\rho} \in \mathcal{S}(\mathcal{H}_1 \otimes \mathcal{H}_2)$, which we briefly prove in lemma 3.5 below.

(iv) The entropy is *concave* [18, Theorem 5.23], i.e.,

$$S\Big(\sum_{i=1}^{n} p_i \hat{\rho}_i\Big) \geq \sum_{i=1}^{n} p_i S(\hat{\rho}_i) \tag{3.39}$$

for all $(\hat{\rho}_i) \subset \mathcal{S}(\mathcal{H})$ and probability vectors $p \in [0,1]^n$.

We denote the *kernel* of an operator $\hat{X} \in \mathrm{L}(\mathcal{H})$ by

$$\ker(\hat{X}) \coloneqq \{|\psi\rangle \in \mathcal{H} :\ \hat{X}|\psi\rangle = 0\}\,. \tag{3.40}$$

Similarly to how the von Neumann entropy generalizes the Shannon entropy, the *relative entropy* generalizes the Kullback–Leibler divergence (supplementary material, section 1.4.2).

Definition 3.3 (Relative entropy)**.** *The* relative entropy *of two density operators $\hat{\rho}, \hat{\sigma} \in \mathcal{S}(\mathcal{H})$ is*

$$S(\hat{\rho}\|\hat{\sigma}) \coloneqq \begin{cases} k\,\mathrm{Tr}[\hat{\rho}\ln(\hat{\rho}) - \hat{\rho}\ln(\hat{\sigma})] & \text{if } \ker(\hat{\sigma}) \subset \ker(\hat{\rho})\,, \\ \infty & \text{otherwise,} \end{cases} \tag{3.41}$$

where the unit constant k is chosen according to the context.

Properties:

- The relative entropy of density operators $\hat{\rho}$ and $\hat{\sigma}$ with spectral decompositions $\hat{\rho} = \sum_i \lambda_i |\lambda_i\rangle\langle\lambda_i|$ and $\hat{\sigma} = \sum_j \xi_j |\xi_j\rangle\langle\xi_j|$ is

$$S(\hat{\rho}\|\hat{\sigma}) = k \sum_i \lambda_i \Big(\ln(\lambda_i) - \sum_j |\langle\xi_j\,|\,\lambda_i\rangle|^2 \ln(\xi_j)\Big) \tag{3.42}$$

(short exercise).

- In general, $S(\hat{\rho}\|\hat{\sigma}) \neq S(\hat{\sigma}\|\hat{\rho})$.

With the following lemma, the relative entropy can be regarded as a non-symmetric distance function on $\mathcal{S}(\mathcal{H})$.

Lemma 3.4 (Klein's inequality)**.** *For all $\hat{\rho}, \hat{\sigma} \in \mathcal{S}(\mathcal{H})$ we have (with $k > 0$)*

$$S(\hat{\rho}\|\hat{\sigma}) \geq 0 \tag{3.43}$$

and

$$S(\hat{\rho}\|\hat{\sigma}) = 0 \quad \Leftrightarrow \quad \hat{\rho} = \hat{\sigma}\,. \tag{3.44}$$

Proof. We use complete orthonormal eigenbases $(|\lambda_i\rangle)$ and $(|\xi_j\rangle)$ of $\hat{\rho}$ and $\hat{\sigma}$, i.e., $\sum_i |\lambda_i\rangle\langle\lambda_i| = \sum_j |\xi_j\rangle\langle\xi_j| = \mathbb{1}$. We assume that $\ker(\hat{\sigma}) \subset \ker(\hat{\rho})$, since otherwise $S(\hat{\rho}\|\hat{\sigma}) = \infty > 0$. Then

$$\begin{aligned}
\frac{1}{k} S(\hat{\rho}\|\hat{\sigma}) &= \sum_i \lambda_i \Big(\ln(\lambda_i) - \sum_j |\langle \xi_j | \lambda_i \rangle|^2 \ln(\xi_j) \Big) && (3.45)\\
&= \sum_i \lambda_i \Bigg(\Big(\sum_j |\langle \xi_j | \lambda_i \rangle|^2 \Big) \ln(\lambda_i) - \sum_j |\langle \xi_j | \lambda_i \rangle|^2 \ln(\xi_j) \Bigg) && (3.46)\\
&= \sum_{i,j} \lambda_i |\langle \xi_j | \lambda_i \rangle|^2 \big(\ln(\lambda_i) - \ln(\xi_j) \big) && (3.47)\\
&= - \sum_{i,j} \lambda_i |\langle \xi_j | \lambda_i \rangle|^2 \ln\Big(\frac{\xi_j}{\lambda_i} \Big) && (3.48)\\
&\geq - \sum_{i,j} \lambda_i |\langle \xi_j | \lambda_i \rangle|^2 \Big(1 - \frac{\xi_j}{\lambda_i} \Big) && (3.49)\\
&= \sum_{i,j} |\langle \xi_j | \lambda_i \rangle|^2 (\xi_j - \lambda_i) && (3.50)\\
&= \sum_j \Big(\sum_i |\langle \xi_j | \lambda_i \rangle|^2 \Big) \xi_j - \sum_i \Big(\sum_j |\langle \xi_j | \lambda_i \rangle|^2 \Big) \lambda_i && (3.51)\\
&= 1 - 1 = 0\,. && (3.52)
\end{aligned}$$

In eq. (3.46) as well as eq. (3.52) we have used $\sum_i |\langle \xi_j | \lambda_i \rangle|^2 = \sum_j |\langle \xi_j | \lambda_i \rangle|^2 = 1$ (normalization, complete bases), and in eq. (3.49) that the first-order Taylor expansion (tangent) of a concave function yields an upper bound. Moreover, the normalization of the density operators ($\sum_i \lambda_i = \sum_j \xi_j = 1$) was used in eq. (3.52).
The inequality (3.49) is satisfied with equality if for all i, j we have that either $|\langle \xi_j | \lambda_i \rangle|^2 = 0$ or $\ln(\xi_j/\lambda_i) = 0$, i.e., if $\hat{\rho} = \hat{\sigma}$. □

As a simple application of the lemma, we show that the upper bound in eq. (3.34) holds. From

$$\begin{aligned}
0 &\leq S(\hat{\rho}\|\mathbb{1}/\dim(\mathcal{H})) \\
&= -k \operatorname{Tr}[\hat{\rho} \ln(\mathbb{1}/\dim(\mathcal{H}))] - S(\hat{\rho}) \\
&= k \ln(\dim(\mathcal{H})) - S(\hat{\rho})
\end{aligned} \tag{3.53}$$

the upper bound (3.34) follows.
One can argue that the subadditivity of the von Neumann entropy follows from the subadditivity of the Shannon entropy, or use Klein's inequality again:

Lemma 3.5 (Subadditivity of the entropy)**.** *For all $\hat{\rho} \in \mathcal{S}(\mathcal{H}_1 \otimes \mathcal{H}_2)$,*

$$S(\hat{\rho}) \leq S(\operatorname{Tr}_2[\hat{\rho}]) + S(\operatorname{Tr}_1[\hat{\rho}])\,. \tag{3.54}$$

Proof. With the choice

$$\hat{\sigma} = \operatorname{Tr}_2[\hat{\rho}] \otimes \operatorname{Tr}_1[\hat{\rho}] \tag{3.55}$$

we have

$$0 \leq S(\hat{\rho}\|\hat{\sigma}) = -k \operatorname{Tr}\big[\hat{\rho} \ln(\operatorname{Tr}_2[\hat{\rho}] \otimes \operatorname{Tr}_1[\hat{\rho}])\big] - S(\hat{\rho})\,. \tag{3.56}$$

Because of $\ln(\hat{A} \otimes \hat{B}) = \ln(\hat{A}) \otimes \mathbb{1} + \mathbb{1} \otimes \ln(\hat{B})$, this yields

$$\begin{aligned}
S(\hat{\rho}) &\leq -k \operatorname{Tr}\big[\hat{\rho}\big(\ln(\operatorname{Tr}_2[\hat{\rho}]) \otimes \mathbb{1}\big)\big] - k \operatorname{Tr}\big[\hat{\rho}\big(\mathbb{1} \otimes \ln(\operatorname{Tr}_1[\hat{\rho}])\big)\big] \\
&= -k \operatorname{Tr}\big[\operatorname{Tr}_2[\hat{\rho}] \ln(\operatorname{Tr}_2[\hat{\rho}])\big] - k \operatorname{Tr}\big[\operatorname{Tr}_1[\hat{\rho}] \ln(\operatorname{Tr}_1[\hat{\rho}])\big] \\
&= S(\operatorname{Tr}_2[\hat{\rho}]) + S(\operatorname{Tr}_1[\hat{\rho}])\,,
\end{aligned} \tag{3.57}$$

where we have used eq. (3.31). □

For the derivation of the generalized canonical distribution in the quantum-mechanical case, we need the following statement.

Lemma 3.6 (Pinching inequality)**.** *Let* $(\hat{P}_j) \subset \mathrm{Herm}(\mathcal{H})$ *be orthogonal projectors with*

$$\sum_j \hat{P}_j = \mathbb{1}\,. \tag{3.58}$$

We define the pinching map $\mathcal{P} : \mathrm{L}(\mathcal{H}) \to \mathrm{L}(\mathcal{H})$ *via*

$$\mathcal{P}(X) \coloneqq \sum_j \hat{P}_j X \hat{P}_j\,. \tag{3.59}$$

Then $\mathcal{P}(\hat{\rho}) \in \mathcal{S}(\mathcal{H})$ *and*

$$S(\hat{\rho}) \leq S(\mathcal{P}(\hat{\rho})) \tag{3.60}$$

for all $\hat{\rho} \in \mathcal{S}(\mathcal{H})$*. Moreover,* $S(\hat{\rho}) = S(\mathcal{P}(\hat{\rho}))$ *if and only if* $\hat{\rho} = \mathcal{P}(\hat{\rho})$*.*

Proof. One can directly verify that $\mathcal{P}(\hat{\rho})$ is a density operator.
Furthermore, we have

$$\begin{aligned} S(\hat{\rho}\|\mathcal{P}(\hat{\rho})) &= k\,\mathrm{Tr}\left[\hat{\rho}\ln(\hat{\rho}) - \hat{\rho}\ln\left(\sum_j \hat{P}_j\hat{\rho}\hat{P}_j\right)\right] \\ &= -k\,\mathrm{Tr}\left[\hat{\rho}\sum_k \hat{P}_k \ln\left(\sum_j \hat{P}_j\hat{\rho}\hat{P}_j\right)\hat{P}_k\right] - S(\hat{\rho}) \\ &= -k\,\mathrm{Tr}[\mathcal{P}(\hat{\rho})\ln(\mathcal{P}(\hat{\rho}))] - S(\hat{\rho}) \\ &= S(\mathcal{P}(\hat{\rho})) - S(\hat{\rho}) \end{aligned} \tag{3.61}$$

and, by the nonnegativity (3.43),

$$S(\hat{\rho}) \leq S(\mathcal{P}(\hat{\rho}))\,. \tag{3.62}$$

If $\mathcal{P}(\hat{\rho}) \neq \hat{\rho}$, then eq. (3.44) also implies $S(\mathcal{P}(\hat{\rho})) > S(\hat{\rho})$, which also proves the last claim. □

3.3 Analogy table: classical mechanics vs. quantum mechanics

The descriptions of classical mechanics and of quantum mechanics exhibit far-reaching analogies, which we briefly list here.

	Classical mechanics	Quantum mechanics
Configuration space	Phase space Γ, e.g., $\Gamma = \mathbb{R}^{6N}$	Hilbert space $\mathcal{H}$ e.g., $\mathcal{H} = \mathcal{L}^2(\mathbb{R}^{3N})$
Coordinates	Canonical coord. $p_1, \ldots, q_{3N}$	Orthogonal basis
States	PDFs $\rho \geq 0$, $\int \mathrm{d}\xi\, \rho(\xi) = 1$	Density operators $\mathcal{S}(\mathcal{H})$ $\hat{\rho} \succeq 0$, $\mathrm{Tr}[\hat{\rho}] = 1$
Observables	Phase-space function $M : \Gamma \to \mathbb{R}$	Self-adj. operator $\hat{A} = \hat{A}^\dagger$
Expectation values	Integral $\langle M\rangle_\rho = \int \mathrm{d}\xi\, \rho(\xi) M(\xi)$	Trace $\langle \hat{A}\rangle_{\hat{\rho}} = \mathrm{Tr}[\hat{\rho}\hat{A}]$

Pure states	Dirac measure $\rho = \delta_{\xi_0}$	State vector $\hat{\rho} = \lvert\psi\rangle\langle\psi\rvert$
One particle	$\Gamma = \{(q,p)^\mathsf{T} :\ q,p \in \mathbb{R}^3\}$	$\mathcal{H} = \mathcal{L}^2(\mathbb{R}^3)$
Composition	$\Gamma = \Gamma_1 \times \Gamma_2$	$\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$
Local observables	$M(\xi_1,\xi_2) = M_1(\xi_1)$	$\hat{A} = \hat{A}_1 \otimes \mathbb{1}$
Product observables	$(M_1 \times M_2)(\xi_1,\xi_2) = M_1(\xi_1)M_2(\xi_2)$	$\hat{A}_1 \otimes \hat{A}_2$
Independence	$\rho(\xi_1,\xi_2) = \rho_1(\xi_1)\rho_2(\xi_2)$	$\hat{\rho} = \hat{\rho}_1 \otimes \hat{\rho}_2$
Marginals	$\rho_1(\xi_1) = \int \mathrm{d}\xi_2\, \rho(\xi_1,\xi_2)$	$\hat{\rho}_1 = \mathrm{Tr}_2[\hat{\rho}]$
Energy	Hamilton function H	Hamiltonian H
Dynamics	$\dot{\rho}_t = \{\rho_t, H\}$ (Poisson bracket) $\dot{p}_i = -\frac{\partial H}{\partial q_i}, \dot{q}_i = \frac{\partial H}{\partial p_i}$ $\rho_t(\xi) = \rho(\mathcal{F}_{-t}(\xi))$	$\dot{\hat{\rho}}_t = -\frac{\mathrm{i}}{\hbar}[\hat{H}, \hat{\rho}]$ $\mathrm{i}\hbar\lvert\dot{\psi}(t)\rangle = \hat{H}\lvert\psi(t)\rangle$ $U_t = \mathrm{e}^{-\mathrm{i}Ht/\hbar}$
Independent dynamics	$H(\xi_1,\xi_2) = H_1(\xi_1) + H_2(\xi_2)$	$\hat{H} = \hat{H}_1 \otimes \mathrm{id} + \mathrm{id} \otimes \hat{H}_2$
Entropy	Shannon $S(p) = -k\sum_i p_i \ln(p_i)$ Differential $S(\rho) = -k\int \mathrm{d}\xi\, \rho(\xi)\ln\rho(\xi)$	Von Neumann $S(\hat{\rho}) = -k\,\mathrm{Tr}[\hat{\rho}\ln(\hat{\rho})]$
Gen. canonical distr. (ν: Einstein sum.)	$\rho(\xi) = \frac{1}{Z}\,\mathrm{e}^{-\lambda_\nu M^{(\nu)}(\xi)}$ (PDF)	$\hat{\rho} = \frac{1}{Z}\mathrm{e}^{-\lambda_\nu \hat{M}^{(\nu)}} \in \mathcal{S}(\mathcal{H})$, $\hat{M}^{(\nu)} \in \mathrm{Herm}(\mathcal{H})$

3.4 The generalized canonical density operator

We can now extend the principle of maximum entropy (section 2.1) to quantum systems, which was likewise initiated by Jaynes [19]. To describe a quantum many-body system, we assume that it is described by observables $\hat{M}^{(\nu)} \in \mathrm{Herm}(\mathcal{H})$ with $\nu \in [m]$. In order to arrive at a stationary equilibrium state, we assume that these observables are conserved quantities, i.e.,

$$[\hat{M}^{(\nu)}, \hat{H}] = 0 \tag{3.63}$$

for all ν, where $\hat{H} \in \mathrm{Herm}(\mathcal{H})$ is the Hamiltonian. Furthermore, we again assume that their expectation values

$$\langle \hat{M}^{(\nu)} \rangle = \mathsf{M}^{(\nu)} \tag{3.64}$$

are known.

Moreover, we make an assumption that will massively simplify the analysis of the maximum-entropy states and that is satisfied in many important situations: we assume that the observables also commute among each other,

$$[\hat{M}^{(\nu)}, \hat{M}^{(\mu)}] = 0 \tag{3.65}$$

for all ν and μ. We note that this assumption is automatically satisfied if the Hamiltonian has no degenerate eigenvalues. It should also be mentioned that a generalization of maximum-entropy states to noncommuting conserved quantities has recently been formulated [20].

Since all operators involved commute, we can find an orthonormal basis of energy eigenstates $\{\lvert j\rangle\} \subset \mathcal{H}$ in which they are all simultaneously diagonal. Thus, the arguments that led to the generalized canonical distribution largely carry over to the quantum case.

The *diagonal* density operator that maximizes the entropy under the constraints

$\hat{\rho} \in \mathcal{S}(\mathcal{H})$ and eq. (3.64) is of the form

$$\hat{\rho} = \frac{1}{Z} \mathrm{e}^{-\lambda_\nu \hat{M}^{(\nu)}} \qquad \text{(Einstein summation)}\,, \tag{3.66}$$

i.e., it has the diagonal entries

$$\hat{\rho}_{j,j} = \frac{1}{Z} \exp\Big(-\sum_\nu \lambda_\nu \hat{M}^{(\nu)}_{j,j}\Big)\,, \tag{3.67}$$

which follows from section 2.1 (the restriction that $\hat{\rho}$ be diagonal reduces the entropy maximization problem to the classical entropy maximization problem). This density operator is also called the *generalized Gibbs ensemble*.

Theorem 3.7 (Quantum generalized canonical distribution)**.** *Let $\hat{H}$ be a Hamiltonian on $\mathcal{H}$ and let $(\hat{M}^{(\nu)})_{\nu\in[m]} \subset \mathrm{Herm}(\mathcal{H})$ be pairwise commuting conserved quantities. The state $\hat{\rho} \in \mathcal{S}(\mathcal{H})$ that maximizes the entropy (3.32) under the constraints*

$$\langle \hat{M}^{(\nu)} \rangle = \mathsf{M}^{(\nu)} \qquad \forall \nu \in [m] \tag{3.68}$$

is

$$\hat{\rho} = \frac{1}{Z} \mathrm{e}^{-\lambda_\nu \hat{M}^{(\nu)}} \quad \textit{(Einstein summation)}, \tag{3.69}$$

where $Z = \mathrm{Tr}[\mathrm{e}^{-\lambda_\nu \hat{M}^{(\nu)}}]$ and $\lambda \in \mathbb{R}^m$ is implicitly given by eq. (3.68).

Proof. We have $\hat{\rho} \in \mathcal{S}(\mathcal{H})$ and $\langle \hat{M}^{(\nu)} \rangle_{\hat{\rho}} = \mathsf{M}^{(\nu)}$ for all ν (short exercise).
It remains to show that $\hat{\rho}$ maximizes the entropy. To this end, we choose a joint orthonormal eigenbasis $(|j\rangle) \subset \mathcal{H}$ of $\hat{H}$ and $(\hat{M}^{(\nu)})$, i.e.,

$$\begin{aligned} \hat{H} &= \sum_j E_j |j\rangle\langle j|\,, \\ \hat{M}^{(\nu)} &= \sum_j \mu_j^{(\nu)} |j\rangle\langle j| \end{aligned} \tag{3.70}$$

with eigenvalues $(E_j), (\mu_j^{(\nu)}) \subset \mathbb{R}$. We now define a pinching map $\mathcal{P} : \mathrm{L}(\mathcal{H}) \to \mathrm{L}(\mathcal{H})$ via

$$\mathcal{P}(\hat{X}) \coloneqq \sum_j |j\rangle\langle j|\hat{X}|j\rangle\langle j|\,. \tag{3.71}$$

Then

$$\mathcal{P}(\hat{\rho}) = \hat{\rho}\,. \tag{3.72}$$

With lemma 3.6 it follows that an entropy-maximizing density operator must satisfy this equation. Under this restriction, the entropy maximization yields the generalized canonical state (3.69), see section 2.1. □

The normalization factor

$$Z(\lambda) = \mathrm{Tr}\big[\mathrm{e}^{-\lambda_\nu \hat{M}^{(\nu)}}\big] \tag{3.73}$$

is here again called the *partition function*. The entropy of the generalized canonical density operator $\hat{\rho}$ is again

$$S(\mathsf{M}) \coloneqq S(\hat{\rho}) = k\langle \lambda, \mathsf{M}\rangle - k\Psi(\lambda) \tag{3.74}$$

with

$$\Psi = -\ln(Z) \tag{3.75}$$

(quick exercise) and Lagrange parameters λ_ν, which are again given as

$$\frac{\partial S(\mathsf{M})}{\partial \mathsf{M}^{(\nu)}} = k\lambda_\nu\,. \tag{3.76}$$

Completely analogously to the classical case, we again obtain

$$-\frac{\partial \ln(Z)}{\partial \lambda_\nu} = \mathsf{M}^{(\nu)} \,. \tag{3.77}$$

3.5 Dynamical equilibration and thermalization (supplementary material)

As in section 2.2.2, we want to motivate that equilibrium states given by generalized canonical distributions frequently occur in nature. To this end, we consider a state $\hat{\rho}(t) \in \mathcal{S}(\mathcal{H})$ evolved in time according to the von Neumann equation (3.15) and define the *time-averaged state* as

$$\hat{\omega} \coloneqq \overline{\hat{\rho}(t)} \coloneqq \lim_{T\to\infty} \frac{1}{T} \int_0^T \hat{\rho}(t)\, \mathrm{d}t \,. \tag{3.78}$$

We first want to characterize the time-averaged state more precisely. For this purpose, we write the Hamiltonian in terms of the energy eigenprojectors $\hat{P}_j$ as

$$\hat{H} = \sum_j E_j \hat{P}_j \tag{3.79}$$

with $E_j \neq E_i$ for $j \neq i$. With these, we again define a pinching map $\mathcal{P} : \mathrm{L}(\mathcal{H}) \to \mathrm{L}(\mathcal{H})$ via

$$\mathcal{P}(\hat{X}) \coloneqq \sum_j \hat{P}_j \hat{X} \hat{P}_j \,. \tag{3.80}$$

Proposition 3.8 (Time average)**.** *The time-averaged state is*

$$\overline{\hat{\rho}(t)} = \mathcal{P}(\hat{\rho}(0)) \,. \tag{3.81}$$

Proof. We consider the block matrix element (i, j) in the energy eigenbasis:

$$\begin{aligned}
\hat{P}_i \overline{\hat{\rho}(t)} \hat{P}_j &= \lim_{T\to\infty} \frac{1}{T} \int_0^T \hat{P}_i \mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar} \hat{\rho}(0) \mathrm{e}^{\mathrm{i}\hat{H}t/\hbar} \hat{P}_j \,\mathrm{d}t \\
&= \lim_{T\to\infty} \frac{1}{T} \int_0^T \hat{P}_i \mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar} \hat{P}_i \hat{\rho}(0) \hat{P}_j \mathrm{e}^{\mathrm{i}\hat{H}t/\hbar} \hat{P}_j \,\mathrm{d}t \\
&= \lim_{T\to\infty} \frac{1}{T} \int_0^T \mathrm{e}^{-\mathrm{i}(E_i - E_j)t/\hbar} \,\mathrm{d}t\, \hat{P}_i \hat{\rho}(0) \hat{P}_j \\
&= \delta_{i,j} \hat{P}_i \hat{\rho}(0) \hat{P}_j \,,
\end{aligned} \tag{3.82}$$

i.e., the time-averaged state $\overline{\hat{\rho}(t)}$ is block diagonal in the energy eigenbasis. This implies the claim. □

We note that if a dynamics equilibrates in the sense that expectation values of relevant observables equilibrate, then the equilibrium state must have the same expectation values as the time-averaged state $\overline{\hat{\rho}(t)}$. If the observables belong to a system Σ, the following definition suggests itself.

