Lecture Notes on Statistical Mechanics and Thermodynamics

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1. Introduction and Historical Overview

As the name suggests, **thermodynamics** historically developed as an attempt to understand phenomena involving **heat**. This notion is intimately related to irreversible processes involving typically *many*, essentially randomly excited, degrees of freedom. The proper understanding of this notion as well as the 'laws' that govern it took the better part of the 19$^{\text{th}}$ century. The basic rules that were, essentially empirically, observed were clarified and laid out in the so-called "laws of thermodynamics". These laws are still useful today, and will, most likely, survive most microscopic models of physical systems that we use.

Before the laws of thermodynamics were identified, other theories of heat were also considered. A curious example from the 17$^{\text{th}}$ century is a theory of heat proposed by J. Becher. He put forward the idea that heat was carried by special particles he called "phlogistons" ($\varphi\lambda o\gamma\iota\sigma\tau\acute{o}\varsigma$: "burned")[1]. His proposal was ultimately refuted by other scientists such as A.L. de Lavoisier[2], who showed that the existence of such a particle did not explain, and was in fact inconsistent with, the phenomenon of burning, which he instead correctly associated also with chemical processes involving oxygen. Heat had already previously been associated with friction, especially through the work of B. Thompson, who showed that in this process work (mechanical energy) is converted to heat. That heat transfer can generate mechanical energy was in turn exemplified through the steam engine as developed by inventors such as J. Watt, J. Trevithick, and T. Newcomen - the key technical invention of the 18$^{\text{th}}$ and 19$^{\text{th}}$ century. A broader theoretical description of processes involving heat transfer was put forward in 1824 by N.L.S. Carnot, who emphasized in particular the importance of the notion of equilibrium. The quantitative understanding of the relationship between heat and energy was found by J.P. Joule and R. Mayer, who were the first to state clearly that heat is a form of energy. This finally lead to the principle of conservation of energy put forward by H. von Helmholtz in 1847.

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[1] Of course this theory turned out to be incorrect. Nevertheless, we nowadays know that heat can be radiated away by particles which we call "photons". This shows that, in science, even a wrong idea can contain a germ of truth.

[2] It seems that Lavoisier's foresight in political matters did not match his superb scientific insight. He became very wealthy owing to his position as a tax collector during the "Ancien Régime" but got in trouble for this lucrative but highly unpopular job during the French Revolution and was eventually sentenced to death by a revolutionary tribunal. After his execution, one onlooker famously remarked: "It takes one second to chop off a head like this, but centuries to grow a similar one."

Parallel to this largely phenomenological view of heat, there were also early attempts to understand this phenomenon from a microscopic angle. This viewpoint seems to have been first stated in a transparent fashion by D. Bernoulli in 1738 in his work on hydrodynamics, in which he proposed that heat is transferred from regions with energetic molecules (high internal energy) to regions with less energetic molecules (low energy). The microscopic viewpoint ultimately lead to the modern 'bottom up' view of heat by J.C. Maxwell, J. Stefan and especially L. Boltzmann. According to Boltzmann, heat is associated with a quantity called "entropy" which increases in irreversible processes. In the context of equilibrium states, entropy can be understood as a measure of the number of accessible states at a defined energy according to his famous formula

$$\boxed{S = k_{\mathrm{B}} \ \log W(E)},$$

which Planck had later engraved in Boltzmann's tomb on Wiener Zentralfriedhof:

Figure 1.1.: Boltzmann's tomb with his famous entropy formula engraved at the top.

The formula thereby connects a *macroscopic*, phenomenological quantity S to the *microscopic* states of the system (counted by $W(E)$ = number of accessible states of energy E). His proposal to relate entropy to counting problems for microscopic configurations and thereby to ideas from probability theory was entirely new and ranks as one of the major intellectual accomplishments in Physics. The systematic understanding of the relationship between the distributions of microscopic states of a system and macroscopic quantities such as S is the subject of **statistical mechanics**. That subject nowadays goes well beyond the original goal of understanding the phenomenon of heat but is more broadly aimed at the analysis of systems with a large number of, typically interacting, degrees of freedom and their description in an "averaged", or "statistical", or "coarse grained" manner. As such, statistical mechanics has found an ever growing number of applications to many diverse areas of science, such as

- Neural networks and other networks

- Financial markets

- Data analysis and mining

- Astronomy

- Black hole physics

and many more. Here is an, obviously incomplete, list of some key innovations in the subject:

Timeline

17$^{\text{th}}$ century:

   Ferdinand II, Grand Duke of Tuscany: Quantitative measurement of temperature

18$^{\text{th}}$ century:

   A.Celsius, C. von Linné: Celsius temperature scale
   A.L. de Lavoisier: basic calometry
   D. Bernoulli: basics of kinetic gas theory
   B. Thompson (Count Rumford): mechanical energy can be converted to heat

19$^{\text{th}}$ century:

1802 *J. L. Gay-Lussac:* heat expansion of gases

1824 *N.L.S.Carnot:* thermodynamic cycles and heat engines

1847 *H. von Helmholtz:* energy conservation (1$^{\text{st}}$ law of thermodynamics)

1848 *W. Thomson (Lord Kelvin):* definition of absolute thermodynamic temperature scale based on Carnot processes

1850 *W. Thomson and H. von Helmholtz:* impossibility of a perpetuum mobile (2$^{\text{nd}}$ law)

1857 *R. Clausius:* equation of state for ideal gases

1860 *J.C. Maxwell:* distribution of the velocities of particles in a gas

1865 *R.Clausius:* new formulation of 2$^{\text{nd}}$ law of thermodynamics, notion of entropy

1877 *L. Boltzmann:* $S = k_{\text{B}} \log W$

1876 (as well as 1896 and 1909) controversy concerning entropy, Poincaré recurrence is not compatible with macroscopic behavior

1894 *W. Wien:* black body radiation

20th century:

20$^{\text{th}}$ century:

1900 *M. Planck:* radiation law → Quantum Mechanics

1911 *P. Ehrenfest:* foundations of Statistical Mechanics

1924 Bose-Einstein statistics

1925 Fermi-Pauli statistics

1931 *L. Onsager:* theory of irreversible processes

1937 *L. Landau:* phase transitions, later extended to superconductivity by Ginzburg

1930's *W. Heisenberg, E. Ising, R. Peierls,...:* spin models for magnetism

1943 *S. Chandrasekhar, R.H. Fowler:* applications of statistical mechanics in astrophysics

1956 *J. Bardeen, L.N. Cooper, J.R. Schrieffer:* explanation of superconductivity

1956-58 *L. Landau:* theory of Fermi liquids

1960's *T. Matsubara, E. Nelson, K. Symanzik,...:* application of Quantum Field Theory methods to Statistical Mechanics

1970's *L. Kadanoff, K.G. Wilson, W. Zimmermann, F. Wegner,...:* renormalization group methods in Statistical Mechanics

1973 *J. Bardeen, B. Carter, S. Hawking, J. Bekenstein, R.M. Wald, W.G. Unruh,...:* laws of black hole mechanics, Bekenstein-Hawking entropy

1975 - Neural networks

1985 - Statistical physics in economy

2. Basic Statistical Notions

2.1. Probability Theory and Random Variables

Statistical mechanics is an intrinsically *probabilistic* description of a system, so we do *not* ask questions like "What is the velocity of the Nth particle?" but rather questions of the sort "What is the probability for the Nth particle having velocity between v and $v + \Delta v$?" in an ensemble of particles. Thus, basic notions and manipulations from probability theory can be useful, and we now introduce some of these, without any attention paid to mathematical rigor.

- A **random variable** x can have different outcomes forming a set $\Omega = \{x_1, x_2, \ldots\}$, e.g. for tossing a coin $\Omega_{\text{coin}} = \{\text{head,tail}\}$ or for a dice $\Omega_{\text{dice}} = \{1, 2, 3, 4, 5, 6\}$, or for the velocity of a particle $\Omega_{\text{velocity}} = \{\vec{v} = (v_x, v_y, v_z) \in \mathbb{R}^3\}$, etc.

- An **event** is a subset $E \subset \Omega$ (not all subsets need to be events).

- A **probability measure** is a map that assigns a number $P(E)$ to each event, subject to the following general rules:

  (i) $P(E) \geq 0$.

  (ii) $P(\Omega) = 1$.

  (iii) If $E \cap E' = \varnothing \Rightarrow P(E \cup E') = P(E) + P(E')$.

In mathematics, the data $(\Omega, P, \{E\})$ is called a **probability space** and the above axioms basically correspond to the axioms for such spaces. For instance, for a fair dice the probabilities would be $P_{\text{dice}}(\{1\}) = \ldots = P_{\text{dice}}(\{6\}) = \frac{1}{6}$ and E would be any subset of $\{1, 2, 3, 4, 5, 6\}$. In practice, probabilities are determined by repeating the experiment (independently) *many* times, e.g. throwing the dice very often. Thus, the "empirical definition" of the probability of an event E is

$$P(E) = \lim_{N \to \infty} \frac{N_E}{N}, \tag{2.1}$$

where N_E = number of times E occurred, and N = total number of experiments.

For one real variable $x \in \Omega \subset \mathbb{R}$, it is common to write the probability of an event $E \subset \mathbb{R}$ formally as

$$P(E) = \int_E p(x)dx. \tag{2.2}$$

Here, $p(x)$ is the **probability density "function"**, defined formally by:

$$\text{``}p(x)dx = P((x, x + dx))\text{''}.$$

The axioms for p formally imply that we should have

$$\int_{-\infty}^{\infty} p(x)dx = 1, \quad 0 \le p(x) \le \infty.$$

A mathematically more precise way to think about the quantity $p(x)dx$ is provided by measure theory, i.e. we should really think of $p(x)dx = d\mu(x)$ as defining a measure and of $\{E\}$ as the corresponding collection of measurable subsets. A typical case is that p is a smooth (or even just integrable) function on $\mathbb{R}$ and that dx is the Lebesgue measure, with E from the set of all Lebesgue measurable subsets of $\mathbb{R}$. However, we can also consider more pathological cases, e.g. by allowing p to have certain singularities. It is possible to define "singular" measures $d\mu$ relative to the Lebesgue measure dx which are not writable as $p(x)dx$ and p an integrable function which is non-negative almost everywhere, such as e.g. the **Dirac measure**, which is formally written as

$$p(x) = \sum_{i=1}^{N} p_i \delta(x - y_i), \tag{2.3}$$

where $p_i \ge 0$ and $\sum_i p_i = 1$. Nevertheless, we will, by abuse of notation, stick with the informal notation $p(x)dx$. We can also consider several random variables, such as $x = (x_1, \ldots, x_N) \in \Omega = \mathbb{R}^N$. The probability density function would now be – again formally – a function $p(x) \ge 0$ on $\mathbb{R}^N$ with total integral of 1.