Definition 3.9 (Equilibration on time average)**.** *Let $\hat{H} \in \mathrm{Herm}(\mathcal{H}_\Sigma \otimes \mathcal{H}_\mathcal{E})$ be a Hamiltonian acting on a system Σ and an environment $\mathcal{E}$. We call a time-evolved state $\mathrm{Tr}_\mathcal{E}[\hat{\rho}(t)]$ on Σ* equilibrated (on time average) *if, for most t, $\hat{\rho}(t)$ is indistinguishable on Σ from the time-averaged state $\overline{\hat{\rho}(t)}$, i.e.,*

$$\mathrm{Tr}_\mathcal{E}[\hat{\rho}(t)] \approx \mathrm{Tr}_\mathcal{E}[\mathcal{P}(\hat{\rho}(0))] \,. \tag{3.83}$$

Examples of non-equilibrating systems

- Let $|E\rangle, |E'\rangle \in \mathcal{H}_\Sigma \otimes \mathcal{H}_\mathcal{E}$ be energy eigenstates with energies $E < E'$ and $|\psi(0)\rangle \coloneqq (|E\rangle + |E'\rangle)/\sqrt{2}$. Then

$$|\psi(t)\rangle = \mathrm{e}^{-\mathrm{i}Et/\hbar}\big(|E\rangle + \mathrm{e}^{-\mathrm{i}(E'-E)t/\hbar}|E'\rangle\big)/\sqrt{2} \tag{3.84}$$

  and therefore

$$|\psi(t)\rangle\langle\psi(t)| = \tfrac{1}{2}(|E\rangle\langle E| + |E'\rangle\langle E'| + \mathrm{e}^{\mathrm{i}(E'-E)t/\hbar}|E\rangle\langle E'| + \mathrm{e}^{-\mathrm{i}(E'-E)t/\hbar}|E'\rangle\langle E|)\,. \tag{3.85}$$

  It follows that certain matrix entries of the system state $\mathrm{Tr}_\mathcal{E}[|\psi(t)\rangle\langle\psi(t)|]$ oscillate with frequency $(E'-E)/\hbar$, and thus no equilibration takes place.

- Let $\hat{H} = \hat{H}_1 \otimes \mathbb{1} + \mathbb{1} \otimes \hat{H}_2$ be a Hamiltonian of a noninteracting system. Then a nonequilibrium state on one system cannot equilibrate.

Fully interacting systems with an initial state $\hat{\rho}(0)$ that has a significant overlap with many energy eigenstates (large *effective dimension* of $\hat{\rho}(0)$) provably equilibrate in the following sense [21]. If $\dim(\mathcal{H}_\mathcal{E})$ is large, then the time average of the distance between $\mathrm{Tr}_\mathcal{E}[\hat{\rho}(t)]$ and the time-averaged state $\mathrm{Tr}_\mathcal{E}[\hat{\omega}]$ is vanishingly small, i.e.,

$$\overline{\|\mathrm{Tr}_\mathcal{E}[\hat{\rho}(t)] - \mathrm{Tr}_\mathcal{E}[\hat{\omega}]\|} \to 0 \tag{3.86}$$

for $\dim(\mathcal{H}_\mathcal{E}) \to \infty$.

We note that for every observable $\hat{A} \in \mathrm{Herm}(\mathcal{H})$ the equivalence

$$[\hat{H}, \hat{A}] = 0 \quad \Leftrightarrow \quad \mathcal{P}(\hat{A}) = \hat{A} \tag{3.87}$$

holds, i.e., $\hat{A}$ is a conserved quantity if and only if $\mathcal{P}(\hat{A}) = \hat{A}$.
The states that have the same conserved-quantity expectation values as the initial state are

$$\{\hat{\sigma} \in \mathcal{S}(\mathcal{H}) :\ \mathrm{Tr}[\hat{\sigma}\hat{A}] = \mathrm{Tr}[\hat{\rho}(0)\hat{A}]\ \forall \hat{A} = \mathcal{P}(\hat{A})\}\,. \tag{3.88}$$

Among these states, the time-averaged state $\hat{\sigma} = \overline{\hat{\rho}(t)}$ is the one that maximizes the entropy (lemma 3.6).
In short: entropy maximization given all conserved quantities yields the same state as time averaging, i.e., the equilibrium state, provided it exists.

Note that eq. (3.87) characterizes at least $\dim(\mathcal{H})$ many conserved quantities. That is exponentially many in the particle number! Next, we consider situations in which an equilibrium state $\hat{\omega}$ is already uniquely determined by a few relevant macroscopic expectation values (3.64).

Definition 3.10 (Thermalization / equilibration to thermodynamic equilibrium)**.** *We say that a system* thermalizes *to a generalized canonical distribution* (3.69) *(i.e., equilibrates to a thermodynamic equilibrium) if it (i) equilibrates and (ii) the equilibrium state $\hat{\omega}$ coincides with the distribution* (3.69)*.*

There are various models and assumptions that lead from equilibration to thermalization. An overview of different approaches can be found in [14, Chapter 7].

3.6 Indistinguishable particles

We consider a quantum system of N indistinguishable particles. We denote the single-particle Hilbert space by $\mathcal{H}$. Then the N-particle Hilbert space is $\mathcal{H}^{\otimes N}$.
First, we consider $N = 2$. We denote by $\mathbb{F} \in \mathrm{U}(\mathcal{H} \otimes \mathcal{H})$ the flip operator, which is defined via

$$\mathbb{F}|\psi\rangle|\phi\rangle \coloneqq |\phi\rangle|\psi\rangle\,. \tag{3.89}$$

Now let $|\psi\rangle \in \mathcal{H}^{\otimes 2}$ be a state vector of 2 indistinguishable particles. Indistinguishability means that

$$\mathbb{F}|\psi\rangle = \mathrm{e}^{\mathrm{i}\varphi}|\psi\rangle \tag{3.90}$$

for a phase φ that depends on the particle species. Because of

$$\mathbb{F}^2 = \mathbb{1}\,, \tag{3.91}$$

$+1$ and -1 are the only eigenvalues of $\mathbb{F}$ and therefore

$$\mathrm{e}^{\mathrm{i}\varphi} = 1 \qquad \text{or} \qquad \mathrm{e}^{\mathrm{i}\varphi} = -1\,. \tag{3.92}$$

In the case $\mathrm{e}^{\mathrm{i}\varphi} = 1$ one calls $|\psi\rangle$ *symmetric* and in the case $\mathrm{e}^{\mathrm{i}\varphi} = -1$ *antisymmetric*. This consideration can be generalized to N particles. We denote by S_N the symmetric group, i.e., the group of permutations of N elements. For a permutation $\sigma \in \mathsf{S}_N$, we denote by $\hat{U}_\sigma \in \mathrm{U}(\mathcal{H}^{\otimes N})$ the unitary representation with

$$\hat{U}_\sigma |\psi_1\rangle \dots |\psi_N\rangle \coloneqq |\psi_{\sigma(1)}\rangle \dots |\psi_{\sigma(N)}\rangle\,. \tag{3.93}$$

If $|\psi\rangle \in \mathcal{H}^{\otimes N}$ describes indistinguishable particles, then

$$\hat{U}_\sigma |\psi\rangle = |\psi\rangle \tag{3.94}$$

or

$$\hat{U}_\sigma |\psi\rangle = \mathrm{sign}(\sigma)|\psi\rangle \tag{3.95}$$

for all $\sigma \in \mathsf{S}_N$, where

$$\mathrm{sign}(\sigma) \coloneqq \begin{cases} +1 & \text{if } \sigma \text{ is a product of an even number of transpositions,} \\ -1 & \text{if } \sigma \text{ is a product of an odd number of transpositions} \end{cases} \tag{3.96}$$

(a transposition is an exchange of only 2 of the N elements). If a vector $|\psi\rangle \in \mathcal{H}^{\otimes N}$ satisfies eq. (3.94) it is called *symmetric*, and if it satisfies eq. (3.95), *antisymmetric*.

Definition 3.11 (Bosons and fermions)**.** *Indistinguishable particles that are described by symmetric state vectors are called* bosons*, and indistinguishable particles that are described by antisymmetric state vectors are called* fermions*.*

In relativistic quantum field theory, the following important physical statement is proven, which connects the discussed symmetry properties with the spin of the particles.

Theorem 3.12 (Spin–statistics theorem)**.** *State vectors describing identical particles with* integer *spin are* symmetric *under exchange of the particles (bosons).*
State vectors describing identical particles with half-integer *spin are* antisymmetric *under exchange of the particles (fermions).*

We note that the sets of symmetric and antisymmetric vectors form two linear subspaces of $\mathcal{H}^{\otimes N}$. We denote these subspaces by $\mathcal{H}_N^+$ and $\mathcal{H}_N^-$. The orthogonal projectors onto the symmetric and the antisymmetric subspace are denoted by $\hat{P}_N^+, \hat{P}_N^- \in \mathrm{Herm}(\mathcal{H}^{\otimes N})$, respectively. The projectors are given by

$$\hat{P}_N^+ |\psi_1\rangle \dots |\psi_N\rangle = c_\psi^+ \sum_{\sigma \in \mathsf{S}_N} |\psi_{\sigma(1)}\rangle \dots |\psi_{\sigma(N)}\rangle \tag{3.97}$$

and

$$\hat{P}_N^- |\psi_1\rangle \dots |\psi_N\rangle = c_\psi^- \sum_{\sigma \in \mathsf{S}_N} \mathrm{sign}(\sigma)|\psi_{\sigma(1)}\rangle \dots |\psi_{\sigma(N)}\rangle\,, \tag{3.98}$$

where $c_\psi^\pm > 0$ are normalization factors such that $(\hat{P}_N^\pm)^2 = \hat{P}_N^\pm$ (projector property).

If $|\psi_j\rangle = |\psi_{j'}\rangle$ for a pair $j \neq j'$, it interestingly follows that

$$\hat{P}_N^- |\psi_1\rangle \dots |\psi_N\rangle = 0\,, \tag{3.99}$$

i.e., $|\psi_1\rangle \dots |\psi_N\rangle$ cannot define an antisymmetric quantum state. This insight yields the following result.

Pauli principle

Two identical fermions cannot occupy the same single-particle state.

In order to be able to extend the grand canonical ensemble to fermions and bosons, we carry out the following construction. With the direct sum over different particle numbers,

$$\begin{aligned} \mathcal{F}_+ &\coloneqq \overline{\bigoplus_{N=0}^{\infty} \mathcal{H}_N^+} \\ \mathcal{F}_- &\coloneqq \overline{\bigoplus_{N=0}^{\infty} \mathcal{H}_N^-} \end{aligned} \tag{3.100}$$

we form the Hilbert spaces for variable particle number, which are called *Fock spaces*; the bar means that the spaces are topologically closed with respect to the induced inner product, which shall be mentioned as a mathematical detail. The Fock spaces $\mathcal{F}_\pm$ are the Hilbert spaces for a variable number of bosons/fermions with single-particle Hilbert space $\mathcal{H}$. We note that the Hilbert space $\mathcal{H}_0^\pm$ is one-dimensional; the corresponding state $|\emptyset\rangle \in \mathcal{F}_\pm$ is called the *vacuum state*.
Now we choose an orthonormal basis $\{|k\rangle\} \subset \mathcal{H}$. From this we obtain a basis for the Fock spaces $\mathcal{F}_\pm$ by specifying how many particles are in each state $|k\rangle$. We write

$$|N_1, N_2, \dots\rangle \in \mathcal{F}_\pm \qquad \text{in } \textit{occupation number representation} \tag{3.101}$$

for the state with N_k particles in the single-particle state $|k\rangle$. For $\sum_k N_k = N$, the state $|N_1, N_2, \dots\rangle$ is given as $\hat{P}_N^\pm |k_1\rangle^{\otimes N_1} |k_2\rangle^{\otimes N_2} \dots$. We have

$$\begin{aligned} N_k &\in \{0, 1, 2, \dots\} \qquad \text{for bosons,} \\ N_k &\in \{0, 1\} \qquad\quad\;\; \text{for fermions,} \end{aligned} \tag{3.102}$$

for all k, where the restriction of the particle number for fermions follows from the Pauli principle. In this basis, the *particle number operators* $\hat{N}_j$ are defined as

$$\hat{N}_j |N_1, N_2, \dots\rangle = N_j |N_1, N_2, \dots\rangle \tag{3.103}$$

and

$$\hat{N} \coloneqq \sum_j \hat{N}_j\,. \tag{3.104}$$

In short: A choice of basis for the single-particle Hilbert space $\mathcal{H}$ thus fixes the occupation number representation and the particle number operators on $\mathcal{F}_\pm$.

3.7 Ideal quantum gases I

We consider a quantum many-body system of non-interacting indistinguishable particles. Then the Hamiltonian $\hat{H}$ is determined by the single-particle Hamiltonian $\hat{H}_1$ with eigenenergies $\{E_j\}$. As the basis of the single-particle Hilbert space, we choose the eigenbasis $|E_j\rangle$ of $\hat{H}_1$.

3.7.1 Grand canonical ensemble

As an example of the generalized canonical distribution in the quantum case, we consider the grand canonical ensemble for non-interacting fermions and bosons. This yields the Fermi and Bose distributions for the particle number.
Analogously to the classical grand canonical ensemble, we choose the macroscopic constraints

$$\begin{aligned} \langle \hat{H} \rangle &= U \,, \\ \langle \hat{N} \rangle &= N \,, \end{aligned} \tag{3.105}$$

which leads to the grand canonical density operator

$$\hat{\rho} = \frac{1}{\mathcal{Z}} \, \mathrm{e}^{-\beta(\hat{H} - \mu \hat{N})} \tag{3.106}$$

(section 3.4). The probability of measuring the particle numbers $\mathbf{N} = (N_1, N_2, \dots)$ in a particle-number measurement is

$$\mathbb{P}[\mathbf{N}] = \langle \mathbf{N} \, | \hat{\rho} | \mathbf{N} \rangle = \frac{1}{\mathcal{Z}} \exp\left(-\beta \sum_j (E_j - \mu) N_j \right) . \tag{3.107}$$

The grand canonical partition function is

$$\mathcal{Z} = \sum_{\mathbf{N}} \exp\left(-\beta \sum_j (E_j - \mu) N_j \right) . \tag{3.108}$$

Exercise: Show that

$$\mathcal{Z} = \prod_j (1 + t_j) \qquad \text{for fermions,} \tag{3.109}$$

$$\mathcal{Z} = \prod_j \frac{1}{1 - t_j} \qquad \text{for bosons} \tag{3.110}$$

with

$$t_j \coloneqq \mathrm{e}^{-\beta(E_j - \mu)} \,, \tag{3.111}$$

where for bosons one has to assume $E_j > \mu$ (why?).
Here we can identify the *single-particle partition function*

$$\mathcal{Z}_j = \sum_{N_j} \mathrm{e}^{-\beta(E_j - \mu) N_j} \tag{3.112}$$

$$= \begin{cases} 1 + t_j & \text{(fermions)} \\ \frac{1}{1 - t_j} & \text{(bosons)} \end{cases} \tag{3.113}$$

such that $\mathcal{Z} = \prod_j \mathcal{Z}_j$.
With eq. (3.112), the *mean occupation number* in the single-particle state $|E_j\rangle$ is given as

$$\begin{aligned} \langle \hat{N}_j \rangle &= \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln(\mathcal{Z}_j) \\ &= \begin{cases} \frac{t_j}{1 + t_j} = \frac{1}{1/t_j + 1} & \text{(fermions),} \\ \frac{t_j}{1 - t_j} = \frac{1}{1/t_j - 1} & \text{(bosons).} \end{cases} \end{aligned} \tag{3.114}$$

With eq. (3.111) we obtain the distributions

$$\langle \hat{N}_j \rangle = \frac{1}{\exp\left(\frac{E_j - \mu}{kT} \right) - \sigma} \,, \tag{3.115}$$

with

$$\sigma = \begin{cases} -1 & \text{(Fermi–Dirac, fermions)}, \\ 0 & \text{(Boltzmann, classical)}, \\ 1 & \text{(Bose–Einstein, bosons)}. \end{cases} \tag{3.116}$$

Exercise: Sketch $\langle \hat{N}_j \rangle$ as a function of E_j for different temperatures.
Similarly, for the internal energy we obtain (eq. (2.20) with $\lambda_N = -\beta\mu$)

$$U = -\left(\frac{\partial \ln(\mathcal{Z})}{\partial \beta} \right)_{\beta\mu} = \sum_j E_j \langle \hat{N}_j \rangle \,. \tag{3.117}$$

3.7.1.1 Connection to classical statistical mechanics

We assume that the non-interacting spinless particles are confined to a cube with edge length L and that each of them is described by the single-particle Hamiltonian $\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m}$ with single-particle momentum operator $\hat{\mathbf{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z)^\mathsf{T}$. In quantum mechanics it is shown that the momentum eigenvalues are given by

$$\mathbf{p} = \frac{2\pi\hbar}{L}\nu = \frac{h}{L}\nu \quad \text{with} \quad \nu \in \mathbb{Z}^3 \,; \tag{3.118}$$

we recall that the corresponding eigenfunctions of $\hat{\mathbf{p}}$ for periodic boundary conditions are given by $\psi_{\mathbf{p}}(\mathbf{x}) = L^{-3/2} \mathrm{e}^{\mathrm{i}\mathbf{p}\cdot\mathbf{x}/\hbar}$. With this, e.g., the single-particle partition function can be approximated as

$$\sum_{\mathbf{p}} \mathrm{e}^{-\beta(E_{\mathbf{p}} - \mu)} \approx \frac{L^3}{h^3} \int \mathrm{d}^3 p \, \mathrm{e}^{-\beta(E_{\mathbf{p}} - \mu)} \tag{3.119}$$

when L is large and β is small. A similar, though slightly more technical, argument can be made for absorbing boundary conditions, where ψ vanishes on the boundary of the cube.
The argument can also be extended to the N-particle partition function, where the factor $1/N!$ must be taken into account in the integration because of the indistinguishability of the particles. Together with

$$V = L^3 = \int \mathrm{d}^3 x \, \mathrm{e}^{-\beta V_{\text{wall}}(\mathbf{x})} \tag{3.120}$$

and the approximation (3.119), this justifies the definition of the classical phase-space volume element (2.32).
The energy eigenvalues of non-interacting particles are, for the given momentum eigenvalues (3.118), given as

$$E_{\mathbf{p}} = \frac{\mathbf{p}^2}{2m} \,. \tag{3.121}$$

Exercise: Show that inserting $E_{\mathbf{p}}$ into eq. (3.108) again yields the classical partition function in the classical limit.

3.7.1.2 Spin

The theory of quantum-mechanical angular momenta implies that a particle with total spin $s \in \mathbb{Z}/2$ has $2s + 1$ spin degrees of freedom with associated state vectors

$$\{|m_s\rangle\}_{m_s = -s, -s+1 \ldots, s} \subset \mathcal{H}_{\text{spin}} \,, \tag{3.122}$$

which form an orthonormal basis of the spin Hilbert space $\mathcal{H}_{\text{spin}}$, i.e., $\mathcal{H}_{\text{spin}} \cong \mathbb{C}^{2s+1}$. Including further degrees of freedom (e.g., momentum) yields the single-particle Hilbert space

$$\mathcal{H}_1 = \mathcal{H}_{\text{spin}} \otimes \mathcal{H}_{\text{momentum}} \,. \tag{3.123}$$

Now we assume that a spin-s particle is described by a Hamiltonian of the form

$$H = \mathbb{1}_{\text{spin}} \otimes H_{\text{momentum}} \tag{3.124}$$

with $H_{\text{momentum}} \in \text{Herm}(\mathcal{H}_{\text{momentum}})$, i.e., the energy of the particle is independent of its spin, which is a good approximation in many situations.
Now we consider 2 particles with single-particle Hilbert space $\mathcal{H}_1$. If s is half-integer, the particles are fermions. Hence, they are described by antisymmetric state vectors $\psi \in \mathcal{H}_2^-$, i.e.,

$$\psi((m_{s1}, \mathbf{p}_1), (m_{s2}, \mathbf{p}_2)) = -\psi((m_{s2}, \mathbf{p}_2), (m_{s1}, \mathbf{p}_1)) \,. \tag{3.125}$$

A generalized version of this of course also holds for N fermions, and an analogous consideration can be made for particles with integer spin, i.e., bosons.
In any case, because of eq. (3.124), the $2s + 1$ spin degrees of freedom lead to an (additional) degeneracy $g_s = 2s + 1$ of every momentum and hence also energy eigenstate.

4 Thermodynamics

A central original goal of thermodynamics is the description of steam engines and of how heat can optimally be converted into mechanical work. Nowadays, more general cycles are the focus of attention, in which chemical reactions can also play a role. Moreover, specific properties of substances are analyzed and classified, for instance by means of susceptibilities. These can help, e.g., to better understand different states of matter.
Thermodynamics can be built up as a largely self-contained theory on the basis of its laws. Here, however, we will introduce the most important concepts of thermodynamics starting from statistical mechanics. We again consider systems that are described by equilibrium states. The macroscopic properties of these states can in turn be described by a few state variables. These are typically the internal energy U, the volume V, and the particle number N (or $\mathbf{N}$ for multi-component systems). As is common in the literature, from now on we no longer distinguish between the random variable N and its expected value, i.e., $\mathbb{E}[\mathbf{N}] = \mathbf{N}$, and similarly for the volume V.
We assume that the systems under consideration are so large that all fluctuations can be neglected (the ensembles from section 2.3 are then equivalent). Furthermore, we consider *quasi-static* situations, i.e., measurements on and changes of the thermodynamic systems take very long compared to the time the respective system needs to equilibrate.
In this way, temporal changes of thermodynamic variables can also be considered. Frequently, one variable is held constant. Corresponding frequently occurring processes are:

Process	constant quantity
Isobaric	pressure p
Isochoric	volume V
Isothermal	temperature T
Isentropic	entropy S
Adiabatic	heat $\delta Q = 0$

The simplest cycles are composed of precisely such processes.
First, we will find a closed expression for the internal energy $U(S, V, \mathbf{N})$ that unifies

the corresponding relations from the different ensembles of section 2.3. Subsequently, we will complete the list of thermodynamic potentials (see section 2.3). With them, the thermodynamic variables can be written as derivatives in many different ways. This leads to additional relations between these derivatives (Maxwell relations) and to the system-specific *susceptibilities* (e.g., the heat capacity). By means of the dissipation–fluctuation theorem (theorem 2.1), the latter lead to stability criteria that are automatically satisfied in equilibrium and yield constraints on the susceptibilities. Building on this, we will encounter various reversible and irreversible processes (e.g., the Carnot cycle and the Gay-Lussac experiment) and discuss them together with the laws of thermodynamics.
Unless explicitly specified otherwise, in this chapter we consider systems that are described by the extensive thermodynamic variables S, U, V, and N and the associated intensive variables T, p, and μ.

4.1 Euler equation and Gibbs-Duhem relation

In the Gibbs ensemble, $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$ is the differential of the internal energy $U(S, V; N)$ from eq. (2.100); in the grand canonical ensemble, on the other hand, $\mathrm{d}U = T\mathrm{d}S + \mu\mathrm{d}N$ is the differential of $U(S, N; V)$ from eq. (2.110). The respective roles of V and N as macro and micro constraints are thus interchanged. The equivalence of the ensembles implies that, more generally,

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N \tag{4.1}$$

must hold. More generally, we can derive the following equation for U from the extensivity of the quantities S, U, V, and N.

Euler equation

The internal energy is

$$U(S, V, \mathsf{N}) = TS - pV + \mu_j \mathsf{N}^{(j)} \qquad \text{(ESC)}. \tag{4.2}$$

Proof. The internal energy is a homogeneous function of first degree, i.e.,

$$U(\alpha S, \alpha V, \alpha \mathbf{N}) = \alpha U(S, V, \mathbf{N})\,. \tag{4.3}$$

Euler's theorem (theorem 1.13), the fundamental equation (2.111), and $\frac{\partial U}{\partial V} = -p$ therefore yield the claimed equation. □

The Euler equation implies

$$U - TS + pV - \mu N = 0 \qquad \text{(ESC)}, \tag{4.4}$$

i.e., the intensive quantities $T = T(S, V, N)$, $p = p(S, V, N)$, and $\mu = \mu(S, V, N)$ are not independent; rather, from two of them one can obtain the value of the third.
The Euler equation yields the differential

$$\mathrm{d}U = T\,\mathrm{d}S + S\,\mathrm{d}T - p\,\mathrm{d}V - V\,\mathrm{d}p + \mu_j\,\mathrm{d}N^{(j)} + N^{(j)}\,\mathrm{d}\mu_j \qquad \text{(ESC)}, \tag{4.5}$$

which together with eq. (4.1) yields the following equation.

Gibbs-Duhem relation

$$S\,\mathrm{d}T - V\,\mathrm{d}p + N^{(j)}\,\mathrm{d}\mu_j = 0 \qquad \text{(ESC)} \tag{4.6}$$

We recall the definition (2.112) of the grand canonical potential

$$\Phi = kT\Psi = U - TS - \mu_j N^{(j)}\,, \tag{4.7}$$

where we have used eq. (2.110). The fundamental relation (4.1) and the Euler equation (4.2) yield the fundamental relation for Φ:

$$\begin{aligned} \mathrm{d}\Phi &= \mathrm{d}(U - TS - \mu_j N^{(j)}) \qquad\qquad (\text{ESC}) \\ &= T\mathrm{d}S - p\,\mathrm{d}V + \mu_j \mathrm{d}N^{(j)} - T\mathrm{d}S - S\mathrm{d}T - \mu_j \mathrm{d}N^{(j)} + N^{(j)}\mathrm{d}\mu_j \\ &= -S\mathrm{d}T - p\,\mathrm{d}V - N^{(j)}\mathrm{d}\mu_j\,. \end{aligned} \tag{4.8}$$

Moreover, the Euler equation yields

$$\Phi(T, \mu; V) = -p(T, \mu)\, V\,, \tag{4.9}$$

where we still have to show that $p(T, \mu)$ does not depend on V. The fundamental relation (4.8) implies

$$\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} = -p\,. \tag{4.10}$$

On the other hand, the product rule gives

$$\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} = -\left(\frac{\partial p}{\partial V}\right)_{T,\mu} V - p\,, \tag{4.11}$$

which implies

$$\left(\frac{\partial p}{\partial V}\right)_{T,\mu} = 0\,. \tag{4.12}$$

Similarly, using the Euler equation, we obtain for the Gibbs energy (2.102)

$$G(T, p; \mathbf{N}) = \mu_j(T, p, \mathbf{N})\, N^{(j)} \quad (\text{ESC}), \tag{4.13}$$

where, for a single particle species,

$$\left(\frac{\partial \mu}{\partial N}\right)_{T,p} = 0\,. \tag{4.14}$$

The other thermodynamic potentials with their fundamental equations can be treated analogously to one another, as we have seen here exemplarily for the grand canonical potential. We will list them in completed form in section 4.2.

4.1.1 Example: ideal gas

We recall that for the grand canonical ensemble

$$\frac{\partial \ln(\mathcal{Z})}{\partial \mu} = \frac{1}{\mathcal{Z}} \sum_N \int \mathrm{d}\xi_N \beta N \mathrm{e}^{-\beta(H(\xi) - \mu N)} = \beta \mathbb{E}[N] = \beta N \tag{4.15}$$

holds. With the grand canonical potential $\Phi = -kT \ln(\mathcal{Z})$ from eq. (2.112) this gives

$$\frac{\partial \Phi(T, \mu; V)}{\partial \mu} = -N\,. \tag{4.16}$$

The grand canonical partition function of an ideal gas was computed in the exercises as

$$\mathcal{Z} = \exp(zV/\lambda^3)\,, \quad z = \mathrm{e}^{\beta\mu}\,, \quad \lambda = \frac{h}{\sqrt{2\pi m k T}}\,, \tag{4.17}$$

cf. eq. (2.117). It follows that

$$\frac{\partial \Phi}{\partial \mu} = -kT \frac{V}{\lambda^3} \frac{\partial z}{\partial \mu} = \beta \Phi \,, \tag{4.18}$$

i.e.,

$$\Phi = -NkT \,. \tag{4.19}$$

With eq. (4.9) we obtain the *thermal equation of state*

$$pV = NkT \,. \tag{4.20}$$

4.1.2 First law of thermodynamics

The fundamental equation

$$\mathrm{d}U = T\mathrm{d}S - p\,\mathrm{d}V + \mu_j \mathrm{d}N^{(j)} \qquad \text{(ESC)} \tag{4.21}$$

from eq. (4.1) is the *first law of thermodynamics* for quasi-static processes. The change in energy is composed of the following three parts:

- The heat contribution
$$\delta Q = T\mathrm{d}S \tag{4.22}$$
is a non-exact 1-form (section 1.6); the second law states that $\mathrm{d}S \geq 0$ for isolated systems.
- The mechanical work
$$\delta W = -p\,\mathrm{d}V \tag{4.23}$$
corresponds to the energy contribution supplied to the system by mechanical work ("system-egoistic" sign convention) and is likewise not exact.
- The increase in energy due to the addition of particles is given by $\mu \mathrm{d}N$. The chemical potential μ is the increase in energy per particle at constant entropy and constant volume.
- Extensions with other forms of energy, such as electric and magnetic work as well as deformation work, are also possible but will not be considered here.

4.2 Thermodynamic potentials

In section 2.3 we encountered the canonical ensemble, the Gibbs ensemble, and the grand canonical ensemble with the respective partition functions Z (canonical), Z_G (Gibbs), and $\mathcal{Z}$ (grand canonical). Moreover, we have already encountered some of the thermodynamic potentials. It should be added that the internal energy U and the entropy S are also referred to as *potentials*, since in certain situations they quantify the available energy. Since the ensembles are equivalent in thermodynamics, we will no longer strictly separate macro and micro constraints and mostly list variables in a fixed order.

	Potential/ variables	Relation to other variables	Fundamental equation	Relations w.r.t. partition function
Internal energy	$U(S,V,N)$	$U = TS - pV + \mu N$	$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$	$U = TS - kT\ln(Z)$
Free energy	$F(T,V,N)$	$F = U - TS$	$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V + \mu\mathrm{d}N$	$F = -kT\ln(Z)$
Gibbs energy	$G(T,p,N)$	$G = U - TS + pV$	$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}N$	$G = -kT\ln(Z_G) = \mu N$
Grand canon. pot.	$\Phi(T,V,\mu)$	$\Phi = U - TS - \mu N$	$\mathrm{d}\Phi = -S\mathrm{d}T - p\mathrm{d}V - N\mathrm{d}\mu$	$\Phi = -kT\ln(\mathcal{Z}) = -pV$
Enthalpy (new)	$H(S,p,N)$	$H \coloneqq U + pV$	$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p + \mu\mathrm{d}N$	

Remark:

- Z: canonical partition function, Z_G: partition function of the Gibbs ensemble, $\mathcal{Z}$: grand canonical partition function
- The equation $U = TS - pV + \mu N$ is to be understood as the functional relation

$$U(S,V,N) = T(S,V,N)S - p(S,V,N)V + \mu(S,V,N)N\,. \tag{4.24}$$

  Analogous statements hold for the other columns and rows of the table.
- The fundamental relations for F, G, Φ, and H each follow with the Euler equation (4.2), cf. eq. (4.8).
- The derivatives of the potentials can be read off from the fundamental equations; e.g., from $\mathrm{d}U = T\mathrm{d}S + \ldots$ together with eq. (1.3) it follows that $\frac{\partial U}{\partial S} = T$.
- The enthalpy is the only genuinely newly introduced potential. For isobaric processes (p constant) without particle exchange (N constant),

$$\mathrm{d}H = T\mathrm{d}S = \delta Q\,, \tag{4.25}$$

  i.e., the heat absorbed by the system.
- The table also holds for the multi-component case if one replaces μN by $\sum_j \mu_j N^{(j)}$.

Comprehension questions:

- List some derivatives of the potentials with respect to their natural variables.
- Express the internal energy U (i) via a derivative of the free energy F and (ii) as the Legendre transform of F. In what respect do the functions U computed in these two ways differ?
- Carry out considerations similar to eq. (4.25) for some of the other potentials.

Theorem 4.1 (Convexity of the internal energy)**.** *Let* $\left(\frac{\partial S}{\partial U}\right)_{V,N} > 0$ *and let* S *be a concave and homogeneous function of* (U,V,N)*. Then* $(S,V,N) \mapsto U(S,V,N)$ *is a convex function.*

Proof. The concavity of S means that for all (U_1,V_1,N_1) and (U_2,V_2,N_2) and $\alpha \in [0,1]$,

$$\begin{aligned} S\big(\alpha U_1 + (1-\alpha)U_2,\ \alpha V_1 + (1-\alpha)V_2,\ \alpha N_1 + (1-\alpha)N_2\big) \\ \geq \alpha S(U_1,V_1,N_1) + (1-\alpha)S(U_2,V_2,N_2)\,. \end{aligned} \tag{4.26}$$

We now set $S_i \coloneqq S(U_i,V_i,N_i)$ for $i = 1,2$, and for each $X \in \{S,V,N\}$ we set $X = \alpha X_1 + (1-\alpha)X_2$.

The function $U(S,V,N)$ is obtained from the entropy S by solving $S(U,V,N)$ for U (by the implicit function theorem, this is always possible locally if $\frac{\partial S}{\partial U} \neq 0$). By the homogeneity of S we then have

$$\begin{aligned} S(U(S,V,N),V,N) &= \alpha S(U(S_1,V_1,N_1),V_1,N_1) \\ &\quad + (1-\alpha)S(U(S_2,V_2,N_2),V_2,N_2) \\ &\leq S(\alpha U(S_1,V_1,N_1) + (1-\alpha)U(S_2,V_2,N_2),V,N)\,. \end{aligned} \tag{4.27}$$

Because of $\frac{\partial S}{\partial U} > 0$, the above relation can therefore be (locally) inverted to give

$$U(S,V,N) \leq \alpha U(S_1,V_1,N_1) + (1-\alpha)U(S_2,V_2,N_2)\,. \tag{4.28}$$

□

Remarks:

- Since the entropy S is maximal in equilibrium under the constraints given by U,V,N, and was defined here as the concave differential or von Neumann entropy, it is also a concave function according to theorem 1.11.
- For systems of non-interacting particles, the entropy is homogeneous.
- $\left(\frac{\partial S}{\partial U}\right)_{V,N} > 0$ is a physically motivated condition: at higher energies more states are accessible, so the entropy also increases with the energy.

In the abstract general case (2.74) we regard $S(U,\mathsf{M})$ and $U(S,\mathsf{M})$ as potentials. The other potentials are obtained by Legendre transforming with respect to some of the variables S and $\mathsf{M}^{(1)},\ldots,\mathsf{M}^{(m)}$; here with the convex version of the Legendre transformation, which, however, makes no difference to the concave version for the concrete computation, see section 1.5.1. The corresponding new variables are then the corresponding variables from $\{T,\lambda_1,\ldots,\lambda_m\}$.
In this way we represented the potentials F, G, and Φ in section 2.3. From $\mathrm{d}U$ in the list above we can read off

$$\left(\frac{\partial U}{\partial V}\right)_{S,N} = -p \tag{4.29}$$

(other derivatives of the potentials can be read off in a similar way). This implies that the enthalpy is the Legendre transform of the internal energy $U(S,V,N)$ with respect to the variable V. Strictly speaking, the enthalpy is thus a function of $(S,-p;N)$, but the minus sign is usually suppressed in the notation; we will indicate such a sign suppression by a + in the following list.
In summary, we obtain the following relations via the Legendre transformation.

Function f	New variable(s)	LT of f
$U(S,V,N)$	$\frac{\partial U}{\partial S} = T$	$-F(T,V,N)$
$U(S,V,N)$	$\frac{\partial U}{\partial V} = -p$	$-H(S,+p,N)$
$U(S,V,N)$	$\frac{\partial U}{\partial S} = T$, $\frac{\partial U}{\partial V} = -p$	$-G(T,+p,N)$
$U(S,V,N)$	$\frac{\partial U}{\partial S} = T$, $\frac{\partial U}{\partial N} = \mu$	$-\Phi(T,V,\mu)$
$-F(T,V,N)$	$-\frac{\partial F}{\partial T} = S$	$U(S,V,N)$
$F(T,V,N)$	$-\frac{\partial F}{\partial V} = p$	$-G(T,+p,N)$
$-G(T,p,N)$	$-\frac{\partial G}{\partial T} = S$	$H(S,p,N)$

Remarks:

- Here we have exclusively used the definition of the Legendre transformation for convex functions, see section 1.5.1 and cf. [4, Chapter 5.2]. For the concrete

computation, however, this makes no difference to the concave version, since in both cases the critical points of eq. (1.91) are the same.

- Hence, the thermodynamic potentials are convex in their extensive variables and concave in the intensive variables.
- In the special cases considered here, one can transform different variables one after the other and thereby obtain the same result as when performing the multi-dimensional Legendre transformation; e.g., G can be represented as the Legendre transform of U with respect to (S, V) or of F with respect to V.
- The corresponding inverse transformations are also possible; e.g., U is the Legendre transform of F with respect to S. Note that the list given above is not complete.

Short exercise: Add corresponding rows to the list.

4.2.1 Maxwell relations

The Gibbs-Duhem relation provides a relation between the first derivatives of the fundamental relations. The Maxwell relations, in contrast, provide relations between the second derivatives. From the fact that second partial derivatives of smooth functions commute (Schwarz's theorem), the second derivatives of the potentials yield relations for the derivatives of the respective thermodynamic variables, e.g.:

$$-\left(\frac{\partial p}{\partial S}\right)_{V,N} = \left(\frac{\partial T}{\partial V}\right)_{S,N} = \left(\frac{\partial^2 U}{\partial S \partial V}\right)_N, \tag{4.30}$$

$$\left(\frac{\partial \mu}{\partial S}\right)_{V,N} = \left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial^2 U}{\partial S \partial N}\right)_V, \tag{4.31}$$

$$\left(\frac{\partial \mu}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial N}\right)_{S,V} = \left(\frac{\partial^2 U}{\partial V \partial N}\right)_S, \tag{4.32}$$

$$\left(\frac{\partial p}{\partial T}\right)_{V,N} = \left(\frac{\partial S}{\partial V}\right)_{T,N} = -\left(\frac{\partial^2 F}{\partial T \partial V}\right)_N, \tag{4.33}$$

$$-\left(\frac{\partial S}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{p,N} = \left(\frac{\partial^2 G}{\partial T \partial p}\right)_N. \tag{4.34}$$

Such relations are called *Maxwell relations*. They are the *integrability conditions* for the existence of the potentials. Conversely, they establish important connections between different thermodynamic variables (here between pairs of conjugate pairs of variables).
The *Guggenheim square* (thermodynamic square) is a popular mnemonic for the Maxwell relations, see Wikipedia.
In the next section we will see that some of the Maxwell relations make a direct statement about the so-called susceptibilities.

Exercise: Derive some further Maxwell relations.

4.2.1.1 Useful identities from calculus

The *inverse function theorem* from calculus states that if the derivative $\mathrm{d}_a f \in \mathrm{L}(\mathbb{R}^n)$ of a smooth function $f : \mathbb{R}^n \to \mathbb{R}^n$ at a point $a \in \mathbb{R}^n$ is invertible, then the map f is also locally invertible and

$$(\mathrm{d}_a f)^{-1} = \mathrm{d}_{f(a)}\left(f^{(-1)}\right) \tag{4.35}$$

holds.

We now consider real variables x, y, z that are dependent in the sense that $z = z(x, y)$ can be regarded as a function of x and y. From eq. (4.35) we can deduce the following relation.

Lemma 4.2. *Let $z(x, y)$ be a smooth function with $\left(\frac{\partial z}{\partial x}\right)_y \neq 0$. Then, locally,*

$$\left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{\left(\frac{\partial x}{\partial z}\right)_y} \,. \tag{4.36}$$

Alternative "proof" of eq. (4.36). We keep y constant and assume that $z(\,\cdot\,, y)$ is smooth and invertible. Then

$$\mathrm{d}x = \frac{\partial x}{\partial z}\,\mathrm{d}z = \frac{\partial x}{\partial z}\frac{\partial z}{\partial x}\,\mathrm{d}x \tag{4.37}$$

and hence

$$\frac{\partial x}{\partial z}\frac{\partial z}{\partial x} = 1 \,. \tag{4.38}$$

□

The *implicit function theorem* states that, under the condition that the derivative of a function $f(\,\cdot\,, \mathbf{y})$ is invertible at a point $\mathbf{y}$, for a given value $\mathbf{z}$ one can find a unique function $\mathbf{y} = g_{\mathbf{z}}(\mathbf{x})$ such that locally $f(\mathbf{x}, g_{\mathbf{z}}(\mathbf{x})) = \mathbf{z}$ and

$$\frac{\partial g_{\mathbf{z}}}{\partial x_j}(\mathbf{x}) = -\big(D_{g_{\mathbf{z}}(\mathbf{x})} f(\mathbf{x}, \,\cdot\,)\big)^{-1} \nabla_{\mathbf{x}} f(\,\cdot\,, g_{\mathbf{z}}(\mathbf{x})) \tag{4.39}$$

holds, where the derivatives each act on the function arguments indicated by the dots, see Wikipedia. With one-dimensional variables x, y, z and the choices $f(x, y) = z(x, y)$ and $g_z(x) = y(x, z)$ it follows that

$$\left(\frac{\partial y}{\partial x}\right)_z = -\frac{\left(\frac{\partial z}{\partial x}\right)_y}{\left(\frac{\partial z}{\partial y}\right)_x} \tag{4.40}$$

holds, which by means of eq. (4.36) we can write in the following form, which is easier to remember.

Lemma 4.3. *Locally,*

$$\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial z}{\partial y}\right)_x = -1 \tag{4.41}$$

holds under the condition that two of the three partial derivatives do not vanish (the third one then automatically does not vanish either).

Alternative proof of eq. (4.41). We have

$$\begin{aligned} \mathrm{d}y &= \left(\frac{\partial y}{\partial x}\right)_z \mathrm{d}x + \left(\frac{\partial y}{\partial z}\right)_x \mathrm{d}z \\ &= \left(\frac{\partial y}{\partial x}\right)_z \left(\left(\frac{\partial x}{\partial y}\right)_z \mathrm{d}y + \left(\frac{\partial x}{\partial z}\right)_y \mathrm{d}z\right) + \left(\frac{\partial y}{\partial z}\right)_x \mathrm{d}z \\ &= \mathrm{d}y + \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \mathrm{d}z + \left(\frac{\partial y}{\partial z}\right)_x \mathrm{d}z \end{aligned} \tag{4.42}$$

and comparing the coefficient functions of $\mathrm{d}z$ yields

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y = -\left(\frac{\partial y}{\partial z}\right)_x , \tag{4.43}$$

where we have used the assumption that $\left(\frac{\partial x}{\partial y}\right)_z \neq 0$. The identity (4.36) yields eq. (4.41). □

4.2.1.2 Further Maxwell relations

With eq. (4.36) the Maxwell relations can be rewritten; e.g., eq. (4.30) yields

$$-\left(\frac{\partial S}{\partial p}\right)_{V,N} = -\frac{1}{\left(\frac{\partial p}{\partial S}\right)_{V,N}} = \frac{1}{\left(\frac{\partial T}{\partial V}\right)_{S,N}} = \left(\frac{\partial V}{\partial T}\right)_{S,N}, \tag{4.44}$$

which results in up to three further Maxwell relations. Similarly, one can use eq. (4.41) to establish further Maxwell relations.