Of course, as the example of the coin shows, one can and should also consider discrete probability spaces such as $\Omega = \{1, \ldots, N\}$, with the events E being all possible subsets. For the elementary event $\{n\}$ the probability $p_n = P(\{n\})$ is then a non-negative number and $\sum_i p_i = 1$. The collection of $\{p_1, \ldots, p_N\}$ completely characterizes the probability distribution.

Let us collect some standard notions and terminology associated with probability spaces:

- The **expectation value** $\langle F(x) \rangle$ of a function $\mathbb{R}^N = \Omega \ni x \mapsto F(x) \in \mathbb{R}$ ("observable") of a random variable is

$$\langle F(x) \rangle := \int\limits_{-\infty}^{\infty} F(x)p(x)d^N x. \tag{2.4}$$

  Here, the function $F(x)$ should be such that this expression is actually well-defined, i.e. F should be integrable with respect to the probability measure $d\mu = p(x)d^N x$.

- The **moments** m_n of a probability density function p of one real variable x are defined by

$$m_n := \langle x^n \rangle = \int\limits_{-\infty}^{\infty} x^n p(x)dx. \tag{2.5}$$

  Note that it is not automatically guaranteed that the moments are well-defined, and the same remark applies to the expressions given below. The probability distribution p can be reconstructed from the moments under certain conditions. This is known as the "Hamburger moment problem".

- The **characteristic function** $\tilde{p}$ of a probability density function of one real variable is its Fourier transform, defined as

$$\tilde{p}(k) = \int\limits_{-\infty}^{\infty} dx\ e^{-ikx}p(x) = \left\langle e^{-ikx} \right\rangle = \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} \langle x^n \rangle. \tag{2.6}$$

  From this it is easily seen that

$$p(x) = \frac{1}{2\pi} \int\limits_{-\infty}^{\infty} dk\ e^{ikx}\tilde{p}(k). \tag{2.7}$$

- The **cumulants** $\langle x^n \rangle_c$ are defined via

$$\log \tilde{p}(k) = \sum_{n=1}^{\infty} \frac{(-ik)^n}{n!} \langle x^n \rangle_c. \tag{2.8}$$

The first four are given in terms of the moments by

$$\langle x \rangle_c = \langle x \rangle$$

$$\langle x^2 \rangle_c = \langle x^2 \rangle - \langle x \rangle^2 = \langle (x - \langle x \rangle)^2 \rangle$$

$$\langle x^3 \rangle_c = \langle x^3 \rangle - 3 \langle x^2 \rangle \langle x \rangle + 2 \langle x \rangle^3$$

$$\langle x^4 \rangle_c = \langle x^4 \rangle - 4 \langle x^3 \rangle \langle x \rangle - 3 \langle x^2 \rangle^2 + 12 \langle x^2 \rangle \langle x \rangle^2 - 6 \langle x \rangle^4 .$$

There is an important combinatorial scheme relating moments to cumulants. The result expressed by this combinatorial scheme is called the **linked cluster theorem**, and a variant of it will appear when we discuss the cluster expansion. In order to state and illustrate the content of the linked cluster theorem, we represent the first four moments graphically as follows:

Figure 2.1.: Graphical expression for the first four moments.

A blob indicates a connected moment, also called 'cluster'. The linked cluster theorem states that the numerical coefficients in front of the various terms can be obtained by finding the number of ways to break points into clusters of this type. A proof of the linked cluster theorem can be obtained as follows: we write

$$\sum_0^\infty \frac{(-ik)^m}{m!} \langle x^m \rangle = e^{\sum_{n=1}^\infty \frac{(-ik)^n}{n!} \langle x^n \rangle_c} = \prod_{n=1}^\infty {\sum_{i_n}}' \left[\frac{(-ik)^{n i_n}}{i_n!} \left(\frac{\langle x^n \rangle_c}{n!} \right)^{i_n} \right], \qquad (2.9)$$

from which we conclude that

$$\langle x^m \rangle = {\sum_{\{i_n\}}}' \, m! \prod_n \frac{\langle x^n \rangle_c^{i_n}}{i_n! \, (n!)^{i_n}}, \qquad (2.10)$$

where $\sum'$ is restricted to $\sum n i_n = m$. The claimed graphical expansion follows because $\frac{m!}{\prod_n i_n! (n!)^{i_n}}$ is the number of ways to break m points into $\{i_n\}$ clusters of n points.

We next give some **important examples of probability distributions**:

(i) The **Gaussian distribution** for one real random variable $x \in \Omega = \mathbb{R}$:

The density is given by the Gauss function

$$p(x) = \frac{1}{\sqrt{2\pi}\sigma} \, e^{-\frac{(x-\mu)^2}{2\sigma^2}}. \tag{2.11}$$

We find $\mu = \langle x \rangle$ and $\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2 = \langle x \rangle_c^2$. The higher moments are all expressible in terms of μ and σ in a systematic fashion. For example:

$$\langle x^2 \rangle = \sigma^2 + \mu^2$$
$$\langle x^3 \rangle = 3\sigma^2\mu + \mu^3$$
$$\langle x^4 \rangle = 3\sigma^4 + 6\sigma^2\mu^2 + \mu^4$$
$$\vdots$$

The generating functional for the moments is $\langle e^{-ikx} \rangle = e^{ik\mu}e^{-\sigma^2 k^2/2}$. The N-dimensional generalization of the Gaussian distribution ($\Omega = \mathbb{R}^N$) is expressed in terms of a "covariance matrix", C, which is symmetric, real, with positive eigenvalues. It is

$$p(\vec{x}) = \frac{1}{(2\pi)^{N/2}(\det C)^{1/2}} e^{-\frac{1}{2}(\vec{x}-\vec{\mu})\cdot C^{-1}(\vec{x}-\vec{\mu})}. \tag{2.12}$$

The first two moments are $\langle x_i \rangle = \mu_i, \langle x_i x_j \rangle = C_{ij} + \mu_i \mu_j$.

(ii) The **binomial distribution**:

Fix N and let $\Omega = \{1, \ldots, N\}$. Then the events are subsets of Ω, such as $\{n\}$. We think of $n = N_A$ as the number of times an outcome A occurs in N trials, where $0 \le q \le 1$ is the probability for the event A.

$$P_N(\{n\}) = \binom{N}{n} q^n (1-q)^{N-n} \tag{2.13}$$

$$\Rightarrow \quad \tilde{p}_N(k) = \langle e^{-ikn} \rangle = \left(q e^{-ik} + (1-q) \right)^N \tag{2.14}$$

(iii) The **Poisson distribution**:

This is the limit of the binomial distribution for $N \to \infty$ when $x = n, \alpha$ are fixed where $q = \frac{\alpha}{N}$ (rare events). It is given by ($x \in \mathbb{R}_+ = \Omega$):

$$p(x) = \frac{\alpha^x}{\Gamma(x+1)} e^{-\alpha}, \tag{2.15}$$

where Γ is the Gamma function[1]. In order to derive this as a limit of the binomial

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[1] For natural numbers n, we have $\Gamma(n+1) = n!$. For $x \ge 0$, we have $\Gamma(x+1) = \int_0^\infty dt \, t^x \, e^{-t}$.

distribution, we start with the characteristic function of the latter, given by:

$$\tilde{p}_N(k) = \left(\frac{\alpha}{N} e^{-ik} + \left(1 - \frac{\alpha}{N}\right)\right)^N \longrightarrow e^{\alpha\left(e^{-ik}-1\right)} = \tilde{p}(k), \quad \text{as } N \to \infty. \qquad (2.16)$$

The formula for the Poisson distribution then follows from $p(x) = (1/2\pi) \int dk\, \tilde{p}(k)e^{ikx}$ (one might use the residue theorem to evaluate this integral). Alternatively, one may start from

$$p_N(x) = \frac{N\,(N-1)\dots(N-x+1)}{\Gamma(x+1)N^x}\alpha^x \left(1 - \frac{\alpha}{N}\right)^{N-x} \to \frac{\alpha^x}{\Gamma(x+1)}e^{-\alpha}, \quad \text{as } N \to \infty. \qquad (2.17)$$

A standard *application* of the Poisson distribution is radioactive decay: let $q = \lambda\Delta t$ the decay probability in a time interval $\Delta t = \frac{T}{N}$. If x denotes the number of decays, then the probability is obtained as:

$$p(x) = \frac{(\lambda T)^x}{\Gamma(x+1)}e^{-\lambda T}. \qquad (2.18)$$

- (iv) The **Ising model:**

  The Ising model is a probability distribution for spins on a lattice. For each lattice site i (atom), there is a spin taking values $\sigma_i \in \{\pm 1\}$. In d dimensions, the lattice is usually taken to be a volume $V = [0, L]^d \subset \mathbb{Z}^d$. The number of lattice sites is then $|V| = \lceil L \rceil^d$, and the set of possible configurations $\{\sigma_i\}$ is $\Omega = \{-1, 1\}^{|V|}$ since each spin can take precisely two values. In the Ising model, one assigns to each configuration an energy

  $$H(\{\sigma_i\}) = -J \sum_{ik} \sigma_i\sigma_k - h \sum_i \sigma_i \ , \qquad (2.19)$$

  where J, h are parameters, and where the first sum is over all lattice bonds ik in the volume V. The second sum is over all lattice sites in V. The probability of a configuration is then given by the Boltzmann weight

  $$H(\{\sigma_i\}) = \frac{1}{Z} \exp[-\beta H(\{\sigma_i\})]. \qquad (2.20)$$

  A large coupling constant $J \gg 1$ favors adjacent spins to be parallel and a large $h \gg 1$ favors spins to be preferentially up (+1). The coupling h can thus be thought of as an external magnetic field. $Z = Z(V, J, h)$ is a normalization constant ensuring that all the probabilities add up to unity. Of particular interest in the Ising model are the mean magnetization $m = |V|^{-1} \sum\langle\sigma_i\rangle$, the free energy density $f = |V|^{-1} \log Z$ or the two-point function $\langle\sigma_i\sigma_j\rangle$ in the limit of large $V \to \mathbb{Z}^d$ (called "thermodynamic limit") and a large separation between i and j. (See exercises.)