4.2.2 Susceptibilities and thermodynamic stability

A *susceptibility* is a measure for the change of an extensive quantity upon variation of an intensive quantity.
In this section we keep the particle number constant, i.e.,

$$\mathrm{d}N = 0 \qquad \text{(in this section)}. \tag{4.45}$$

We can thus describe the thermodynamic state with two variables.

- Since the temperature T and the pressure p can be written as derivatives of the internal energy U, we can regard them as functions

$$T = T(S,V) \qquad \text{and} \qquad p = p(S,V)\,. \tag{4.46}$$

- Typically, these functions are strictly monotonic in their variables. Hence they can be inverted, i.e., solved to give the functions

$$S = S(T,p) \qquad \text{and} \qquad V = V(T,p) \tag{4.47}$$

  (inverse function theorem from calculus). Alternatively, we can regard $-S$ and V as derivatives of the Gibbs energy $G(T,p)$.

- Similarly, we obtain the coordinates

$$S = S(T,V) \qquad \text{and} \qquad p = p(T,V) \tag{4.48}$$

  by taking partial derivatives of the free energy $F(T,V)$.

The parametrization (4.47) in terms of (T,p) yields

$$\frac{\mathrm{d}V}{V} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T + \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p\,. \tag{4.49}$$

The relative volume change $\mathrm{d}V/V$ and the heat supply $\delta Q = T\mathrm{d}S$ lead to

- *Thermal expansion coefficient*

$$\alpha \coloneqq \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N} = \frac{1}{V}\frac{\partial^2 G}{\partial T \partial p} \tag{4.50}$$

- *Isothermal compressibility*

$$\kappa_T \coloneqq -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = -\frac{1}{V}\frac{\partial^2 G}{\partial p^2} \tag{4.51}$$

Since G is concave in p, it follows that

$$\kappa_T \geq 0\,. \tag{4.52}$$

The property (4.52) is also called *mechanical stability*, since otherwise the substance would keep expanding and the pressure would keep increasing.

With $\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_{p,N}\mathrm{d}T + \left(\frac{\partial V}{\partial p}\right)_{T,N}\mathrm{d}p$ we thus have

$$\frac{\mathrm{d}V}{V} = \alpha \mathrm{d}T - \kappa_T \mathrm{d}p\,. \tag{4.53}$$

- *Heat capacity at constant pressure*

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,N} = -T\frac{\partial^2 G}{\partial T^2}\,. \tag{4.54}$$

With $\mathrm{d}H = T\mathrm{d}S + \mu\mathrm{d}N + V\mathrm{d}p$ we have

$$\frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_{p,N}\mathrm{d}T = \frac{1}{T}\,\mathrm{d}H = \mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_{p,N}\mathrm{d}T\,, \tag{4.55}$$

hence also

$$C_p = \left(\frac{\partial H}{\partial T}\right)_{p,N}\,. \tag{4.56}$$

Moreover,

$$\delta Q = T\mathrm{d}S = C_p \mathrm{d}T\,, \tag{4.57}$$

i.e., C_p specifies the amount of heat that is required to warm the body by 1 Kelvin when p and N are held fixed. Along a path with constant pressure p we then have

$$Q(T) - Q(T_0) = \int_{T_0}^{T} \delta Q = \int_{T_0}^{T} \mathrm{d}T\, C_p(T)\,. \tag{4.58}$$

We will also find that

$$C_p \geq C_V \geq 0\,. \tag{4.59}$$

Starting from the coordinates (4.48), we define the following further susceptibilities.

- *Heat capacity at constant volume V*:

$$C_V \coloneqq T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \left(\frac{\partial U}{\partial T}\right)_{V,N} = -T\frac{\partial^2 F}{\partial T^2}\,, \tag{4.60}$$

where in the second step

$$\mathrm{d}S = (\mathrm{d}U + p\mathrm{d}V - \mu\mathrm{d}N)/T = (1/T)\mathrm{d}U \tag{4.61}$$

was used.

From the concavity of F in T it follows that

$$C_V \geq 0\,. \tag{4.62}$$

The property (4.62) is also called *thermal stability*, since otherwise supplying heat would lower the temperature of the body and the substance would thus "soak up" all the heat.

- *Isochoric pressure coefficient* at constant volume V:

$$\beta_{\text{sp}} \coloneqq \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_{V,N} = -\frac{1}{p}\frac{\partial^2 F}{\partial T \partial V} \tag{4.63}$$

The specific heats c_V, c_p follow by dividing by the mass of the substance.
Starting from the coordinates (p, S), the *adiabatic (isentropic) compressibility* is defined as

$$\kappa_S \coloneqq -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{S,N} = -\frac{1}{V}\frac{\partial^2 H}{\partial p^2}\,. \tag{4.64}$$

Since H is concave in p, we have

$$\kappa_S \geq 0\,. \tag{4.65}$$

The Maxwell relations lead to *general relations between the susceptibilities* (exercise):

$$\frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_S} \tag{4.66}$$

$$C_p - C_V = \frac{TV\alpha^2}{\kappa_T} \qquad \text{(Exercise 10.1c)} \tag{4.67}$$

$$\kappa_T - \kappa_S = \frac{TV\alpha^2}{C_p} \tag{4.68}$$

$$p\beta_{\text{sp}} = \frac{\alpha}{\kappa_T} \tag{4.69}$$

With eq. (4.67) it indeed follows that $C_p \geq C_V$.

Exercise: Compute some of these susceptibilities for an ideal gas, i.e., for the thermal and caloric equations of state $pV = NkT$ and $U = \frac{3}{2}NkT$. For example,

$$\alpha = \frac{1}{T}\,, \tag{4.70}$$

$$\kappa_T = \frac{1}{p}\,, \tag{4.71}$$

$$C_V = \frac{3}{2}Nk\,. \tag{4.72}$$

With eq. (4.67) it follows that

$$C_p - C_V = Nk \tag{4.73}$$

and therefore

$$C_p = \frac{5}{2}Nk\,. \tag{4.74}$$

4.2.2.1 Adiabatic equation

We consider an ideal gas,

$$U = \frac{3}{2}NkT\,, \quad pV = NkT\,, \tag{4.75}$$

with constant particle number N. Because of $\left(\frac{\partial U}{\partial V}\right)_T = 0$ we then have

$$\begin{aligned} \mathrm{d}S &= \frac{1}{T}(\mathrm{d}U + p\mathrm{d}V) \\ &= C_V\frac{\mathrm{d}T}{T} + \frac{p}{T}\mathrm{d}V \\ &= C_V\frac{\mathrm{d}T}{T} + Nk\frac{\mathrm{d}V}{V} \end{aligned} \tag{4.76}$$

In the following, $C_1, C_2, \ldots$ denote constants. With $C_p - C_V = Nk$ this gives

$$S(T,V) = C_V \ln(T) + (C_p - C_V)\ln(V) + C_1\,, \tag{4.77}$$

which can be checked by differentiation. The ideal gas law yields

$$S = C_V \ln(p) + C_p \ln(V) + C_2 \tag{4.78}$$

with the constant $C_2 = C_1 - C_V \ln(Nk)$. Now we keep S constant. Then

$$\ln(p) + \kappa \ln(V) = C_3 \tag{4.79}$$

with the *isentropic exponent* $\kappa = C_p/C_V$. Put differently, the *adiabatic equation*

$$pV^\kappa = C_4 \tag{4.80}$$

holds, where $\kappa > 1$ because of eq. (4.67). Thus $p(V)$ is given as

$$p(V) \propto \begin{cases} \frac{1}{V^\kappa} & \text{in the adiabatic case,} \\ \frac{1}{V} & \text{in the isothermal case.} \end{cases} \tag{4.81}$$

4.2.3 Equilibrium conditions

We consider a thermodynamic system in equilibrium and now change some of the thermodynamic variables. How will the other variables react to this? What is the new equilibrium state? These are the questions we want to pursue in this section. To this end, we introduce a thermodynamic quantity, the *exergy*, which cannot increase during equilibration.
The content of this section builds on [1, Chapter 2.3].

4.2.3.1 Exergy

We consider systems Σ, Σ_E, and Σ_W that are not in equilibrium. Furthermore, we regard Σ_E as the environment/bath of Σ with temperature T_E and pressure p_E, which do not change since we assume Σ_E to be very large. Another system Σ_W serves as a work reservoir for Σ, i.e., work $W' \geq 0$ can be transferred adiabatically from Σ to Σ_W. (It is helpful to draw a schematic sketch of the overall setup.)
Now we consider a change of state of Σ and Σ_E with corresponding changes $\Delta U, \Delta U_E$, $\Delta V, \Delta V_E$, and $\Delta S, \Delta S_E$ of energy, volume, and entropy (final value minus initial value). We assume that Σ_E is in equilibrium throughout, i.e., that the change of state of Σ_E proceeds quasi-statically. The particle numbers are assumed to remain constant. In total, we obtain the balance

$$\begin{aligned} \Delta V + \Delta V_E &= 0\,, \\ \Delta U + \Delta U_E &= -W'\,. \end{aligned} \tag{4.82}$$

Hence, the work released by Σ_E to Σ is

$$W = p_E \Delta V_E \tag{4.83}$$

and

$$Q = -T_E \Delta S_E \tag{4.84}$$

is the released heat. Thus,

$$\Delta U_E = -W - Q = -p_E \Delta V_E + T_E \Delta S_E \tag{4.85}$$

and so

$$\begin{aligned}\Delta S_E &= \frac{1}{T_E}(\Delta U_E + p_E \Delta V_E) \\ &= \frac{1}{T_E}(-\Delta U - W' - p_E \Delta V)\,,\end{aligned} \tag{4.86}$$

where eq. (4.82) was used in the second step. Since $\Sigma \times \Sigma_E$ was assumed to be adiabatically closed, i.e., $T\mathrm{d}S + T_E \mathrm{d}S_E = 0$, we have

$$\Delta S + \Delta S_E \geq 0\,, \tag{4.87}$$

i.e., the entropy increases when $\Sigma \times \Sigma_E$ equilibrates. To be precise, we consider the case $T \leq T_E$. Then $0 = \frac{T}{T_E}\mathrm{d}S + \mathrm{d}S_E \leq \mathrm{d}S + \mathrm{d}S_E$. The case $T \geq T_E$ follows analogously, and with it eq. (4.87).
Altogether,

$$\Delta S + \frac{1}{T_E}(-\Delta U - W' - p_E \Delta V) \geq 0 \tag{4.88}$$

and thus

$$W' \leq -\Delta U + T_E \Delta S - p_E \Delta V =: -\Delta \Lambda\,. \tag{4.89}$$

This motivates the definition of the *exergy* (availability)

$$\Lambda := U - U_0 - T_E(S - S_0) + p_E(V - V_0)\,, \tag{4.90}$$

as the maximal available work, where (S_0, U_0, V_0) describes the equilibrium state of Σ with Σ_E. In equilibrium, $\Lambda = 0$ holds automatically. In general we have $\Delta\Lambda \leq -W' \leq 0$ and therefore $\Lambda \geq 0$.

Exercise: The situation is described by Gibbs ensembles with distributions (2.98). Show that

$$S(\rho\|\rho_0) = \frac{\Lambda}{T_E}\,, \tag{4.91}$$

where ρ is the initial state of Σ and ρ_0 is the equilibrium state of Σ with Σ_E; $S(\rho\|\rho_0)$ denotes their relative entropy (1.84) or (3.43), depending on whether the computation is classical or quantum mechanical.

The relation (4.91) shows from an information-theoretic point of view that $\Lambda \geq 0$ and that $\Lambda = 0$ in equilibrium.

4.2.3.2 Equilibrium conditions

To introduce the exergy while taking the particle number into account, we use the quantum mechanical framework, i.e., density operators, observables, and the quantum relative entropy. However, all arguments and computations apply analogously to continuous classical distributions as well (with section 1.4). We now consider two generalized canonical density operators (section 3.4)

$$\begin{aligned}\hat\rho &= \exp(\Psi - \lambda_\nu \hat M^{(\nu)})\,, \\ \hat\rho_0 &= \exp(\Psi_0 - \lambda_\nu^0 \hat M^{(\nu)}) \quad \text{(ESC)}\end{aligned} \tag{4.92}$$

on the same Hilbert space and with the same observables $\hat M^{(\nu)}$. Then their relative entropy (3.41) is

$$\begin{aligned}S(\hat\rho\|\hat\rho_0) &= k\,\mathrm{Tr}\big[\hat\rho\big(\ln(\hat\rho) - \ln(\hat\rho_0)\big)\big] \\ &= -S(\hat\rho) + S(\hat\rho_0) + k\lambda_\nu^0\big(\mathsf{M}^{(\nu)} - \mathsf{M}_0^{(\nu)}\big) \qquad \text{(ESC)}\end{aligned} \tag{4.93}$$

with $\mathsf{M}^{(\nu)} = \mathrm{Tr}[\hat\rho \hat M^{(\nu)}]$ and $\mathsf{M}_0^{(\nu)} = \mathrm{Tr}[\hat\rho_0 \hat M^{(\nu)}]$.
With the usual choice $\mathsf{M} = (U, V, \mathbf{N})$ and $\lambda = (\beta, \beta p, -\beta\mu)$, this suggests the following

generalization of the *exergy*:

$$\Lambda \coloneqq T_0\, S(\rho\|\rho_0) = U - U_0 + p_0(V - V_0) - \mu_{0,j}(N^{(j)} - N_0^{(j)}) - T_0(S - S_0)\,. \quad (4.94)$$

Because of eq. (1.85) we have

$$\Lambda \geq 0\,. \quad (4.95)$$

Two thermodynamic systems, each of which is in an equilibrium state ρ and ρ_0, respectively, are in equilibrium with each other if and only if $\rho = \rho_0$, which is equivalent to $S(\rho\|\rho_0) = 0$, cf. eq. (3.44). Hence, we can use the exergy to characterize equilibrium situations. To this end, in the following we consider situations where some of the thermodynamic variables are not in equilibrium, with U_0, V_0, $\mathbf{N}_0$, etc. denoting the respective thermodynamic quantities in equilibrium. Some of the variables are now held constant at their equilibrium values. Via the exergy (4.94), for such situations we can draw conclusions about the extremality of the potential matching the respective variables.

Examples:

(i) Isolated systems: for constant U, V, $\mathbf{N}$ we have

$$S - S_0 \leq 0 \quad (4.96)$$

and S is *maximal in equilibrium*.

(ii) Isentropic-isochoric system: for constant S, V, $\mathbf{N}$ we have

$$U - U_0 \geq 0 \quad (4.97)$$

and $U(S, V, \mathbf{N})$ is *minimal in equilibrium*.

(iii) Isothermal-isochoric system: for constant T, V, $\mathbf{N}$ we have

$$\begin{aligned} 0 &\leq \Lambda \\ &= \underbrace{(U - TS)}_{=F} - \underbrace{(U_0 - T_0 S_0)}_{=F_0} + S\,\underbrace{(T - T_0)}_{=0} + p_0\,\underbrace{(V - V_0)}_{=0} - \mu_{0j}\,\underbrace{(N^{(j)} - N_0^{(j)})}_{=0} \\ &= F - F_0 \end{aligned} \quad (4.98)$$

(with ESC) and $F(T, V, \mathbf{N})$ is *minimal in equilibrium*.

(iv) Isothermal-isobaric system: for constant T, p, $\mathbf{N}$ we have

$$\begin{aligned} 0 &\leq \Lambda \\ &= \underbrace{(U - TS + pV)}_{=G} - \underbrace{(U_0 - T_0 S_0 + p_0 V_0)}_{=G_0} - V\,\underbrace{(p - p_0)}_{=0} + S\,\underbrace{(T - T_0)}_{=0} - \mu_{0j}\,\underbrace{(N^{(j)} - N_0^{(j)})}_{=0} \\ &= G - G_0 \end{aligned} \quad (4.99)$$

(with ESC) and $G(T, p, \mathbf{N})$ is *minimal in equilibrium*.

(v) Isentropic-isobaric system: for constant S, p, $\mathbf{N}$ we have

$$\begin{aligned} 0 &\leq \Lambda \\ &= \underbrace{(U + pV)}_{=H} - \underbrace{(U_0 + p_0 V_0)}_{=H_0} - V\,\underbrace{(p - p_0)}_{=0} - T_0\,\underbrace{(S - S_0)}_{=0} - \mu_{0j}\,\underbrace{(N^{(j)} - N_0^{(j)})}_{=0} \\ &= H - H_0 \end{aligned} \quad (4.100)$$

(with ESC) and $H(S, p, \mathbf{N})$ is *minimal in equilibrium*; cf. Exercise 9.4.

(vi) Isothermal-isochoric system: for constant T, V, μ we have

$$\begin{aligned} 0 &\leq \Lambda \\ &= \underbrace{(U - TS - \mu_j N^{(j)})}_{=\Phi} - \underbrace{(U_0 - T_0 S_0 - \mu_{0j} N_0^{(j)})}_{=\Phi_0} + S \underbrace{(T - T_0)}_{=0} + p_0 \underbrace{(V - V_0)}_{=0} + N^{(j)} \underbrace{(\mu_j - \mu_{0j})}_{=0} \\ &= \Phi - \Phi_0 \end{aligned} \tag{4.101}$$

(with ESC) and $\Phi(T, V, \mu)$ is *minimal in equilibrium.*

4.2.3.3 Application example: vapor pressure

We consider two phases of the same substance in equilibrium, N_1 particles in a gas phase and N_2 particles in a liquid phase. By coupling to a larger bath Σ_E, p and T are held constant. At the same time, the total particle number $N = N_1 + N_2$ is to be conserved.
We now seek the *vapor pressure* $P(T) = p$ at which a coexistence of gas and liquid, i.e., $N_1, N_2 > 0$, is possible.
To this end, we first introduce molar quantities: $n = N/N_\mathrm{A}$ is the particle number in moles, where N_A is the Avogadro constant, and similarly for n_1 and n_2. By g, g_1, g_2 we denote the *molar Gibbs energy*, i.e., the Gibbs energy of one mole. An analogous notation can be used for other extensive quantities.
In equilibrium, the total Gibbs energy $G(T, p)$ with $G = n_1 g_1 + n_2 g_2$ is minimal. Admissible deviations from equilibrium satisfy

$$\Delta n_1 + \Delta n_2 = 0\,. \tag{4.102}$$

Due to the minimality of G, the corresponding deviation of the Gibbs energy must satisfy

$$\Delta G = g_1 \Delta n_1 + g_2 \Delta n_2 = (g_1 - g_2)\Delta n_1 \overset{!}{=} 0 \tag{4.103}$$

(minimality of G and first-order Taylor expansion around the equilibrium value of n_1), i.e.,

$$g_1(T, P(T)) \overset{!}{=} g_2(T, P(T))\,, \tag{4.104}$$

provided that the vapor pressure curve $P(T)$ exists locally as a function (implicit function theorem, section 4.2.1.1). With $\mathrm{d}n = \mathrm{d}n_1 + \mathrm{d}n_2 = 0$ the fundamental equation is

$$\mathrm{d}g = -s\mathrm{d}T + v\mathrm{d}p \tag{4.105}$$

and with $g_1 = g_2$ we have

$$-(s_2 - s_1)\mathrm{d}T + (v_2 - v_1)\mathrm{d}p = 0\,. \tag{4.106}$$

Hence,

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{s_2 - s_1}{v_2 - v_1} \qquad \text{(Clausius-Clapeyron equation).} \tag{4.107}$$

With the *molar heat of vaporization* $q \coloneqq (s_1 - s_2)T$ we write this as

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{q}{(v_1 - v_2)T}\,. \tag{4.108}$$

Example: Ideal gas (a gas far away from the critical point). With the ideal *gas constant* $R = N_\mathrm{A} k$ we have $v_1 = \frac{RT}{P(T)} \gg v_2$, and thus we obtain the differential equation

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{q}{RT^2} P(T)\,, \tag{4.109}$$

which is solved by

$$P(T) = C \exp\Big(-\frac{q}{RT}\Big) \qquad \text{(vapor pressure of an ideal gas).} \tag{4.110}$$

4.2.3.4 Application example: Gibbs energy in chemical reactions

The Gibbs energy $G(T,p) = H - TS$ indicates whether a reaction proceeds "spontaneously". If $\Delta G = \Delta H - T\Delta S < 0$, the reaction is *exergonic*. At constant T and p, the reaction thus lowers the Gibbs energy and could therefore take place from a thermodynamic point of view. With $G = H - TS$, this can be interpreted as saying that the increase in entropy can be regarded as the driving "force" of a chemical reaction, which must overcompensate the heat production measured by H. (Cf. Exercise 9.3.)

4.2.3.5 Application example: law of mass action

Exercise 11.3

4.3 Thermodynamic processes

4.3.1 Basic notions

- In *equilibrium*, a system can be described by $U, V, \mathbf{N}$ or correspondingly conjugate variables. All other quantities then follow from equations of state.
- Conversely, a system that is not in equilibrium cannot be described by thermodynamic state variables.
- A *thermodynamic process* is a process in which at least the initial and final states are thermodynamic equilibrium states.
- A *reversible process* is a thermodynamic change of state that could at any time also run in reverse without the system or its environment undergoing any permanent changes. The definition of reversibility here is somewhat narrower than in statistical mechanics (section 2.2.3).
- Reversible processes are quasi-static (non-equilibrium processes are not reversible) and isentropic (second law). For subsystems the entropy can increase or decrease, but the total entropy must remain the same.
- There are quasi-static (i.e., arbitrarily slow) irreversible processes (Gay-Lussac experiment). Non-quasi-static processes are always irreversible.
- Irreversible processes thus cannot be reversed, e.g., a transition from an equilibrium state to a non-equilibrium state. Experience shows that the non-equilibrium system then passes into a new equilibrium state, but the transition between initial and final state is irreversible (the entropy has increased). The system no longer spontaneously returns to the intermediate non-equilibrium state.
- If a process is reversible and the heat Q is exchanged, then energy conservation implies

  $$T\mathrm{d}S_{\mathrm{rev}} = \delta Q_{\mathrm{rev}}\,, \tag{4.111}$$

  where "rev" emphasizes that the process is reversible. One also speaks of *reversibly exchanged heat*.