- (v) **Random walk** on a lattice:

  A walk ω in a volume V of a lattice as in the Ising model can be characterized by the sequence of sites $\omega = (x, i_1, i_2, \ldots, i_{N-1}, y)$ encountered by the walker, where x is the fixed beginning and y the fixed endpoint. The number of sites in the walk is denoted $l(\omega)$ ($= N + 1$ in the example), and the number of self-intersections is denoted by $n(\omega)$. The set of walks from x to y is our probability space $\Omega_{x,y}$, and a natural probability distribution is

  $$P(\omega) = \frac{1}{Z} e^{-\mu l(\omega) - g n(\omega)} \ . \tag{2.21}$$

  Here, μ, g are positive constants. For large $\mu \gg 1$, short walks between x and y are favored, and for large $g \gg 1$, self-avoiding walks are favored. $Z = Z_{x,y}(V, \mu, g)$ is a normalization constant ensuring that the probabilities add up to unity. Of interest are e.g. the "free energy density" $f = |V|^{-1} \log Z$, or the average number of steps the walk spends in a given subset $S \subset V$, given by $\langle \#\{S \cap \omega\}\rangle$.

  In general, such observables are very difficult to calculate, but for $g = 0$ (unconstrained walks) there is a nice connection between Z and the Gaussian distribution, which is the starting point to obtain many further results. Let $\partial_\alpha f(i) = f(i + \vec{e}_\alpha) - f(i)$ be the "lattice partial derivative" of a function $f(i)$ defined on the lattice sites $i \in V$, in the direction of the α-th unit vector, $\vec{e}_\alpha, \alpha = 1, \ldots, d$. Let $\sum \partial_\alpha^2 = \Delta$ be the "lattice Laplacian". The lattice Laplacian can be identified with a matrix Δ_{ij} of size $|V| \times |V|$ defined by $\Delta f(i) = \sum_j \Delta_{ij} f(j)$. Define the covariance matrix as $C = (-\Delta + m^2)^{-1}$ and consider the corresponding Gaussian measure for the variables $\{\phi_i\} \in \mathbb{R}^{|V|}$ (one real variable per lattice site in V). One shows that

  $$Z_{x,y} = \langle \phi_x \phi_y \rangle \equiv \frac{1}{(2\pi)^{|V|/2} (\det C)^{1/2}} \int \phi_x \phi_y \ e^{-\frac{1}{2} \sum \phi_i (-\Delta + m^2)_{ij} \phi_j} \ d^{|V|}\phi \tag{2.22}$$

  for $g = 0, \mu = \log(2d + m^2)$ (exercises).

  Let p be a probability density on the space $\Omega = \mathbb{R}^N$. If the density is factorized, as in

  $$p(x) = p_1(x_1) \ldots p_n(x_N) \ , \tag{2.23}$$

then we say that the variables $x = (x_1, \ldots, x_N)$ are **independent**. This notion can be generalized immediately to any "Cartesian product" $\Omega = \Omega_1 \times \ldots \times \Omega_N$ of probability spaces. In the case of independent identically distributed real random variables $x_i, \ i = 1, \ldots, N$, there is an important theorem characterizing the limit as $N \to \infty$, which is treated in more detail in the homework assignments. Basically it says that (under certain assumptions about p) the random variable $y = \frac{\sum(x_i - \mu)}{\sqrt{N}}$ has Gaussian distribution for large N with mean 0 and spread $\sigma/\sqrt{N}$. Thus, in this sense, a sum of a large number

of arbitrary random variables is approximately distributed as a Gaussian random variable. This so called "**Central Limit Theorem**" explains, in some sense, the empirical evidence that the random variables appearing in various applications are distributed as Gaussians.

A further important quantity associated with a probability distribution is its "information entropy", which is defined as follows:

Definition: Let Ω be a subset of $\mathbb{R}^N$, and let $p(x)$ be a, say continuous, probability density. The quantity

$$S_{\text{inf}}(p) := -k_{\text{B}} \int_{\Omega} p(x) \, \log p(x) \, d^N x \tag{2.24}$$

is called **information entropy**.

In the context of computer science, the factor k_{B} is dropped, and the natural log is replaced by the logarithm with base 2, which is natural to use if we think of information encoded in bits (k_{B} is merely inserted here to be consistent with the conventions in statistical physics).

More or less evident generalizations exist for more general probability spaces. For example, for the discrete probability space such as $\Omega = \{1, ..., N\}$ with probabilities $\{p_1, \ldots, p_N\}$ for the elementary events, i.e. $P(\{i\}) = p_i$, the information entropy is given by $S_{\text{inf}} = -k_{\text{B}} \sum_i p_i \log p_i$. It can be shown that the information entropy (in computer science normalization) is roughly equal to the average (with respect to the given probability distribution) number of yes/no questions necessary to determine whether a given event has occurred (cf. exercises).

A practical application of information entropy is as follows: suppose one has an ensemble whose probability distribution $p(x)$ is not completely known. One would like to make a good guess about $p(x)$ based on some partial information such as a finite number of moments, or other observables. Thus, suppose that $F_i(x)$, $i = 1, ..., n$ are observables for which $\langle F_i(x) \rangle = f_i$ are known. Then a good guess, representing in some sense a minimal bias about $p(x)$, is to minimize S_{inf}, subject to the n constraints $\langle F_i(x) \rangle = f_i$. In the case when the observables are μ and σ, the distribution obtained in this way is the Gaussian. So the Gaussian is, in this sense, our best guess if we only know μ and σ (cf. exercises).

2.2. Ensembles in Classical Mechanics

The basic ideas of probability theory outlined in the previous sections can be used for the statistical description of systems obeying the laws of classical mechanics. Consider a classical system of N particles, described by $6N$ phase space coordinates[2] which we abbreviate as

$$(P, Q) = (\vec{p}_1, \ldots, \vec{p}_N; \vec{x}_1, \ldots, \vec{x}_N) \in \mathbb{R}^{(3+3)N} = \Omega. \tag{2.25}$$

A **classical ensemble** is simply a probability density function $\rho(P, Q)$, i.e.

$$\int_{\Omega} \rho(P, Q) d^{3N} P d^{3N} Q = 1, \quad 0 \le \rho(P, Q) \le \infty. \tag{2.26}$$

According to the basic concepts of probability theory, the ensemble average of an observable $F(P, Q)$ is then simply

$$\langle F(P, Q) \rangle = \int_{\Omega} F(P, Q) \, \rho(P, Q) \, d^{3N} Q \, d^{3N} P. \tag{2.27}$$

The probability distribution $\rho(P, Q)$ represents our limited knowledge about the system which, in reality, is of course supposed to be described by a single trajectory $(P(t), Q(t))$ in phase space. In practice, we cannot know what this trajectory is precisely other than for a very small number of particles N and, in some sense, we do not really want to know the precise trajectory at all. The idea behind ensembles is rather that the time evolution (=phase space trajectory $(Q(t), P(t))$) typically scans the entire accessible phase space (or sufficiently large parts of it) such that the time average of F equals the ensemble average of F, i.e. in many cases we expect to have:

$$\lim_{T \to \infty} \frac{1}{T} \int_0^T F\left(P(t), Q(t)\right) dt = \langle F(P, Q) \rangle, \tag{2.28}$$

for a suitable (stationary) probability density function. This is closely related to the "ergodic theorem" and is related to the fact that the equations of motion are derivable from a (time independent) Hamiltonian. Hamilton's equations are

$$\dot{x}_{i\alpha} = \frac{\partial H}{\partial p_{i\alpha}} \qquad \dot{p}_{i\alpha} = -\frac{\partial H}{\partial x_{i\alpha}}, \tag{2.29}$$

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[2]This description is not always appropriate, as the example of a rigid body shows. Here the phase space coordinates take values in the co-tangent space of the space of all orthogonal frames describing the configuration of the body, i.e. $\Omega \cong T^* SO(3)$, with $SO(3)$ the group of orientation preserving rotations.

where $i = 1, \ldots, N$ and $\alpha = 1, 2, 3$. The Hamiltonian H is typically of the form

$$H = \underbrace{\sum_i \frac{\vec{p}_i^2}{2m}}_{\text{kinetic energy}} + \underbrace{\sum_{i<j} \mathcal{V}\left(\vec{x}_i - \vec{x}_j\right)}_{\text{interaction}} + \underbrace{\sum_j \mathcal{W}\left(\vec{x}_j\right)}_{\text{external potential}} , \qquad (2.30)$$

if there are no internal degrees of freedom. It is a standard theorem in classical mechanics that $E = H(P, Q)$ is conserved under time evolution. Let us imagine a well-potential $\mathcal{W}(\vec{x})$ as in the following picture:
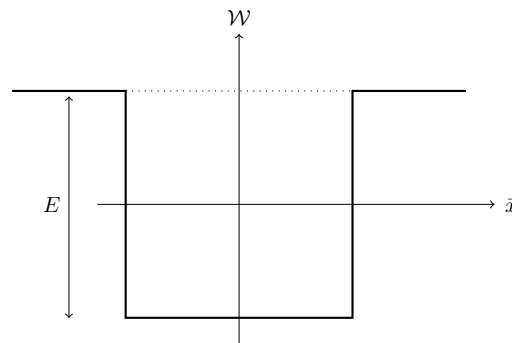
Figure 2.2.: Sketch of a well-potential $\mathcal{W}$.

Then $\Omega_E = \left\{(P, Q) | H(P, Q) = E\right\}$ is compact. We call Ω_E the **energy surface**. Particle trajectories do not leave this surface by energy conservation. If Hamilton's equations admit other constants of motion, then it is natural to define a corresponding surface with respect to all constants of motion.