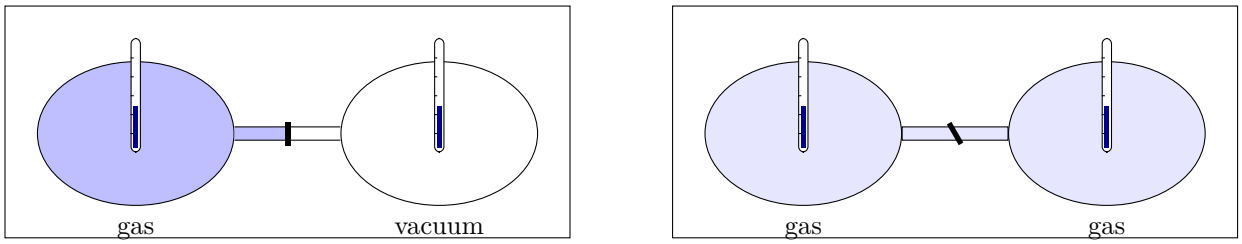

Figure 4.1: In the Gay-Lussac experiment, a gas expands into a vacuum.

Irreversible processes

4.3.2 Irreversible expansion of a gas: Gay-Lussac experiment (1807)

We had said that $T\mathrm{d}S$ can be interpreted as *heat* δQ in certain situations. The Gay-Lussac experiment (with the experiment of 1807) describes the irreversible expansion of a gas and provides more detailed insight into the relation between $\mathrm{d}S$ and δQ.
The Gay-Lussac experiment must not be confused with the *Joule-Thomson effect* (later) or with *Gay-Lussac's law*, which also concern the expansion of gases.
In this experiment, a gas expands adiabatically (fig. 4.1). The process takes place at constant internal energy $U = U_1 + U_2$. One uses an insulated vessel with volume $V = V_1 + V_2$. Initially, the volumes V_1 and V_2 are separated by a partition; V_1 contains a gas of temperature T and V_2 is evacuated. Then the partition is removed and gas also flows into V_2. What do the thermodynamic state variables look like after equilibration?

Remark: After the removal of the partition, irreversible (turbulent) processes set in (even if the process is conducted very slowly, i.e., quasi-statically), which cannot be described thermodynamically. Only the initial and final states can be described thermodynamically. In particular, the relation $\delta Q = T\mathrm{d}S$ has no meaning here (i.e., it does not hold).

4.3.2.1 Ideal gas

Before the expansion, entropy, pressure, and internal energy are given by

$$S = Nk\left(\frac{5}{2} + \ln\left[\frac{V_1}{N\lambda^3}\right]\right) \tag{4.112}$$

with thermal wavelength $\lambda = h/\sqrt{2\pi mkT}$ [see the Sackur-Tetrode equation (2.91)], $p = NkT/V_1$, and $U = \frac{3}{2}NkT$. Since $U(T,V)$ obviously does not depend on the volume, the same temperature prevails after the expansion, and hence also the same thermal wavelength.
The only change in the entropy (4.112) is given by $V_1 \to V = V_1 + V_2$, and the pressure after the expansion is $p = NkT/V$. The entropy thus increases by

$$\Delta S = Nk\ln(V/V_1) > 0\,. \tag{4.113}$$

The entropy has thus increased without any heat being supplied, i.e., with $\Delta Q = 0$.
We will see that the second law for thermodynamic processes in a closed total system states that

$$T\mathrm{d}S \geq \delta Q_{\mathrm{rev}}\,, \tag{4.114}$$

where irreversible processes are characterized by $T\mathrm{d}S > \delta Q_{\mathrm{rev}}$. The process considered here is thus irreversible although it can be conducted quasi-statically. Lifting the constraint (partition) leads to a higher entropy. A spontaneous reversal of the process

is not possible (the system does not by itself return to the state before the constraint was lifted).

4.3.2.2 General gas

For general gases one can show the following: (i) the temperature can change, and (ii) the entropy always increases in the Gay-Lussac experiment. This follows from the equations

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{p - T\left(\frac{\partial p}{\partial T}\right)_V}{C_V} \tag{4.115}$$

and

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{p}{T} > 0\,, \tag{4.116}$$

which are to be derived on problem sheet 11.
The entropy must therefore always increase in an expansion at constant energy U. This confirms that the outflow of a gas is always irreversible.

4.3.3 Mixing of gases

In Exercise 6.2 it was shown for the mixing of two ideal distinguishable gases that the entropy change is

$$\Delta S = N_1 k \ln\left(\frac{V}{V_1}\right) + N_2 k \ln\left(\frac{V}{V_2}\right) \tag{4.117}$$

with $V = V_1 + V_2$, where initially the N_1 particles occupy the volume V_1 and the N_2 particles occupy the volume V_2. The mixing entropy of ideal gases thus equals the entropy production of two corresponding Gay-Lussac experiments!
In the case of gases of indistinguishable particles,

$$\Delta S = Nk \ln\left(\frac{V}{N}\right) - N_1 k \ln\left(\frac{V_1}{N_1}\right) - N_2 k \ln\left(\frac{V_2}{N_2}\right) = N_1 k \ln(p_1) + N_2 k \ln(p_2) - Nk \ln(p) \tag{4.118}$$

with $N = N_1 + N_2$ and $p_x = N_x kT/V_x$. This means that, as expected, there is no entropy change for equal pressures $p_1 = p_2$. For this, the $1/N!$ factor in the phase-space volume element (2.32) is necessary.

Reversible processes

Isothermal and adiabatic volume changes can be combined into a reversible cycle – the Carnot cycle.

4.3.4 Isothermal expansion of an ideal gas

The isothermal process with $p = NkT/V$ is the reversible variant of the Gay-Lussac experiment. Here, in a (quasi-static) expansion from V_0 to V, the energy

$$\begin{aligned} -W &= \int_{V_0}^{V} p(V)\,\mathrm{d}V \\ &= NkT \int_{V_0}^{V} \frac{\mathrm{d}V}{V} \\ &= NkT \ln(V/V_0) > 0 \end{aligned} \tag{4.119}$$

is delivered as work (task: mark the work in a p-V diagram). Since the internal energy $U = \frac{3}{2}NkT$ remains constant, heat $Q = -W$ was released from the reservoir to the

system, which corresponds to an entropy increase of

$$\Delta S = \frac{Q}{T} = -\frac{W}{T} > 0\,. \tag{4.120}$$

However, no heat was supplied to the *total system* (ideal gas). We will see that this change of state can be made reversible as part of a Carnot cycle: the work can be "used" to compress the gas isothermally back to its original volume.

4.3.5 Adiabatic expansion of an ideal gas

From section 4.2.2 we know that for an ideal gas

$$C_p = \frac{5}{2}Nk\,, \quad C_V = \frac{3}{2}Nk\,. \tag{4.121}$$

The isentropic exponent $\kappa = C_p/C_V$ is therefore

$$\kappa = \frac{5}{3}\,. \tag{4.122}$$

Hence, for an adiabatic process,

$$p \propto V^{-5/3}\,. \tag{4.123}$$

With $p(V) = p_0(V/V_0)^{-\kappa}$, the work generated by a (quasi-static) expansion is given by

$$\begin{aligned} -W &= \int_{V_0}^{V} p\,\mathrm{d}V \\ &= p_0 V_0^{5/3} \int_{V_0}^{V} V^{-5/3}\,\mathrm{d}V \\ &= \frac{3}{2}NkT_0\big(1-(V/V_0)^{-2/3}\big)\,, \end{aligned} \tag{4.124}$$

where we have used $p_0V_0 = NkT_0$. Because of $T\mathrm{d}S = \delta Q = 0$, the entropy remains constant, and the release of the mechanical work is accompanied by a change in temperature. In the Gay-Lussac experiment, in contrast, the work is "dissipated" and T remains constant.
Finally, let us note that the adiabatic exponent κ depends on the type of gas. In Exercise 11.2, κ is to be determined from "mechanical properties" of a gas.

4.3.6 The Carnot cycle

We consider a system that couples to heat baths of temperatures $T_2 > T_1$ and to a work reservoir. We assume that the system undergoes a reversible (in particular quasi-static) cycle (periodic process). The heats Q_2, Q_1 and the performed work $-W$ are released to the respective reservoirs. We choose the signs such that energies transferred to the system are counted positively and released amounts of energy are counted negatively.
For one cycle we then have

$$\Delta U = W + Q_1 + Q_2 = 0 \tag{4.125}$$

$$\Delta S = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0\,, \tag{4.126}$$

since U and S are state functions and the process is run quasi-statically. The entropy changes of the heat baths are therefore given by

$$\Delta S_1 := -\frac{Q_1}{T_1} = \frac{Q_2}{T_2} =: -\Delta S_2\,. \tag{4.127}$$

The *efficiency* of the cycle is defined as

$$\eta \coloneqq \frac{-W}{Q_2}\,, \tag{4.128}$$

i.e., the ratio of work to "consumed" heat, where the heat released to the colder heat bath is regarded as consumed. With eq. (4.125),

$$\eta = \frac{Q_1 + Q_2}{Q_2} = 1 + \frac{Q_1}{Q_2}\,. \tag{4.129}$$

From eq. (4.126) it follows that

$$\frac{Q_1}{Q_2} = -\frac{T_1}{T_2} \tag{4.130}$$

and thus the maximal efficiency compatible with the first and second laws (Carnot case),

$$\eta_{\mathrm{C}} = 1 - \frac{T_1}{T_2} < 1\,. \tag{4.131}$$

As a reversible cycle, the Carnot cycle can be operated in two directions:

- Forward operation/clockwise cycle (in the T-S and p-V diagrams): for $Q_2 > 0$, the work $-W = \eta Q_2 > 0$ is performed and the heat $-Q_1 = Q_2 T_1/T_2 > 0$ is released to the T_1 heat bath (heat engine).
- Backward operation/counterclockwise cycle: for $Q_2 < 0$, the work $W = -\eta Q_2 > 0$ is absorbed and the heat $Q_1 = -Q_2 T_1/T_2 > 0$ is extracted from the T_1 heat bath and released to the T_2 heat bath (heat pump/refrigerator).

The efficiency of the heat pump is defined as

$$\eta_W \coloneqq \frac{-Q_2}{W} = 1/\eta \tag{4.132}$$

and in the Carnot case gives

$$\eta_{\mathrm{C},W} = \frac{T_2}{T_2 - T_1} > 1\,. \tag{4.133}$$

Analogously, the efficiency of the refrigerator is defined as

$$\eta_K \coloneqq \frac{Q_1}{W} \tag{4.134}$$

and in the Carnot case is

$$\begin{aligned} \eta_{\mathrm{C},K} &= \frac{-Q_2}{W}\frac{T_1}{T_2} = \frac{1}{\eta}\frac{T_1}{T_2} \\ &= \frac{T_1}{T_2 - T_1} = \eta_{\mathrm{C},W} - 1\,. \end{aligned} \tag{4.135}$$

Results:

(i) The Carnot efficiency is universal, i.e., it depends only on the temperatures of the baths.

(ii) Heat cannot be converted completely into work (without further changes occurring). This rules out the existence of *perpetual motion machines of the second kind*.

A Carnot cycle can be explicitly composed of isothermal and adiabatic processes, i.e., there exist idealized cycles with $\eta = \eta_{\mathrm{C}}$.

Exercises (see also problem sheet 12):
Sketch the corresponding T-S and p-V diagrams and verify the efficiency by going through the four phases. Make use of

$$\begin{aligned} -W &= \oint p \, \mathrm{d}V \\ &= Q = \oint T \, \mathrm{d}S \, . \end{aligned} \tag{4.136}$$

4.3.7 The second law

Formulations of the second law

(i) In equilibrium, the intensive variables maximize the entropy (see also the equilibrium conditions in section 4.2.3.2); i.e., in particular, the entropy cannot decrease in isolated thermodynamic systems.

(ii) Heat cannot be converted completely into work without further changes occurring somewhere (Thomson; Planck), i.e., $\eta < 1$.

(iii) Heat cannot pass from a colder to a warmer system without further changes occurring (Clausius 1850). Otherwise one could transfer heat from the T_1 reservoir to the T_2 reservoir and thereby violate $\eta < 1$ (sketch in the lecture).

(iv) All Carnot cycles operating reversibly between the reservoirs with temperatures T_1 and T_2 have the same efficiency η_C; this is the maximal possible efficiency for all forward processes, irreversible processes included. Otherwise one could "chain" the different Carnot machines, one as a heat pump and one as a heat engine, and thereby violate the second law (see lecture).

(v) The Carnot efficiency is the highest possible one, i.e., $\eta \leq \eta_\mathrm{C}$ for all cycles (otherwise one could chain the process with a Carnot cycle and obtain a perpetual motion machine).

Irreversibly operating machines have a forward efficiency η_+ (heat engine) and a backward efficiency η_- (heat pump) with

$$\eta_+ \leq \eta_- \, . \tag{4.137}$$

As above, $\eta_+ > \eta_-$ leads to a contradiction via chaining of these processes.

(vi) There exists a state function S with $\mathrm{d}S = \delta Q_\mathrm{rev}/T$, which is constant in reversible adiabatic processes. In general, $\mathrm{d}S \geq 0$ holds for closed systems.

We have shown that (i) ⇒ (ii).

Exercise: Show that (ii) ⇔ (iii) and (ii) ⇒ (iv) (demonstrated in the lecture).
In section 4.3.9 we will see that (iv) ⇒ (vi). Since (vi) is essentially a reformulation of (i), the different formulations of the second law are equivalent (up to the statistical interpretation of (i)).

4.3.8 Absolute temperature (supplementary material)

What distinguishes our temperature scale? Could we, e.g., also use a scale that uses a Kelvin-squared scale instead of the Kelvin scale (e.g., $10\,\mathrm{K} \to 100\,\mathrm{K}^2$)?
In this section we will show that the Carnot cycle singles out the Kelvin scale up to a constant factor. For this purpose, we start from an arbitrary quantification ϑ of temperature, where ϑ increases monotonically under the supply of heat. Now let $\vartheta_1 < \vartheta_2$. From the Carnot cycle we know that

$$f(\vartheta_1, \vartheta_2) := 1 - \eta_C(\vartheta_1, \vartheta_2) = -\frac{Q_1}{Q_2} \tag{4.138}$$

is a universal function (it depends only on ϑ_1 and ϑ_2). Now we consider two Carnot cycles, one for $\vartheta_1 < \vartheta_2$ and one for $\vartheta_2 < \vartheta_3$. Since we can chain the Carnot machines, we have

$$f(\vartheta_1, \vartheta_3) = -\frac{Q_1}{Q_3'} = \Big(-\frac{Q_1}{Q_2}\Big)\Big(-\frac{Q_2'}{Q_3'}\Big) = f(\vartheta_1, \vartheta_2) f(\vartheta_2, \vartheta_3)\,, \tag{4.139}$$

where for the Carnot machine between $\vartheta_2 < \vartheta_3$ the heat Q_3' plays the role of Q_2 and Q_2' plays the role of Q_1 (sketch). Now we choose ϑ_2 as an arbitrary reference value. Therefore,

$$f(\vartheta_1, \vartheta_3) = a(\vartheta_1) b(\vartheta_3) \tag{4.140}$$

with $a(\vartheta_1) = f(\vartheta_1, \vartheta_2)$ and $b(\vartheta_3) = f(\vartheta_2, \vartheta_3)$. Using $f(\vartheta, \vartheta) = 1$ for all ϑ, one can show that

$$b(\vartheta_3) = \frac{1}{a(\vartheta_3)} =: \frac{1}{T(\vartheta_3)} \tag{4.141}$$

(without the assumption $\vartheta_1 < \vartheta_2 < \vartheta_3$) and thus

$$f(\vartheta_1, \vartheta_3) = \frac{T(\vartheta_1)}{T(\vartheta_3)}\,. \tag{4.142}$$

We call $T(\vartheta)$ the *absolute temperature*. With $T_i \coloneqq T(\vartheta_i)$,

$$\eta = 1 - f(\vartheta_1, \vartheta_2) = 1 - \frac{T_1}{T_2}\,. \tag{4.143}$$

The temperature scale still leaves a factor $\alpha > 0$ open, i.e., the choice $T'(\vartheta) = \alpha T(\vartheta)$ would also be possible. This corresponds to a different choice of the reference value ϑ_2. Usually we choose it such that the melting temperature of water is assigned the value 273.15.

4.3.9 Phenomenological entropy

We assume that formulation (iv) of the second law holds, and in this section we deduce the existence and the basic property of the entropy.
For all reversible cycles we have $\eta \overset{!}{=} \eta_{\mathrm{C}}$, i.e.,

$$\eta = \frac{-W}{Q_2} = \frac{Q_1 + Q_2}{Q_2} \overset{!}{=} 1 - \frac{T_1}{T_2} = \eta_{\mathrm{C}} \tag{4.144}$$

and thus

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0\,. \tag{4.145}$$

More generally, for a quasi-static sequence of equilibrium states with temperatures $T_0, \dots, T_n = T_0$ we have

$$\sum_{i=1}^{n} \frac{\Delta Q_i}{T_i} = 0 \tag{4.146}$$

with $\Delta Q_i = Q_i - Q_{i-1}$, where the initial state with T_0 and the final state coincide. Therefore,

$$\oint \frac{\delta Q_{\mathrm{rev}}}{T} = 0 \quad \forall \text{ reversible cycles}, \tag{4.147}$$

since these integrals can each be approximated arbitrarily well by a discretization (4.146); the index "rev" emphasizes that the process is reversible. It follows that there exists a state function S such that

$$\mathrm{d}S = \frac{1}{T}\,\delta Q_{\mathrm{rev}}\,, \tag{4.148}$$

i.e., $1/T$ is an integrating factor for δQ_{rev}. We call S the *phenomenological entropy*,

which is unique up to a constant and also coincides with our previously defined entropy. Formulation (iv) of the second law moreover states that for arbitrary (non-reversible) cycles

$$\eta = \frac{-W}{Q_2} = \frac{Q_1 + Q_2}{Q_2} \leq 1 - \frac{T_1}{T_2} = \eta_C \tag{4.149}$$

holds and thus

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leq 0\,. \tag{4.150}$$

This implies that

$$\oint \frac{\delta Q}{T} \leq 0 \quad \forall \text{ cycles.} \tag{4.151}$$

If we now have an arbitrary process $A \to B$, we can complete it reversibly to a cycle $A \to B \xrightarrow{\text{rev}} A$. Then

$$0 \geq \oint \frac{\delta Q}{T} = \int_A^B \frac{\delta Q}{T} + \underbrace{\int_B^A \frac{\delta Q_{\text{rev}}}{T}}_{S_A - S_B}\,, \tag{4.152}$$

i.e.,

$$S_B - S_A \geq \int_A^B \frac{\delta Q}{T}\,. \tag{4.153}$$

Since this holds for all processes $A \to B$, we have the following result.

$$\mathrm{d}S \geq \frac{\delta Q}{T} \tag{4.154}$$

Moreover, we have seen that there exists an entropy function that cannot decrease in isolated systems, which largely corresponds to formulation (i).

4.3.10 The third law of thermodynamics

In essence, the third law states that it is *not possible to cool a system down to absolute zero.*

Theorem 4.4 (Third law, Nernst 1905, with Planck's refinement of 1911)**.** *We consider a quantum system with a Hamiltonian $\hat{H}$. Let g_0 be the degeneracy of the ground state of $\hat{H}$. Then the entropy of the generalized canonical density operator (3.66) satisfies*

$$\lim_{T \to 0} S(\mathsf{M}) = k \ln(g_0)\,, \tag{4.155}$$

where $kT = 1/\beta = 1/\lambda_U$.

Proof for the canonical state. We write the Hamiltonian $\hat{H}$ in its eigendecomposition as

$$\hat{H} = \sum_j E_j \hat{P}_j\,, \tag{4.156}$$

where $E_0 < E_1 < \dots$ are the energy eigenvalues and $\hat{P}_j$ the eigenprojectors. By $g_j \coloneqq \mathrm{Tr}[\hat{P}_j]$ we denote the energy degeneracies.
The partition function is

$$Z = \mathrm{Tr}[\mathrm{e}^{-\beta \hat{H}}] = \sum_j \mathrm{e}^{-\beta E_j}\, \mathrm{Tr}[\hat{P}_j] = \sum_j g_j \mathrm{e}^{-\beta E_j} \tag{4.157}$$

and thus the canonical state is

$$\begin{aligned}\hat{\rho} &= \sum_j \frac{\mathrm{e}^{-\beta E_j}}{\sum_k g_k \mathrm{e}^{-\beta E_k}} \hat{P}_j \\ &= \sum_j \frac{\mathrm{e}^{\beta E_0}\mathrm{e}^{-\beta(E_j-E_0)}}{\mathrm{e}^{\beta E_0}\sum_k g_k \mathrm{e}^{-\beta(E_k-E_0)}} \hat{P}_j \\ &= \sum_j \frac{\mathrm{e}^{-\beta(E_j-E_0)}}{\sum_k g_k \mathrm{e}^{-\beta(E_k-E_0)}} \hat{P}_j \\ &= \frac{1}{\sum_k g_k \mathrm{e}^{-\beta(E_k-E_0)}} \hat{P}_0 + \frac{1}{\sum_k g_k \mathrm{e}^{-\beta(E_k-E_0)}} \sum_{j>0} \mathrm{e}^{-\beta(E_j-E_0)} \hat{P}_j \,.\end{aligned} \tag{4.158}$$

Because of

$$\lim_{\beta\to\infty} \mathrm{e}^{-\beta(E_k-E_0)} = \delta_{k,0} \tag{4.159}$$

the state at $T = 0$ is

$$\lim_{\beta\to\infty} \hat{\rho} = \frac{1}{g_0} \hat{P}_0 \,, \tag{4.160}$$

i.e., the maximally mixed state on the ground-state eigenspace. Since the entropy (3.32) is continuous, we thus have

$$\lim_{T\to 0} S(\hat{\rho}) = \lim_{\beta\to\infty} S(\hat{\rho}) = k \ln(g_0) \,. \tag{4.161}$$

The general proof proceeds analogously, or one can argue via the equivalence of the ensembles. □

Remarks and consequences:

- Typically, the degeneracy g_0 is small, so that $\ln(g_0)/N \approx 0$ for macroscopic systems. More precisely: the spectra of many-body Hamiltonians usually look like a suitably rescaled normal distribution, which can be shown rigorously for certain cases by means of a non-commutative **CLT!** [22, 23].

  The molar entropy is then also practically equal to zero.