An important feature of the dynamics given by Hamilton's equations is

Liouville's Theorem: The flow map $\Phi_t : (P, Q) \mapsto \left(P(t), Q(t)\right)$ is area-preserving.
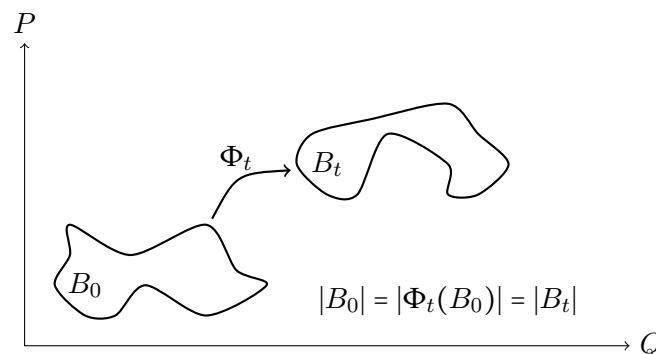
Figure 2.3.: Evolution of a phase space volume under the flow map Φ_t.

Proof of the theorem: Let $(P', Q') = (P(t), Q(t))$, such that $(P(0) = P, \ Q(0) = Q)$. Then we have

$$d^{3N}P' d^{3N}Q' = \frac{\partial(P', Q')}{\partial(P, Q)} d^{3N}P d^{3N}Q \ , \tag{2.31}$$

and we would like to show that $J_{P,Q}(t) = 1$ for all t. Let us write the Jacobian as $J_{P,Q}(t) = \frac{\partial(P', Q')}{\partial(P, Q)}$. Since the flow evidently satisfies $\Phi_{t+t'}(P, Q) = \Phi_{t'}(\Phi_t(P, Q))$, the chain rule and the properties of the Jacobian imply $J_{P,Q}(t + t') = J_{P,Q}(t) J_{P',Q'}(t')$. We now show that $\partial J_{P,Q}(0)/\partial t = 0$. For small t, we can expand as follows:

$$P' = P + t\dot{P} + \mathcal{O}(t^2) = P - t\frac{\partial H}{\partial Q} + \mathcal{O}(t^2),$$

$$Q' = Q + t\dot{Q} + \mathcal{O}(t^2) = Q + t\frac{\partial H}{\partial P} + \mathcal{O}(t^2).$$

It follows that

$$J_{P,Q}(t) = \frac{\partial(P', Q')}{\partial(P, Q)} = \det\left[\mathbb{1}_{3N \times 3N} + t \begin{pmatrix} -\partial_P \partial_Q H & -\partial_Q^2 H \\ \partial_P^2 H & \partial_Q \partial_P H \end{pmatrix} + \mathcal{O}(t^2) \right]$$

$$= 1 + t \left(\underbrace{-\frac{\partial^2 H}{\partial x_{i\alpha} \partial p_{i\alpha}} + \frac{\partial^2 H}{\partial p_{i\alpha} \partial x_{i\alpha}}}_{=0} \right) + \mathcal{O}(t^2)$$

$$= 1 + \mathcal{O}(t^2).$$

This implies $\partial J_{P,Q}(0)/\partial t = 0$ (and $J_{P,Q}(0) = 0$). The functional equation for the Jacobean then implies that the time derivative vanishes for arbitrary t:

$$\frac{\partial}{\partial t} J_{P,Q}(t) = \frac{\partial}{\partial t'} J_{P,Q}(t + t') \bigg|_{t'=0} = J_{P,Q}(t) \frac{\partial}{\partial t'} J_{P',Q'}(t') \bigg|_{t'=0} = 0. \tag{2.32}$$

Together with $J_{P,Q}(0) = 1$, this gives the result $J_{P,Q}(t) = 1$ for all t, i.e. the flow is area-preserving. $\qquad\square$

The flow Φ_t is not only area preserving on the entire phase-space, but also on the energy surface Ω_E (with the natural integration element understood). Such area-preserving flows under certain conditions imply that the phase space average equals the time average, cf. (2.28). This is expressed by the **ergodic theorem**:

Theorem: Let $\big(P(t), Q(t)\big)$ be *dense* in Ω_E and F continuous. Then the time average is equal to the ensemble average:

$$\lim_{T \to \infty} \frac{1}{T} \int_0^T F\big(P(t), Q(t)\big)\, dt = \int_{\Omega_E} F(P, Q). \tag{2.33}$$

The key hypothesis is that the orbit lies dense in Ω_E and that this surface is compact. The first is clearly not the case if there are further constants of motion, since the orbit must then lie on a submanifold of Ω_E corresponding to particular values of these constants. The Kolmogorov-Arnold-Moser (KAM) theorem shows that small perturbations of systems with sufficiently many constants of motion again possess such invariant submanifolds, i.e. the ergodic theorem does not hold in such cases. Nevertheless, the ergodic theorem still remains an important motivation for studying ensembles.