- By means of the heat capacity $C_X = T\left(\frac{\partial S}{\partial T}\right)_X$, the entropy can be written as

  $$S(T) - S(T=0) = \int_0^T \mathrm{d}T' \, \frac{C_X(T')}{T'} \,. \tag{4.162}$$

  It follows that

  $$\lim_{T\to 0} C_X(T) = 0 \,, \tag{4.163}$$

  since otherwise the integral would not have a finite value (Exercise 12.3).

- It is not possible to cool a system down to absolute zero:

  to do so, one would have to extract all entropy from the system. For the known processes and realistic Hamiltonians, however, one can easily argue that this is impossible. Optimally, one would again alternate between isothermal and adiabatic sub-processes. In the S-T diagram one would then move step by step towards $T = 0$ within a "cone", where each step lowers the temperature but does not lead to $T = 0$ (Exercise 12.3).

5 Model Systems and Phase Transitions

In this chapter, we discuss several specific model systems in more detail.

5.1 Ideal Molecular Gas

We have repeatedly discussed the ideal gas as a paradigmatic example. It describes identical microscopic particles without mutual interaction. Hence, dilute gases, where the mean interparticle distance is much larger than the range of the interaction potential, are described correctly.
The canonical partition function (2.88) is

$$Z_N = \frac{(V/\lambda^3)^N}{N!} \tag{5.1}$$

and the grand canonical partition function (2.117)

$$\mathcal{Z} = \exp(zV/\lambda^3) \tag{5.2}$$

with thermal wavelength $\lambda = \frac{h}{\sqrt{2\pi mkT}}$ and fugacity $z = \mathrm{e}^{\beta\mu}$. Moreover, one obtains the following equations of state (sections 2.3.1.1, 2.3.3.2 and 4.1.1)

$$\frac{S}{kN} = \ln\left[\frac{V}{N\lambda^3}\right] + \frac{5}{2} \qquad \text{(Sackur–Tetrode)} \tag{5.3}$$

$$U = \frac{3}{2}\mathsf{N}kT \qquad \text{(caloric equation of state)}, \tag{5.4}$$

$$N = \frac{Vz}{\lambda^3}\,, \tag{5.5}$$

$$pV = NkT \qquad \text{(thermal equation of state)}. \tag{5.6}$$

For ideal molecular gases, the factors of $3/2$ appearing in the derivation must be replaced by $f/2$, where f is the number of non-frozen degrees of freedom of the molecule that appear as quadratic terms in the single-particle Hamiltonian (equipartition principle, Exercises 6.1 and 8.1). For example, a diatomic molecule (dumbbell-shaped) has 3 translational degrees of freedom, 2 rotational degrees of freedom, and 2 vibrational degrees of freedom (kinetic + potential energy). Under standard conditions ($T = 0°\mathrm{C}$, $p = 1\,\mathrm{atm}$), the vibrational degrees of freedom of gases such as oxygen, nitrogen, and hydrogen are frozen out, which leads to $f \approx 5$ and can be confirmed experimentally by measuring the heat capacities.
More precisely, there are temperatures Θ_{rot} and Θ_{vib} at which the freezing-out of the degrees of freedom takes place, which is captured by

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{f}{2}Nk \tag{5.7}$$

see the lecture or [2, Fig. 5.3 and explanations] for more details.

5.2 Real Gases

We now consider the situation where the interactions between the particles can no longer be neglected. Furthermore, we assume that the temperature is so high that quantum effects can be neglected. Accordingly, we write the Hamiltonian of N particles

as

$$H(p,q) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \sum_{i<j} \varphi(\mathbf{q}_i - \mathbf{q}_j) + V_{\text{wall}}(q)\,, \tag{5.8}$$

where m is the particle mass and φ the interaction potential of the particles. With (see, e.g., Exercise 4.3)

$$\frac{1}{h}\int \mathrm{d}p_k\, \exp\Big(-\frac{\beta}{2m}p_k^2\Big) = \frac{1}{\lambda} \tag{5.9}$$

the canonical partition function is

$$Z = \int \mathrm{d}\xi \mathrm{e}^{-\beta H(\xi)} = \frac{1}{h^{3N}N!}\int_{V^N} \mathrm{d}^3\mathbf{p}_1 \ldots \mathrm{d}^3\mathbf{p}_N \mathrm{d}^3\mathbf{q}_1 \ldots \mathrm{d}^3\mathbf{q}_N \mathrm{e}^{-\beta H(p,q)} \tag{5.10}$$

$$= \underbrace{\frac{V^N}{N!\lambda^{3N}}}_{=:Z_{\text{ideal}}} \underbrace{\frac{1}{V^N}\int_{V^N} \mathrm{d}^3\mathbf{q}_1 \ldots \mathrm{d}^3\mathbf{q}_N \exp\Big(-\beta\sum_{i<j}\varphi(\mathbf{q}_i - \mathbf{q}_j)\Big)}_{=:Z_{\text{pot}}}\,, \tag{5.11}$$

i.e., it factorizes into a kinetic part Z_{ideal}, which is identical to the canonical partition function (2.88) of an ideal gas, and a part Z_{pot} accounting for the potential interaction energy.
In order to evaluate the partition function further, we will approximate it for small deviations from the ideal gas by performing the so-called virial expansion of Z. To this end, we introduce

$$f_{i,j} \coloneqq \exp\big(-\beta\varphi(\mathbf{q}_i - \mathbf{q}_j)\big) - 1 \tag{5.12}$$

so that $f_{i,j} \to 0$ for a vanishing interaction potential φ. Now we expand the partition function (5.11) in powers of $f_{i,j}$, which yields the *virial expansion*:

$$\begin{aligned} Z &= \frac{1}{N!\lambda^{3N}}\int_{V^N} \mathrm{d}^3\mathbf{q}_1 \ldots \mathrm{d}^3\mathbf{q}_N \prod_{i<j}(1 + f_{i,j}) \\ &= \frac{1}{N!\lambda^{3N}}\int_{V^N} \mathrm{d}^3\mathbf{q}_1 \ldots \mathrm{d}^3\mathbf{q}_N \Big(1 + \sum_{i<j} f_{i,j} + \sum_{\substack{i<j \\ k<\ell}} f_{i,j}f_{k,\ell} + \ldots\Big). \end{aligned} \tag{5.13}$$

Here we consider the lowest order that deviates from the ideal gas:

$$Z = \frac{1}{N!\lambda^{3N}}\Big[V^N + V^{N-2}\sum_{i<j}\int_{V^2} \mathrm{d}^3\mathbf{q}_i \mathrm{d}^3\mathbf{q}_j f_{i,j}(\mathbf{q}_i - \mathbf{q}_j) + \mathrm{O}(V^{N-2})\Big]. \tag{5.14}$$

Using the relative coordinate $\mathbf{r} \coloneqq \mathbf{q}_1 - \mathbf{q}_2$, the indistinguishability of the particles, the assumption that $\varphi(\mathbf{r} + \mathbf{a}) = \varphi(\mathbf{r}) = \varphi(-\mathbf{r})$ for all $\mathbf{r}$ and $\mathbf{a}$, and the partition function of the ideal gas (5.2), this yields

$$\begin{aligned} Z &= \frac{1}{N!\lambda^{3N}}\Big[V^N + V^{N-2}\frac{N(N-1)}{2}\int \mathrm{d}^3\mathbf{r} f_{i,j}(\mathbf{r}) + \mathrm{O}(V^{N-2})\Big] \\ &= Z_{\text{ideal}} \underbrace{\Big[1 + \frac{N(N-1)}{V}B(T) + \mathrm{O}(1/V^2)\Big]}_{=Z_{\text{pot}}} \end{aligned} \tag{5.15}$$

with the *second virial coefficient*

$$B(T) \coloneqq \tfrac{1}{2}\int \mathrm{d}^3\mathbf{r} f_{1,2}(\mathbf{r})\,, \tag{5.16}$$

which accounts for the intermolecular two-particle interaction.

5.2.1 Thermal Equation of State

We have (see, e.g., the table in section 4.2)

$$p = -\frac{\partial F}{\partial V} = kT\frac{\partial \ln(Z)}{\partial V}\,. \tag{5.17}$$

With eq. (5.15), the free energy is[1]

$$\begin{aligned} F &= -kT\ln(Z) = -kT\big(\ln(Z_{\text{ideal}}) + \ln(Z_{\text{pot}})\big) \\ &\approx F_{\text{ideal}} - kT\ln\Big(1 + \frac{N(N-1)}{V}B(T)\Big) \\ &\approx F_{\text{ideal}} - kT\,\frac{N(N-1)}{V}B(T)\,, \end{aligned} \tag{5.18}$$

where F_{ideal} denotes the free energy of an ideal gas and we have used $\ln(1+x) = x + \mathrm{O}(x^2)$. With $-\frac{\partial F_{\text{ideal}}}{\partial V} = p_{\text{ideal}} = NkT/V$ and $N(N-1) \approx N^2$ we finally obtain

$$\begin{aligned} p &\approx \frac{NkT}{V} - kTB(T)\,\frac{N^2}{V^2} \\ &= \frac{NkT}{V}\Big(1 - \frac{N}{V}B(T)\Big). \end{aligned} \tag{5.19}$$

These are the first two terms of a series expansion in the particle density N/V with first virial coefficient 1 and second virial coefficient $B(T)$. The coefficient $B(T)$ can be determined experimentally or computed via more sophisticated derivations. For this, one has to assume a concrete potential φ. A good model is given by the Lennard-Jones potential

$$\varphi(|\mathbf{r}|) = \frac{c_1}{|\mathbf{r}|^{12}} - \frac{c_2}{|\mathbf{r}|^6}\,. \tag{5.20}$$

The r^6 term arises from a dipole–dipole approximation of attractive interactions, and the r^{12} term provides a strong short-range repulsion (the 12 in the exponent is not a typo!).
A simpler model is one of hard spheres with a fixed proper volume, outside of which an attractive potential decays quickly, i.e.,

$$\varphi(r)\begin{cases} = \infty & \text{for } r \le d \\ < 0 & \text{for } r > d \end{cases}$$

in spherical coordinates. For eq. (5.12), such a potential yields

$$f_{1,2}(r) \approx \begin{cases} -1 & \text{for } r < d\,, \\ -\beta\varphi(r) & \text{for } r > d\,. \end{cases} \tag{5.21}$$

Per mole (i.e., $N \mapsto N_{\text{A}}$), this leads for the second virial coefficient (5.16) to

$$\begin{aligned} B(T) &= -\frac{1}{2}\,\frac{4\pi}{3}d^3 - \frac{1}{2}\int_d^\infty \beta\varphi(r)4\pi r^2\,\mathrm{d}r \\ &= -\frac{b}{N_{\text{A}}} + \frac{a}{kTN_{\text{A}}^2} \end{aligned} \tag{5.22}$$

[1] We have computed Z only approximately. In general, however, $f(x) \approx g(x)$ does not imply that also $\frac{\partial f}{\partial x}(x) \approx \frac{\partial g}{\partial x}(x)$. The approximation of F made here, which is the usual one, additionally relies on the hypothesis that nature behaves sufficiently "benignly" on macroscopic scales.

with the molar *proper volume* (covolume)

$$b := 4N_{\mathrm{A}} \frac{4\pi}{3} \left(\frac{d}{2}\right)^3 \geq 0, \tag{5.23}$$

where d is the diameter of the spheres (sketch), and the *internal pressure*

$$a := \frac{1}{2} N_{\mathrm{A}}^2 \int_d^\infty |\varphi(r)| 4\pi r^2 \, \mathrm{d}r \geq 0 \qquad \text{(spherical coordinates)}. \tag{5.24}$$

With eq. (5.19) and the gas constant $R := kN_{\mathrm{A}}$, this gives

$$p = \frac{RT}{v}\left(1 + \frac{b}{v}\right) - \frac{a}{v^2}\,. \tag{5.25}$$

For *dilute gases*, i.e., $b \ll v$, this equation agrees with the empirical van der Waals equation

$$p = \frac{RT}{v - b} - \frac{a}{v^2} \tag{5.26}$$

(see also [2, Fig. 5.11] or the lecture for a sketch), since then $\frac{1}{1-b/v} \approx 1 + b/v$. It is often also written in the following form.

Van der Waals equation

$$RT = \left(p + \frac{a}{v^2}\right)(v - b) \tag{5.27}$$

Here, a and b can be estimated more precisely by further calculations, and using the leading error from eq. (5.18) one can describe a domain of validity of the van der Waals equation; more precisely: $v \gg b$ and $kT \gg \langle \varphi \mathbf{1}_{[d,\infty)} \rangle := \int_d^\infty r^2 \varphi$. However, one can also determine a and b empirically and thereby enlarge the domain of validity of the van der Waals equation.
For a sufficiently small constant temperature T, the function $p(v)$ from eq. (5.26) has a local maximum, a local minimum, and an inflection point. We will see that the van der Waals gas undergoes phase transitions at these temperatures when the volume is varied suitably. For a sufficiently large constant temperature T, the function $p(v)$ is monotonically decreasing. It follows that there exists a point (T_c, p_c, v_c) at which $p(v)$ has a saddle point, which is also called the *critical point*. At (T_c, v_c) we must have

$$\frac{\partial p}{\partial v} = 0 = \frac{\partial^2 p}{\partial v^2}\,. \tag{5.28}$$

From this, one obtains the values (Exercise 13.1a)

$$v_c = 3b\,, \quad RT_c = \frac{8}{27}\frac{a}{b}\,, \quad p_c = \frac{a}{27b^2} \tag{5.29}$$

for the critical point.

5.2.2 Caloric Equation of State

With eq. (2.20) and eq. (5.15) we have

$$\begin{aligned} U &= -\frac{\partial \ln(Z)}{\partial \beta} \\ &\approx -\frac{\partial \ln(Z_{\text{ideal}})}{\partial \beta} - \frac{\partial}{\partial \beta} \ln\left(1 + \frac{N^2}{V} B(T)\right) \\ &\approx \frac{3}{2} NkT - \frac{N^2}{V} \frac{\partial B(T)}{\partial T} \frac{\partial T}{\partial \beta}\,, \end{aligned} \tag{5.30}$$

where we have again used $\ln(1+x) = x + \mathrm{O}(x^2)$. With $\frac{\partial T}{\partial \beta} = -kT^2$,

$$U = \frac{3}{2}NkT + \frac{N^2kT^2}{V}\frac{\partial B(T)}{\partial T} \tag{5.31}$$

is the caloric equation of state. For the van der Waals case (5.22) we have

$$\frac{\partial B(T)}{\partial T} = -\frac{a}{kT^2N_A^2} \tag{5.32}$$

and thus (in molar notation):

Van der Waals gas: caloric equation of state

$$u = \frac{3}{2}RT - \frac{a}{v}\,. \tag{5.33}$$

5.2.3 The Joule-Thomson Process

This process describes the throttled expansion of a gas (sketch in the lecture).

- Initial state: V_1, U_1
- Final state: V_2, U_2

Here, the gas is pressed by a piston out of the volume V_1 through a throttle into a volume V_2, which in turn is coupled to a piston. The two pistons keep the pressures fixed at p_1 and p_2, respectively. The entire process is adiabatic.
The total change of the internal energy is therefore

$$U_2 - U_1 = \int_{V_1}^{0}(-p_1)\mathrm{d}V + \int_{0}^{V_2}(p_2)\mathrm{d}V = p_1V_1 - p_2V_2\,. \tag{5.34}$$

It follows that the enthalpy $H = U + pV$ remains unchanged during the process. The temperature change is therefore given by the *Joule-Thomson coefficient*

$$\mu_{\mathrm{JT}} \coloneqq \left(\frac{\partial T}{\partial p}\right)_H\,. \tag{5.35}$$

One can show (Exercise 13.3b) that

$$\mu_{\mathrm{JT}} = \frac{V}{C_p}(T\alpha - 1)\,, \tag{5.36}$$

where C_p is the heat capacity (1.14) and α the thermal expansion coefficient (4.50). For an ideal gas, eq. (4.70) gives $\alpha = 1/T$ and no temperature change occurs. For real gases, however, α can be larger or smaller than $1/T$, i.e., both heating (negative Joule-Thomson effect) and cooling (positive Joule-Thomson effect) of the gas are possible. The boundary between these two effects is given by the *inversion curve* $p_{\mathrm{inv}}(V)$, on which

$$\alpha = \frac{1}{T} \tag{5.37}$$

holds.
Example: For a van der Waals gas, eq. (5.26) gives

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \tag{5.38}$$

and differentiating with respect to T yields

$$0 = \frac{R}{v-b} - \frac{RT}{(v-b)^2}\left(\frac{\partial v}{\partial T}\right)_p + \frac{2a}{v^3}\left(\frac{\partial v}{\partial T}\right)_p . \tag{5.39}$$

Inserting the inversion condition $\alpha \coloneqq \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{1}{T}$ gives

$$\begin{aligned} 0 &= \frac{R}{v-b} - \frac{Rv}{(v-b)^2} + \frac{2a}{Tv^2} \\ \Leftrightarrow \quad 0 &= \frac{RT}{v} - \frac{RT}{v-b} + \frac{2a(v-b)}{v^3} = -\frac{b}{v}\frac{RT}{v-b} + \frac{2a(v-b)}{v^3} \end{aligned} \tag{5.40}$$

and with eq. (5.38)

$$\begin{aligned} 0 &= -\frac{b}{v}\left(p_{\text{inv}} + \frac{a}{v^2}\right) + \frac{2a(v-b)}{v^3} \\ \Leftrightarrow \quad p_{\text{inv}} &= \frac{2a}{bv} - \frac{3a}{v^2} . \end{aligned} \tag{5.41}$$

Moreover, one can derive an inversion curve $p_{\text{inv}}(T)$; see Wikipedia for the derivation and [2, Fig. 3.14a] or the lecture for a sketch. Above the curve the Joule-Thomson coefficient is always negative, below it always positive.

5.2.4 Phase Transitions

The van der Waals equation (5.27) can equivalently be written as

$$pv^3 - (RT + pb)v^2 + av - ab = 0 . \tag{5.42}$$

Hence, there are T, p such that three solutions for v exist, which becomes particularly clear from a sketch of $p(v)$ for different values of T; see [2, Fig. 5.11], the lecture, and Exercise 13.1b.
To this end, we recall the critical point (5.29) (cf. Exercise 13.1a). Accordingly, there is a temperature interval with $T < T_c$ for which

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} > 0 . \tag{5.43}$$

In particular, the isothermal compressibility is negative,

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T < 0 . \tag{5.44}$$

Thus, the stability condition (4.52) is violated!
The stability boundary is defined by $\left(\frac{\partial p}{\partial v}\right)_T = 0$, where mechanical stability holds for $\left(\frac{\partial p}{\partial v}\right)_T < 0$ and is violated for $\left(\frac{\partial p}{\partial v}\right)_T > 0$. It follows that, as we approach the stability boundary, the compressibility diverges,

$$\kappa_T \propto -\frac{1}{\left(\frac{\partial p}{\partial v}\right)_T} \to \infty . \tag{5.45}$$

Using eq. (4.40), it also follows that the thermal expansion coefficient and the heat

capacities diverge,

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = -\frac{\left(\frac{\partial p}{\partial T}\right)_V}{v\left(\frac{\partial p}{\partial v}\right)_T} \to \infty \tag{5.46}$$

$$c_p = c_v + \frac{Tv\alpha^2}{\kappa_T} = c_v - T\frac{\left(\frac{\partial v}{\partial T}\right)_p^2}{\left(\frac{\partial v}{\partial p}\right)_T} = c_v + T\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial p}{\partial T}\right)_v \to \infty\,, \tag{5.47}$$

where for c_p and c_V additionally eq. (4.67) was used. In Exercise 13.1d it is shown that the singular behavior can be described by so-called *critical exponents*, i.e., e.g.,

$$\kappa_T \propto \left(\frac{T - T_c}{T_c}\right)^{-\gamma} \tag{5.48}$$

with critical exponent $\gamma = 1$.
By the fluctuation-dissipation theorem (2.43), the volume fluctuations, or density fluctuations, are given by

$$\mathrm{Var}(v) \equiv \langle(\Delta v)^2\rangle = -kT\left(\frac{\partial v}{\partial p}\right)_T = kT\, v\, \kappa_T \to \infty \tag{5.49}$$

and likewise diverge at the stability boundary.
In general, we can note that at the stability boundary the susceptibilities, which are given as second derivatives of the Gibbs energy $G(T, p)$ (see section 4.2.2), diverge. Such singular behavior is, more generally, taken as the definition of a *phase transition*. Physically, a coexistence of different phases is observed at the stability boundary. In the p-V diagram for $T < T_c$, the region between the two local extrema is unstable and "separates" the liquid and the gaseous phase (see the lecture for a sketch).

5.2.4.1 Maxwell Construction for Phase Coexistence

By the equilibrium condition (4.99) for the Gibbs energy,

$$g_1(T, P(T)) = g_2(T, P(T))\,, \tag{5.50}$$

where g_1 and g_2 denote the molar Gibbs energies in the liquid and in the gaseous phase, respectively, and $P(T)$ the equilibrium vapor pressure. In terms of the molar free energy $f = g - pv$, this means that

$$f_2 - f_1 + (v_2 - v_1)P = 0\,. \tag{5.51}$$

With $\left(\frac{\partial f}{\partial v}\right)_T = -p$ it follows that

$$\int_{v_1}^{v_2}\left(\frac{\partial f}{\partial v}\right)_T \mathrm{d}v + (v_2 - v_1)P = 0\,, \tag{5.52}$$

which implies the following *equal-area rule*.

Maxwell construction

The integral

$$(v_2 - v_1)P = \int_{v_1}^{v_2} p\,\mathrm{d}v \tag{5.53}$$

determines the *Maxwell line* $P(T)$ (in the p-V diagram) as well as the molar volumes v_2 and v_1.

See [2, Fig. 5.14] or the lecture for a sketch. It follows that $v(p)$ is discontinuous at constant $T < T_c$. We also recall the vapor-pressure curve (4.110) of an ideal gas, $P(T) \propto \mathrm{e}^{-q/(RT)}$, which approximately describes the temperature dependence.
Metastability refers to phenomena such as *delayed boiling* (superheating) or supersaturated vapor, which are compatible with the van der Waals description. Such metastable states are generally typical for phase transitions.

5.2.4.2 Classification of Phase Transitions (Ehrenfest)

We have seen that in the van der Waals gas, at the phase transition between the liquid and the gaseous phase, the second derivatives of the Gibbs energy diverge and $V = \left(\frac{\partial G}{\partial p}\right)_T$ is discontinuous. This motivates the following definition.

Definition 5.1 (Phase transition of n-th order (Ehrenfest))**.** *At a phase transition of n-th order, at least one of the n-th derivatives of the Gibbs energy G is discontinuous.*

*Remarks*on the van der Waals gas:

- A *first-order phase transition* occurs if $\left(\frac{\partial G}{\partial p}\right)_T = V$ is discontinuous. Here we observe (i) a coexistence of phases and (ii) that *latent heat* occurs at the phase transition (above, the heat of vaporization $q = (s_2 - s_1)T$, cf. the Clausius–Clapeyron equation in section 4.2.3.3). This is because

$$S = -\left(\frac{\partial G}{\partial T}\right)_p \tag{5.54}$$

  is then discontinuous as well.

- A *second-order phase transition* occurs if $\left(\frac{\partial G}{\partial p}\right)_T = V$ is continuous but $\left(\frac{\partial^2 G}{\partial p^2}\right)_T = \left(\frac{\partial V}{\partial p}\right)_T$ is discontinuous. Such a phase transition occurs when, in the p-V diagram, the critical point is traversed vertically, perpendicular to the phase-coexistence region.

  Then there is no phase coexistence and no latent heat occurs, since $S = -\left(\frac{\partial G}{\partial T}\right)_p$ is continuous, and the path must pass through the critical point. This can be described by universal critical exponents, is accompanied by critical fluctuations, and a critical slowing down of the relaxation to equilibrium occurs.

- In an alternative formulation of the Ehrenfest classification, the free energy is used instead of the Gibbs energy.

- The classification does not cover the case that derivatives of the potentials diverge at phase transitions. There is a more modern classification into phase transitions of first and second order. This classification also includes, e.g., *superconductivity*.

5.3 Ideal Quantum Gases II

In section 3.7 we encountered the grand canonical partition function

$$\mathcal{Z} = \sum_{\{N_{\mathbf{p}}\}} \exp\Big(-\beta \sum_{\mathbf{p}} (E_{\mathbf{p}} - \mu) N_{\mathbf{p}}\Big) \tag{5.55}$$

for ideal quantum gases, where $\sum_{\mathbf{p}} N_{\mathbf{p}} = N$; here we have parametrized the sums by the momentum eigenvalues $\mathbf{p} = (p_x, p_y, p_z)$ instead of a counting index j, since we are considering an ideal gas with a Hamiltonian of the form $\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m}$. It should be clear from the context when p denotes the momentum and when it denotes the pressure.

This yields

$$\mathcal{Z} = \prod_{\mathbf{p}} (1 + t_{\mathbf{p}}) \qquad \text{for fermions,} \tag{5.56}$$

$$\mathcal{Z} = \prod_{\mathbf{p}} \frac{1}{1 - t_{\mathbf{p}}} \qquad \text{for bosons} \tag{5.57}$$

with

$$t_{\mathbf{p}} \coloneqq \mathrm{e}^{-\beta(E_{\mathbf{p}} - \mu)} \,, \tag{5.58}$$

where for bosons one has to assume $E_{\mathbf{p}} > \mu$ for all $\mathbf{p}$.
Hence, for an ideal quantum gas the *grand canonical potential* is

$$\Phi(T, V, \mu) = -kT \ln(\mathcal{Z}) = \frac{\xi}{\beta} \sum_{\mathbf{p}} \ln\bigl(1 - \xi \mathrm{e}^{-\beta(E_{\mathbf{p}} - \mu)}\bigr) \,, \tag{5.59}$$

with $\xi = 1$ for bosons and $\xi = -1$ for fermions.
From this, all thermodynamic quantities follow:

- Mean particle number at given μ:

$$N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = \sum_{\mathbf{p}} \frac{\mathrm{e}^{-\beta(E_{\mathbf{p}} - \mu)}}{1 - \xi \mathrm{e}^{-\beta(E_{\mathbf{p}} - \mu)}} = \sum_{\mathbf{p}} N_{\mathbf{p}} \tag{5.60}$$

  with the *Bose–Einstein* and *Fermi–Dirac distribution function*, respectively,

$$N_{\mathbf{p}} = N(E_{\mathbf{p}}) = \frac{1}{\mathrm{e}^{\beta(E_{\mathbf{p}} - \mu)} - \xi} \,. \tag{5.61}$$

  We check that $N_{\mathbf{p}}$ is the mean occupation number of the momentum eigenstate $|\mathbf{p}\rangle$ (discrete, as we are confined to the volume V),

$$N_{\mathbf{p}} = \langle \hat{N}_{\mathbf{p}} \rangle = \mathrm{Tr}[\hat{\rho} \hat{N}_{\mathbf{p}}] = \cdots = N(E_{\mathbf{p}}) \,, \tag{5.62}$$

  where $\hat{\rho}$ is the grand canonical density operator. The energy thus splits into single-particle energies, since we are dealing with an ideal gas.

- Internal energy

$$U = -\left(\frac{\partial \ln(\mathcal{Z})}{\partial \beta}\right)_{\beta\mu} = -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \beta} \tag{5.63}$$

  since $\lambda_U = \beta$ and $\lambda_N = -\beta\mu$; cf. eq. (3.77). With eq. (5.55), taking the corresponding derivative yields

$$U = \frac{1}{\mathcal{Z}} \sum_{\{N_{\mathbf{p}}\}} E_{\mathbf{p}} \exp\Bigl(-\beta \sum_{\mathbf{p}} (E_{\mathbf{p}} - \mu) N_{\mathbf{p}}\Bigr) = \langle \hat{H} \rangle = \sum_{\mathbf{p}} E_{\mathbf{p}} N_{\mathbf{p}} \,. \tag{5.64}$$

Remarks:

- For $N(E_{\mathbf{p}}) \geq 0$ to hold, bosons must satisfy

$$\mu \leq \min(E_{\mathbf{p}}) \,. \tag{5.65}$$

  For fermions, $0 \leq N(E_{\mathbf{p}}) \leq 1$ is automatically satisfied because of the Pauli principle, and μ is thus arbitrary.

- Classical limit: $\mathrm{e}^{-\beta(E_{\mathbf{p}} - \mu)} \ll 1$, that is, high energies $(E_{\mathbf{p}} - \mu) \gg kT$ (not simply high temperature!). Then the Maxwell–Boltzmann distribution follows,

$$N_{\mathbf{p}}^{\mathrm{MB}} = \mathrm{e}^{-\beta(E_{\mathbf{p}} - \mu)} \,, \tag{5.66}$$

as well as (by factorizing eq. (5.55)) the classical potential

$$\Phi = -kT \sum_{\mathbf{p}} \mathrm{e}^{-\beta(E_{\mathbf{p}}-\mu)} \,. \tag{5.67}$$

With the fugacity $z = \exp(\beta\mu)$ it follows (continuum limit: $\sum_{\mathbf{p}} \to (V/h^3) \int \mathrm{d}^3\mathbf{p}$, cf. eq. (3.119)) that

$$\Phi = -kTz \frac{V}{(2\pi\hbar)^3} \int \mathrm{d}^3\mathbf{p}\, \mathrm{e}^{-\beta\mathbf{p}^2/2m} = -kTzV/\lambda^3 \tag{5.68}$$

with $\lambda = h/\sqrt{2\pi mkT}$. This is consistent with the previously computed partition function (2.117).

5.3.1 Equation of State

We will now derive an equation of state in the variables p, V, and U. But we start with the question: What is the mean particle number of an ideal quantum gas? Since $E_{\mathbf{p}}$ is independent of the spin s, the continuum limit is given by

$$\sum_{\mathbf{p}} \ldots \;\to\; g \frac{V}{h^3} \int \mathrm{d}^3\mathbf{p} \ldots \tag{5.69}$$

where here $\int \mathrm{d}^3\mathbf{p} \ldots \to 4\pi \int_0^\infty \mathrm{d}p\, p^2 \ldots$ and the degeneracy factor $g = 2s + 1$ were used. The total particle number is thus

$$N = \frac{gV}{(2\pi\hbar)^3} \int \mathrm{d}^3\mathbf{p}\, N(E_{\mathbf{p}}) = \frac{gV}{2\pi^2\hbar^3} \int_0^\infty \mathrm{d}p\, p^2 N(E_{|\mathbf{p}|}) \,. \tag{5.70}$$

Now we use eq. (5.61) and change to the integration variable $\epsilon = p^2/2m$, where

$$p^2 \mathrm{d}p \mapsto m\sqrt{2m\epsilon}\, \mathrm{d}\epsilon \tag{5.71}$$

(this can be seen from $\mathrm{d}\epsilon = p\,\mathrm{d}p/m$, hence $p^2\mathrm{d}p = pm\,\mathrm{d}\epsilon$), and thus

$$N = \frac{gVm^{3/2}}{\sqrt{2}\,\pi^2\hbar^3} \int_0^\infty \mathrm{d}\epsilon \frac{\epsilon^{1/2}}{\mathrm{e}^{\beta(\epsilon-\mu)} - \xi} \,. \tag{5.72}$$

With $x = \beta\epsilon$ and $v = V/N$ (inverse density), it follows ($z = \mathrm{e}^{\beta\mu}$ is the fugacity and $\lambda = h/\sqrt{2\pi mkT}$ the thermal wavelength) that

$$\frac{1}{v} = \frac{g}{\lambda^3} \begin{cases} g_{3/2}(z) & \text{for bosons} \\ f_{3/2}(z) & \text{for fermions} \end{cases} \tag{5.73}$$

with generalized Riemann ζ-functions[2], also called *polylogarithms*[3] ($x = \beta\epsilon$),

$$g_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty \mathrm{d}x\, \frac{x^{\nu-1}}{z^{-1}\mathrm{e}^x - 1} \,, \tag{5.74}$$

$$f_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty \mathrm{d}x\, \frac{x^{\nu-1}}{z^{-1}\mathrm{e}^x + 1} \tag{5.75}$$

and the Gamma function with, e.g., $\Gamma(3/2) = \sqrt{\pi}/2$, $\Gamma(1) = 1$ and the functional equation

$$\Gamma(z+1) = z\Gamma(z) \,. \tag{5.76}$$

[2] The usual Riemann ζ-function is $\nu \mapsto g_\nu(1)$.
[3] One also writes $g_\nu(z) \equiv \mathrm{Li}_\nu(z)$ for the polylogarithm Li.

The power series expansion of the generalized zeta functions is (without proof):

$$\left\{ \begin{array}{c} g_\nu(z) \\ f_\nu(z) \end{array} \right\} = \sum_{k=1}^{\infty} \xi^{k+1} \frac{z^k}{k^\nu} \,, \tag{5.77}$$

where $\xi = +1$ for bosons (g_ν) and $\xi = -1$ for fermions (f_ν).
In the same way, it follows that

$$\Phi = -\beta^{-1} \ln(\mathcal{Z}) = -pV = \frac{\xi}{\beta} \sum_p \ln(1 - \xi \mathrm{e}^{-\beta(E_p - \mu)}) \,. \tag{5.78}$$

In the continuum limit, this yields

$$\begin{aligned} \Phi &= \xi \frac{gVm^{3/2}}{\sqrt{2}\,\pi^2\hbar^3\beta} \int_0^\infty \mathrm{d}\epsilon \sqrt{\epsilon} \ln[1 - \xi \exp(-\beta(\epsilon - \mu))] && (5.79) \\ &= -\frac{2}{3} \frac{gVm^{3/2}}{\sqrt{2}\,\pi^2\hbar^3} \int_0^\infty \mathrm{d}\epsilon \frac{\epsilon^{3/2}}{\mathrm{e}^{\beta(\epsilon-\mu)} - \xi} \\ &= \frac{-gVkT}{\lambda^3} \begin{cases} g_{5/2}(z) & \text{(bosons)}, \\ f_{5/2}(z) & \text{(fermions)}, \end{cases} && (5.80) \end{aligned}$$

where in the second step integration by parts was used, with the auxiliary relations

$$\sqrt{\epsilon} = \frac{2}{3} \partial_\epsilon \epsilon^{3/2} \tag{5.81}$$

$$\partial_\epsilon \ln\bigl(1 - \xi \mathrm{e}^{-\beta(\epsilon-\mu)}\bigr) = \frac{\xi\beta}{\mathrm{e}^{\beta(\epsilon-\mu)} - \xi} \,, \tag{5.82}$$

i.e., since the boundary term vanishes, integration by parts yields

$$\int_0^\infty \mathrm{d}\epsilon \sqrt{\epsilon} \ln(1 - \xi \mathrm{e}^{-\beta(\epsilon-\mu)}) = -\frac{2}{3} \int_0^\infty \mathrm{d}\epsilon \epsilon^{3/2} \underbrace{\partial_\epsilon \ln(\cdots)}_{\frac{\xi\beta}{\mathrm{e}^{\beta(\epsilon-\mu)} - \xi}}; \tag{5.83}$$

note also $\Gamma(5/2) = (3/2)\Gamma(3/2) = (3/4)\sqrt{\pi}$.
Likewise, the internal energy follows,

$$U = \frac{gV}{(2\pi\hbar)^3} \int \mathrm{d}^3p \, E_{\mathbf{p}} N(E_{\mathbf{p}}) = \frac{gVm^{3/2}}{\sqrt{2}\,\pi^2\hbar^3} \int_0^\infty \mathrm{d}\epsilon \, \frac{\epsilon^{3/2}}{\mathrm{e}^{\beta(\epsilon-\mu)} - \xi} = -\frac{3}{2}\Phi = +\frac{3}{2}pV \,. \tag{5.84}$$

Altogether, as for the classical ideal gas, we obtain the *equation of state of an ideal quantum gas*

$$pV = \frac{2}{3}U \tag{5.85}$$

independently of the statistics. For the classical ideal gas, we also have $pV = NkT = 2U/3$ because $U = (3/2)NkT$. Caution: $U = (3/2)NkT$ holds only for the classical ideal gas, whereas $pV = 2U/3$ holds generally for a quadratic dispersion relation (i.e., massive non-relativistic particles). For photons the equation of state is a different one. In the following section, we will see that the equation of state eq. (5.73) for bosons acquires an additional term, which yields the following equation.

Equation of state of an ideal Bose gas

$$\frac{N}{V} = \frac{1}{\lambda^3} g_{3/2}(z) + \frac{1}{V} \frac{z}{1 - z} \tag{5.86}$$

5.3.2 Classical Limit

In the classical limit, $E - \mu \gg kT$. For low energies E, it follows that $\mu \ll -kT$, so $z = \exp(\mu/kT) \ll 1$. Hence, eq. (5.73) together with eq. (5.77) implies that

$$\frac{\lambda^3}{gv} = \sum_{k=1}^{\infty} \xi^{k+1} z^k k^{-3/2} = z + \xi z^2/\sqrt{8} + \mathrm{O}(z^3)\,. \tag{5.87}$$

Solving the quadratic equation and expanding to second order in $\lambda^3/gv \ll 1$ yields

$$z \approx \frac{\lambda^3}{vg} - \xi \frac{1}{\sqrt{8}} \Big(\frac{\lambda^3}{vg}\Big)^2 . \tag{5.88}$$

Thus, with eq. (5.77), it follows from eq. (5.80) that

$$\begin{aligned} \Phi &= \frac{-gVkT}{\lambda^3}(z + \xi z^2/\sqrt{32} + \cdots) \\ &= -\frac{gVkT}{\lambda^3}\left(\frac{\lambda^3}{vg} - \xi \frac{1}{\sqrt{8}}\Big(\frac{\lambda^3}{vg}\Big)^2 + \xi \frac{1}{\sqrt{32}}\Big(\frac{\lambda^3}{vg}\Big)^2 + \cdots\right), \end{aligned} \tag{5.89}$$

that is, the *equation of state*

$$pV = -\Phi = NkT\Big(1 - \xi \frac{\lambda^3}{\sqrt{32}\, vg} + \cdots\Big) = \frac{2}{3}U\,; \tag{5.90}$$

compare this with the classical ideal gas. Corrections scale as $\hbar^3/T^{3/2}$, since $\lambda = h/\sqrt{2\pi mkT}$.

Leading *quantum corrections* (exchange corrections):

- They are proportional to $\hbar^3$ and depend on the symmetry behavior ($\xi = \pm$) of the wave function.
- For bosons (symmetric state vectors), the pressure is reduced, as if the atoms attracted each other (cf. the van der Waals equation!). There is a tendency toward *cluster formation for bosons*, even though the particles are non-interacting.
- For fermions (antisymmetric state vectors), the pressure is increased, i.e., there is an effective repulsion. The *Pauli principle acts like a repulsive force*, even though the particles are non-interacting.

  This is an effect of quantum statistics.
- The classical limit applies if $\lambda \ll v^{1/3}$ (the typical distance between two particles is $v^{1/3}$, since the inverse density is just v), i.e., for strong dilution and/or high temperature.
- The mean occupation number follows from the Fermi–Dirac and Bose–Einstein distribution, respectively. In the classical limit,

  $$\frac{1}{z^{-1}\mathrm{e}^{\beta E} \pm 1} \to \mathrm{e}^{-\beta(E-\mu)}\,, \tag{5.91}$$

  since then $-\beta\mu \gg 1$ and thus $z = \mathrm{e}^{\beta\mu} \ll 1$. This limit therefore yields exactly the *Maxwell–Boltzmann distribution*

  $$N^{\mathrm{MB}}(E) = \mathrm{e}^{-\beta(E-\mu)}\,. \tag{5.92}$$

  In particular, there is no difference between the distributions for bosons and fermions in the classical limit.

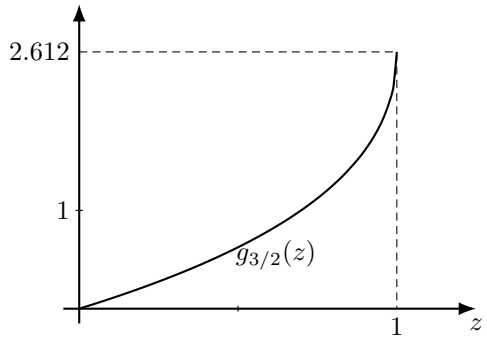

Figure 5.1: Graph of the function $g_{3/2}$; we have $g_{3/2}(1) = \zeta(3/2) \approx 2.612$ (with ζ-function ζ).

5.3.3 Ideal Bose Gases

In the following, we consider some physically relevant special cases, depending on the dispersion relation $p \mapsto E_p$.

5.3.3.1 Bose–Einstein Condensation

We consider an ideal gas of N spinless ($g = 2s+1 = 1$) bosons with dispersion relation

$$E_{\mathbf{p}} = \frac{\mathbf{p}^2}{2m}\,. \tag{5.93}$$

In the ground state, all bosons occupy the single-particle state with $\mathbf{p} = 0$.
BEC! (**BEC!**) refers to the phenomenon that below a certain critical temperature T_c the single-particle state with $\mathbf{p} = 0$ is *macroscopically* occupied, i.e., with a particle number of the order of the total particle number N. Here one observes a separation into a condensate and excited "normal" thermal bosons. This was predicted by Einstein and Bose in 1924 and observed in 1995 by Ketterle, Cornell, and Wieman (Nobel Prize 2001).
For bosons, the inverse specific volume from eq. (5.73) is given by

$$\frac{\lambda^3}{v} = g_{3/2}(z) \qquad \text{(equation of state)}. \tag{5.94}$$

For bosons, $\mu \leq 0$ must hold, hence $0 < z \leq 1$. Thus, the maximal value of $g_{3/2}(z)$ is attained at $z = 1$:

$$g_{3/2}(1) = \zeta(3/2) \approx 2.612\,, \tag{5.95}$$

see fig. 5.1.
In the following, let N, V, and hence also $v = V/N$, be constant. Then eq. (5.94) determines the chemical potential μ, or the fugacity $z = \mathrm{e}^{\beta\mu}$. When T is decreased, both λ^3/v and $z = \exp(-|\mu|/(kT))$ increase (see fig. 5.1). This can only continue up to $z = 1$, i.e., there must be a critical temperature T_c, determined by $\lambda^3 = v g_{3/2}(1)$, below which $z = 1$.
From the existence of the critical temperature T_c at $z = 1$, it follows from eq. (5.94) that

$$kT_c = \frac{2\pi\hbar^2/m}{(2.612v)^{2/3}}\,. \tag{5.96}$$

The higher the density (i.e., the smaller the specific volume v) and the lighter the atoms, the higher T_c. Below T_c, a condensate exists in addition to the thermal Bose gas. In the extreme case $T = 0$, only the condensate would remain.
At T_c, the fugacity z, and hence also the chemical potential μ, is not continuously differentiable. On the other hand, $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,p}$, i.e., a second derivative of the Gibbs

energy has a discontinuity. Hence, the condensation effect is a *second-order phase transition*.
At temperatures that are not substantially larger than T_c, the limiting procedure $d^3p \mapsto d\epsilon$ must be carried out more carefully. We treat the $\mathbf{p} = 0$ mode in eq. (5.60) separately, where below T_c the chemical potential is $\mu = 0$, i.e., $z = 1$. The total particle number is

$$\begin{aligned} N &= N(\mathbf{p}=0) + \sum_{\mathbf{p}\neq 0} N(E_\mathbf{p}) \\ &\approx N_0 + \frac{V}{h^3}\int d^3\mathbf{p}\, N(E_\mathbf{p}) \\ &= N_0 + N\frac{v}{\lambda^3} g_{3/2}(z)\,, \end{aligned} \tag{5.97}$$

where N_0 is the number of condensed atoms and we have already computed the integral in eq. (5.73). We have

$$N_0 = N(\mathbf{p}=0) = \frac{1}{\mathrm{e}^{\beta(0-\mu)} - 1} = \frac{1}{1/z - 1}\,, \tag{5.98}$$

which also implies eq. (5.86).

Remarks:

- Already the closest mode with $\mathbf{p} \neq 0$ has an occupation probability that is smaller by orders of magnitude. At $T = 0$ this behavior is extremal.
- With the definition of the critical temperature, it follows for arbitrary T that

  $$N = N_0 + N(T/T_c)^{3/2}\frac{g_{3/2}(z)}{g_{3/2}(1)}\,. \tag{5.99}$$

  For $T > T_c$, we have $z < 1$, and N_0 is of order 1 and can therefore be neglected compared to the second term. It follows that $g_{3/2}(z) = g_{3/2}(1)(T/T_c)^{-3/2}$, which gives us $\mu(T)$.
- For $T < T_c$, we have $z = 1$, i.e., $\mu(T < T_c) = 0$, and

  $$N = N_0 + N(T/T_c)^{3/2}\,. \tag{5.100}$$

  The *condensate fraction* for large N is thus

  $$\nu_0 \coloneqq \frac{N_0}{N} = 1 - (T/T_c)^{3/2} \tag{5.101}$$

  (see the lecture or [2, Fig. 4.13] for a sketch).
- Specific heat of the Bose gas:
  At low T, $C_V \propto T^{3/2}$ (longer calculation via $S = -\left(\frac{\partial(pV)}{\partial T}\right)_{V,\mu}$). At $T = T_c$, however, there is a sharp peak ('cusp'), which is a signature of the phase transition; see the lecture or [2, Fig. 4.17] for a sketch.

Physical applications of the ideal spinless Bose gas:

- Helium-4. At $T_\lambda = 2.18$ K (lambda temperature), there is a phase transition into a superfluid state. However, interactions are very important here; otherwise it would be "simple" **BEC!**. They cause a strong depletion of the macroscopically occupied mode ("quantum depletion") down to a few percent.
- Atomic hydrogen in a strong magnetic field (spin polarization to prevent recombination into H_2). Here, **BEC!** was demonstrated in 1998 ($T_c = 50\,\mu$K).

- First experimental demonstration of Bose–Einstein condensates in ultracold atomic gases (Rb, Li) in traps (1995). Metastable (the solid is actually the stable form at ultralow temperatures), but with a long lifetime since very dilute, with few three-body collisions. Here, T_c is in the nano-Kelvin range.

5.3.3.2 Photon Gas

The dispersion relation for massless particles is

$$E_{\mathbf{p}} = c|\mathbf{p}| = c\hbar|\mathbf{k}| \tag{5.102}$$

with wave vector $\mathbf{k}$. Photons have spin $s = 1$. However, the degeneracy of the energies is $g = 2$ and not $g = (2s + 1) = 3$, since, due to the propagation at the speed of light, the polarization $\sigma = \pm$ must be perpendicular to $\mathbf{k}$. The Hamiltonian is therefore

$$\hat{H} = \sum_{\mathbf{p},\sigma} E_{\mathbf{p}} \hat{N}(\mathbf{p}, \sigma)\,, \qquad \mathbf{p} \neq 0\,, \tag{5.103}$$

where $\hat{N}(\mathbf{p}, \sigma)$ is the occupation number operator for momentum $\mathbf{p}$ and polarization σ. The partition function is

$$\begin{aligned} Z = \mathrm{Tr}[\mathrm{e}^{-\beta\hat{H}}] &= \sum_{\{N(\mathbf{p},\pm)\}} \mathrm{e}^{-\beta \sum_{\mathbf{p},\sigma} E_{\mathbf{p}} N(\mathbf{p},\sigma)} \\ &= \left(\prod_{\mathbf{p}\neq 0} \frac{1}{1 - \mathrm{e}^{-\beta c|\mathbf{p}|}} \right)^2, \end{aligned} \tag{5.104}$$

where the exponent is precisely $g = 2$. Using the continuum limit (5.69) and subsequently integrating, one can derive the following thermodynamic equations:

$$F = -kT \ln(Z) = -\frac{4\sigma}{3c} V T^4 \qquad \text{(free energy)}, \tag{5.105}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{16\sigma}{3c} V T^3 \qquad \text{(entropy)}, \tag{5.106}$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = \frac{16\sigma}{c} V T^3 \qquad \text{(heat capacity)}, \tag{5.107}$$

$$U = F + TS = \frac{4\sigma}{c} V T^4 \qquad \text{(internal energy)}, \tag{5.108}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{4\sigma}{3c} T^4 \qquad \text{(radiation pressure)}, \tag{5.109}$$

where σ is the *Stefan–Boltzmann constant*

$$\sigma = \frac{2\pi^5 k_{\mathrm{B}}^4}{15 h^3 c^2} = \frac{\pi^2 k_{\mathrm{B}}^4}{60 \hbar^3 c^2}\,. \tag{5.110}$$

For the internal energy, see also Exercise 8.2 (Stefan–Boltzmann law). We observe that, due to the relativistic dispersion relation,

$$U = 3pV \tag{5.111}$$

holds instead of eq. (5.85).
Using the Bose–Einstein distribution (5.61), one can also compute the *spectral energy density* (energy per unit volume and unit frequency)

$$u(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\mathrm{e}^{\hbar\omega/(kT)} - 1}\,, \tag{5.112}$$

which corresponds to the Rayleigh–Jeans law in the classical limit $kT \gg \hbar\omega$ and to Wien's law in the quantum limit $kT \ll \hbar\omega$; see the lecture or [2, Fig. 4.23] for a sketch.

5.3.3.3 Phonon Gas

The "phonon gas" consists of non-interacting quantized lattice vibrations in solids. Here, the dispersion relation is likewise linear. However, there are two transverse plus one longitudinal vibrational modes.

5.3.4 Ideal Fermi Gas

5.3.4.1 Physical Examples

Real fermion systems are interacting; often, Coulomb interactions play little or no role. Theoretical basis: Landau's *Fermi liquid theory*, which would lead too far here. Physical mechanisms for "switching off" the interaction:

- Screening: electrons form polarization clouds around charges. The long-range tail of the Coulomb potential is screened (see electrodynamics).
- We will see that the Pauli principle implies that there are only few states contributing to electron-electron scattering (phase-space argument).

For the ideal Fermi gas, one again assumes non-interacting particles.
The ideal Fermi gas is applicable, to a good approximation, to

- the electron gas in many metals, e.g., alkali metals, noble metals
- Helium-3 (there, interaction effects within Fermi liquid theory are also important)
- nuclear matter: neutrons and protons are fermions. Also in neutron stars.
- white dwarfs (at the end of a star's life), e.g., Sirius B, which consist of ionized nuclei and free electrons (plasma).

The ideal Fermi gas is not applicable to correlation effects such as magnetism or superconductivity.

5.3.4.2 Ground State (Fermi Sea)

We consider the ground state ($T = 0$) of an N-fermion system with spin, having spin $s = 1/2$ in mind (e.g., electrons). Because of the Pauli principle, each momentum eigenstate $|\mathbf{p}\rangle$ is either unoccupied or singly occupied. Each value of $\mathbf{p}$ occurs, e.g., for electrons, exactly twice ($g = 2$).
In the ground state, all momentum eigenstates below $p_F = \hbar k_F$ are occupied such that the particle density N/V is realized. One calls p_F the *Fermi momentum* and

$$E_F = \frac{\hbar^2 k_F^2}{2m} = kT_F \tag{5.113}$$

the *Fermi energy* and *Fermi temperature*, respectively, with the *Fermi wave number* k_F.
A 2D sketch in momentum space is helpful here to visualize which states are occupied (Fermi sphere); see the lecture or [2, Fig. 4.2].
For the so-called *degenerate Fermi gas*, *degenerate* means a deviation from the classical ideal gas.
In the ground state, all single-particle states with energy smaller than the Fermi energy E_F, or momentum $p := |\mathbf{p}|$ smaller than p_F, are thus occupied (Pauli principle!).

Hence, in the continuum limit (5.69), the particle number is

$$\begin{aligned} N &= g \sum_{p \le p_F} 1 = \frac{gV}{h^3} \int_0^\infty \Theta(p_F - p) 4\pi p^2 \mathrm{d}p \qquad \text{(spherical coordinates)} \\ &= \frac{gV p_F^3}{6\pi^2 \hbar^3} , \end{aligned} \tag{5.114}$$

where we have used $h = 2\pi\hbar$. Thus,

$$p_F = \Big(\frac{6\pi^2}{g}\Big)^{1/3} \hbar \varrho^{1/3} \tag{5.115}$$

with particle density $\varrho \coloneqq N/V$. Furthermore, the Fermi energy is

$$E_F = \frac{p_F^2}{2m} = \Big(\frac{6\pi^2}{g}\Big)^{2/3} \frac{\hbar^2}{2m} \varrho^{2/3} . \tag{5.116}$$

The ground-state energy is

$$U = \frac{gV}{h^3} \int_0^\infty \frac{p^2}{2m} \Theta(p_F - p) 4\pi p^2 \mathrm{d}p = \frac{gV p_F^5}{20\pi^2 \hbar^3 m} , \tag{5.117}$$

hence

$$U = \frac{3}{5} E_F N . \tag{5.118}$$

The equation of state eq. (5.85) yields the pressure

$$p = \frac{2}{3} \frac{U}{V} = \frac{2}{5} E_F \varrho = \frac{1}{5} \Big(\frac{6\pi^2}{g}\Big)^{2/3} \frac{\hbar^2}{m} \varrho^{5/3} . \tag{5.119}$$

The degeneracy of the ground state is so small that its entropy vanishes macroscopically (cf. section 4.3.10). The Euler equation (4.2) thus yields

$$\mu = \frac{1}{N}(U + pV - TS) = \ldots = E_F , \tag{5.120}$$

which is consistent with the definition of the chemical potential (it is the energy required to add another particle to the ensemble). Note, however, that the existence of the Fermi energy is rooted in quantum mechanics.

5.3.4.3 Finite Temperatures

Now we consider $T \ll T_F$. Here, the Fermi–Dirac distribution

$$N(E) = \frac{1}{\mathrm{e}^{(E-\mu)/kT} + 1} \tag{5.121}$$

leads to a "smearing" of the *Fermi edge* by $\pm kT$; see the sketch in the lecture or [2, Fig. 4.3]. For $T \to 0$, the edge becomes a step ("degenerate Fermi gas"). One can compute [2, Sec. 4.3] that the effect of the smearing is given by the following correction to the energy,

$$U = U(T = 0) + C \Big(\frac{k_\mathrm{B} T}{E_F}\Big)^2 + \mathrm{O}(T^4) , \tag{5.122}$$

with an absolute constant C. For small temperatures, the heat capacity is thus linear in T,

$$C_V \propto T/T_F , \tag{5.123}$$

and hence usually small, since T_F is very large for metals. More generally, thermal effects in Fermi gases are usually small. Analogously, using $N(T) = N(T = 0) = N(\epsilon_F)$,

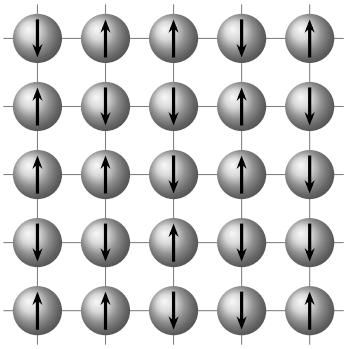

Figure 5.2: Ising model.

one can show that

$$\mu(T) = E_F\left(1 - \frac{\pi^2}{12}\left(\frac{kT}{E_F}\right)^2 + \mathrm{O}(T^4)\right). \tag{5.124}$$

5.4 The Ising Model

The Ising model is a special case of *quantum spin lattice systems*, which also include, e.g., the Heisenberg model. These models form the basis, e.g., for the understanding of magnetism. An overview of the mathematical treatment of the Ising model can be found in [24].
We consider a system of N (classical) spins, each with magnetic moment $\mu_0 s_i$ with $s_i = \pm 1$, on a cubic lattice; see fig. 5.2.

- Here, spins can only point up or down, so the model can be regarded as a strongly anisotropic version of the SU(2)-invariant quantum-mechanical Heisenberg model.
- The quantum-mechanical Heisenberg models with SU(2) symmetry are considerably more complicated to analyze. Written as a quantum model, the Ising model is diagonal in the σ_z basis.
- In solids, the interactions between spins are usually short-ranged.

The *Ising model* is a fundamental model of statistical physics that can explain magnetism. It is a classical model with Hamiltonian

$$H(s) = -J\sum_{\langle i,j\rangle} s_i s_j - \mu_0 B\sum_{i=1}^{N} s_i\,, \tag{5.125}$$

where $s \in \{-1,1\}^N$, B is the external magnetic field strength in the z direction, J is a coupling constant, and $\langle i,j\rangle$ denotes the nearest neighbors on the given interaction graph, which here is a cubic lattice in D spatial dimensions (see fig. 5.2 for $D = 2$).

- If $J > 0$, it is energetically favorable to align the spins in the same direction: tendency toward *ferromagnetism*.
- If $J < 0$, there is correspondingly a tendency toward *antiferromagnetism*.
- An external magnetic field $B > 0$ tries to align the spins upwards.
- We consider $J > 0$. As a function of the temperature, a phase transition between an ordered ferromagnetic phase ($T < T_c$) and a disordered paramagnetic phase ($T > T_c$) should occur at the *Curie temperature* $T = T_c$.

- The ferromagnetic phase has a *spontaneous magnetization*. Cooperative processes set in that make all spins point in the same direction, even though the Hamiltonian H contains only short-range interactions. This means that *long-range correlations* and *long-range order* emerge from rules for the behavior of nearest neighbors!

The *magnetization* is the observable

$$M(s) := \mu_0 \sum_{i=1}^{N} s_i \,. \tag{5.126}$$

A *spontaneous magnetization* is present if

$$\langle M \rangle = \mu_0 \sum_{i=1}^{N} \langle s_i \rangle \tag{5.127}$$

has a macroscopically non-vanishing value for $B = 0$; see fig. 5.3 for the spontaneous magnetization in the 2D Ising model. We often also write

$$\langle M \rangle = \mu_0 (N_+ - N_-) \,, \tag{5.128}$$

where $N_\pm$ is the expected number of spins s_i with value ± 1.
Both directions (signs) of M are possible at $B = 0$; one of them is realized. This is called *spontaneous symmetry breaking:*

- The Hamiltonian possesses full symmetry under $s_i \to -s_i$ (for all spins simultaneously). However, this does not hold for the ground state and the magnetization M.
- Spontaneous symmetry breaking is a very important concept, e.g., in the description of the weak interaction in particle physics, the Meissner effect in superconductivity, and much more.
- The realized sign of M depends on the history.

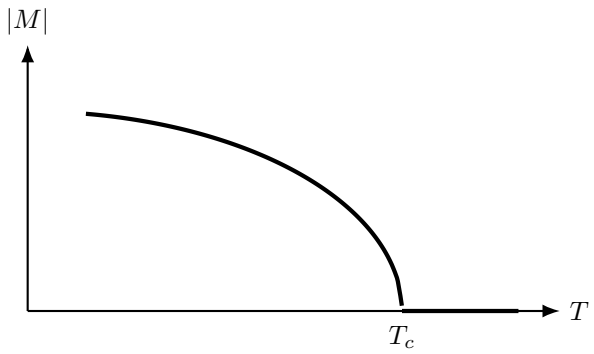

Figure 5.3: Spontaneous magnetization.

5.4.1 Partition Function

Implicitly, we have chosen U as a macroscopic constraint and N and B as microscopic constraints. The partition function is

$$\begin{aligned} Z(\beta; B, N) &= \sum_{s\in\{-1,1\}^N} \mathrm{e}^{-\beta H(s)} \\ &= \sum_{s_1=\pm} \cdots \sum_{s_N=\pm} \mathrm{e}^{\beta\mu_0 B\sum_{i=1}^N s_i}\ \mathrm{e}^{\beta J\sum_{\langle ij\rangle} s_i s_j}\,. \end{aligned} \tag{5.129}$$

The magnetic field plays the role of the chemical potential, which controls the magnetization $\langle M\rangle = N_+ - N_-$.

5.4.2 The 1D Ising Model

In one dimension (Ising chain), the partition function can be computed exactly in an elementary way. For the calculation, it is helpful to set $\mu_0 = 1$. The interaction is the sum over a single index, i.e.,

$$H(s) = -\sum_{i=1}^{N}(Js_is_{i+1} + Bs_i)\,, \tag{5.130}$$

where we choose periodic boundary conditions $s_{N+1} = s_1$. Then the *transfer matrix method* can be applied: We will see shortly that the partition function is the trace of a product of N identical 2×2 matrices

$$A = \begin{pmatrix} \mathrm{e}^{\beta(J+B)} & \mathrm{e}^{-\beta J} \\ \mathrm{e}^{-\beta J} & \mathrm{e}^{\beta(J-B)} \end{pmatrix} \tag{5.131}$$

with entries $A(s_i, s_{i+1})$. The matrix A is called the *transfer matrix*, since it propagates one site further along the Ising chain. The partition function is thus

$$\begin{aligned} Z &= \sum_{s_1=\pm} \cdots \sum_{s_N=\pm} \prod_{i=1}^{N} \mathrm{e}^{\beta(Js_is_{i+1}+Bs_i)} \\ &= \sum_{s_1=\pm} \cdots \sum_{s_N=\pm} \prod_{i=1}^{N} \mathrm{e}^{\beta\left(\frac{B}{2}s_i + Js_is_{i+1} + \frac{B}{2}s_{i+1}\right)} \\ &= \mathrm{Tr}\left[\begin{pmatrix} \mathrm{e}^{\beta(J+B)} & \mathrm{e}^{-\beta J} \\ \mathrm{e}^{-\beta J} & \mathrm{e}^{\beta(J-B)} \end{pmatrix}^N\right] \\ &= \mathrm{Tr}[A^N] \\ &= \lambda_+^N + \lambda_-^N \end{aligned} \tag{5.132}$$

with the eigenvalues $\lambda_\pm$ of the matrix A. Each eigenvalue λ of A must satisfy $\det(A - \lambda\mathbb{1}) = 0$ and hence

$$\lambda^2 - 2\cosh(\beta B)\mathrm{e}^{\beta J}\lambda + \mathrm{e}^{2\beta J} - \mathrm{e}^{-2\beta J} = 0\,. \tag{5.133}$$

Thus,

$$\lambda_\pm = \mathrm{e}^{\beta J}\left(\cosh(\beta B) \pm \sqrt{\cosh^2(\beta B) - 1 + \mathrm{e}^{-4\beta J}}\right). \tag{5.134}$$

For $N\to\infty$, the larger eigenvalue dominates the partition function (5.132). Hence, for large N,

$$\ln Z(T, B, N) \approx N\ln(\lambda_+) \tag{5.135}$$

or, equivalently, $F \approx -kTN \ln(\lambda_+)$. For $B = 0$, it follows that

$$Z = [2\cosh(\beta J)]^N \,. \tag{5.136}$$

We obtain the magnetization as a derivative with respect to B (which again follows from the definition of the partition function),

$$\langle M \rangle =: M = kT \frac{1}{Z} \frac{\partial}{\partial B} Z(T, B, N)\Big|_{B=0} = kT \frac{\partial}{\partial B}\Big|_{B=0} \ln(Z(T, B, N)) \,. \tag{5.137}$$

For $B \to 0, T > 0$, Z and $\ln(Z)$ are analytic functions of B^2 (the Taylor expansion in B^2 exists). It thus follows immediately that

$$M(B = 0) = 0 \,. \tag{5.138}$$

In one dimension, there is no spontaneous magnetization at finite temperature.

This is a special case of the *Mermin–Wagner theorem*. In discrete systems (such as spin systems), fluctuations destroy any order for $T > 0$ in one spatial dimension (completely generally, not restricted to this type of model).
Physical explanation: We consider the spin configuration where the first $N/2$ spins have the value $s_i = +$ and the other spins have the value $s_j = -$. A fully aligned ferromagnet would have energy $-NJ$. However, this state has energy $H(s) = (-N + 4)J$ and magnetization 0 ("disordered"). Here we have two *domain walls* (where the spin orientations change), each with an energy cost of $2J$. For large N, the relative energy change is thus only of order $1/N$, i.e., small energy fluctuations already destroy the magnetic order.

5.4.3 The 2D Ising Model

In two dimensions, domain walls are lines and cost a relative energy $\propto N^{-1/2}$. Here, there is a critical temperature T_c such that for $T < T_c$ a ferromagnetic phase exists (likewise in 3D). This is, however, highly non-trivial and was only shown by the exact solution of the 2D Ising model by Lars Onsager (1944). The derivation would lead too far; the result, with $\beta = 1/(kT)$, is for $B = 0$

$$Z = [2\cosh(\beta J)\mathrm{e}^I]^N = \mathrm{e}^{-\beta F} \tag{5.139}$$

with

$$I = \int_0^\pi \frac{\mathrm{d}\phi}{2\pi} \ln\Big(\frac{1}{2}\big[1 + \sqrt{1 - \kappa^2 \sin^2\phi}\big]\Big) \tag{5.140}$$

and

$$\kappa = 2\frac{\sinh(2\beta J)}{\cosh^2(2\beta J)} \,. \tag{5.141}$$

The free energy F has a *branch cut* for $\kappa > 1$ (non-uniqueness of the logarithm), and hence indeed a spontaneous magnetization. The critical temperature T_c, also called the *Curie temperature*, satisfies

$$\kappa_c = \frac{2\sinh(2J/kT_c)}{1 + \sinh^2(2J/kT_c)} = 1 \,, \tag{5.142}$$

which implies that

$$\sinh(2J/kT_c) = 1 \to \frac{kT_c}{J} = \frac{2}{\ln(1 + \sqrt{2})} \approx 2.269 \,. \tag{5.143}$$

A spontaneous magnetization $M(T)$ near $T = T_c$ (but below) then follows in the form

$$\frac{M}{N} \propto (T_c - T)^\eta \tag{5.144}$$

with *critical exponent* $\eta = 1/8$. The heat capacity C_V follows from the exact solution in the form (near T_c)

$$\frac{C_V}{N} = \frac{k_\mathrm{B}\beta^2}{N} \frac{\partial^2 \ln Z(\beta)}{\partial \beta^2} \approx \frac{8k}{\pi} (\beta J)^2 \ln |1/(T - T_c)| \,, \tag{5.145}$$

i.e., the heat capacity diverges logarithmically.
The canonical distribution is here explicitly given by the probability vector p with components

$$p_s = \frac{\mathrm{e}^{-\beta H(s)}}{Z} \,. \tag{5.146}$$

The *correlation* between two spins $i, j \in [N]$ is

$$\Gamma(i,j) \coloneqq \big\langle (S_i - \langle S_i \rangle)(S_j - \langle S_j \rangle) \big\rangle \tag{5.147}$$

$$= \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle \,, \tag{5.148}$$

where all expectation values are taken with respect to p and S_i is the random variable with values in $\{-1, +1\}$ that describes the i-th spin and is thermally distributed here, i.e., the random vector S is distributed according to the probability vector p. Onsager also showed that the correlations decay as

$$\Gamma_p(i,j) \leq c_\beta \, \mathrm{e}^{-\beta |i-j| / \xi(\beta)} \tag{5.149}$$

with correlation length

$$\xi \propto \frac{1}{|T - T_c|^\nu} \tag{5.150}$$

and critical exponent $\nu = 1$.

The 3D Ising model has not been solved analytically so far. Numerical works show $T_c^{3D} \approx 2T_c^{2D}$ with critical exponent

$$\eta \approx 0.313 \,. \tag{5.151}$$

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