One puzzling consequence of Liouville's theorem is that a trajectory starting at (P_0, Q_0) comes back *arbitrarily close* to that point, a phenomenon called **Poincaré recurrence**. An intuitive "proof" of this statement can be given as follows:
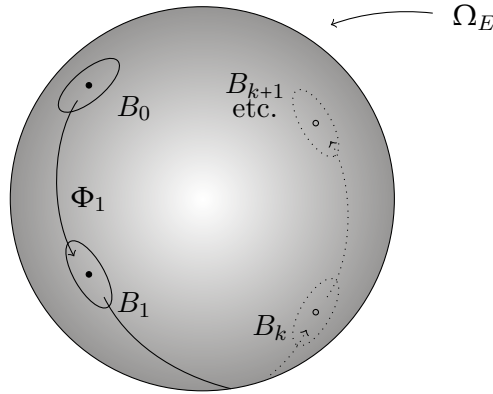
Figure 2.4.: Sketch of the situation described in the proof of Poincaré recurrence.

Let B_0 be an ϵ-neighborhood of a point (P_0, Q_0). For $k \in \mathbb{N}$ define $B_k := \Phi_k(B_0)$, which are ϵ-neighborhoods of $(P_k, Q_k) = \Phi_k((Q_0, P_0))$. Let us assume that the statement of the theorem is wrong. This yields

$$B_0 \cap B_k = \varnothing \qquad \forall k \in \mathbb{N}.$$

Then it follows that

$$B_n \cap B_k = \varnothing \qquad \forall n, k \in \mathbb{N}, n \neq k.$$

Now, by Liouvilles theorem we have

$$|B_0| = |B_1| = \ldots = |B_k| = \ldots,$$

which immediately yields

$$|\Omega_E| \geq |B_0| + \ldots + |B_k| + \ldots = \infty.$$

This clearly contradicts the assumption that Ω_E is compact and therefore the statement of the theorem has to be true. $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\square$

Historically, the recurrence argument played an important role in early discussions of the notion of irreversibility, i.e. the fact that systems generically tend to approach an equilibrium state, whereas they never seem to spontaneously leave an equilibrium state and evolve back to the (non-equilibrium) initial conditions. To explain the origin of resp. the mechanisms behind this irreversibility is one of the major challenges of non-equilibrium thermodynamics and we shall briefly come back to this point later. For the moment, we simply note that in practice the recurrence time $\tau_{\text{recurrence}}$ would be extremely large compared to the natural scales of the system such as the equilibration time. We will verify this by investigating the dynamics of a toy model in the appendix. Here we only give a heuristic explanation. Consider a gas of N particles in a volume V. The volume is partitioned into sub volumes V_1, V_2 of equal size. We start the system in a state where the atoms only occupy V_1. By the ergodic theorem we estimate that the fraction of time the system spends in such a state is $\langle \chi_{Q \in V_1} \rangle = 2^{-3N}$ (for an ideal gas), where $\chi_{Q \in V_1}$ gives 1 if all particles are in V_1, and zero otherwise. For $N = 1$ mol, i.e. $N = \mathcal{O}(10^{23})$, this fraction is astronomically small. So there is no real puzzle!

2.3. Ensembles in Quantum Mechanics (Statistical Operators and Density Matrices)

Quantum mechanical systems are of an intrinsically probabilistic nature, so the language of probability theory is, in this sense, not just optional but actually essential. In fact, to say that the system is in a state $|\Psi\rangle$ really means that, if A is a self adjoint operator and

$$A = \sum_i a_i |i\rangle\langle i| \tag{2.34}$$

its spectral decomposition[3], the probability for measuring the outcome a_i is given by

$$p_{A,\Psi}(a_i) = |\langle \Psi | i \rangle|^2 \equiv p_i.$$

---

[3] A general self-adjoint operator on a Hilbert space will have a spectral decomposition $A = \int_{-\infty}^{\infty} a \, dE_A(a)$. The spectral measure does not have to be atomic, as suggested by the formula (2.34). The corresponding probability measure is in general $d\mu(a) = \langle \Psi | dE_A(a)\Psi \rangle$.

Thus, if we assign the state $|\Psi\rangle$ to the system, the set of possible measuring outcomes for A is the probability space $\Omega = \{a_1, a_2, \dots\}$ with (discrete) probability distribution given by $\{p_1, p_2, \dots\}$.

In statistical mechanics we are in a situation where we have incomplete information about the state of a quantum mechanical system. In particular, we do not want to prejudice ourselves by ascribing a pure state $|\Psi\rangle$ to the system. Instead, we describe it by a **statistical ensemble**. Suppose we believe that the system is in the state $|\Psi_i\rangle$ with probability p_i, where, as usual, $\sum p_i = 1$, $p_i \geq 0$. The states $|\Psi_i\rangle$ should be normalized, i.e. $\langle\Psi_i|\Psi_i\rangle = 1$, but they do *not* have to be orthogonal or complete. Then the expectation value $\langle A\rangle$ of an operator is defined as

$$\langle A\rangle = \sum_i p_i \left\langle\Psi_i|A|\Psi_i\right\rangle. \tag{2.35}$$

Introducing the **density matrix** $\rho = \sum_i p_i |\Psi_i\rangle\langle\Psi_i|$ this may also be written as

$$\langle A\rangle = \mathrm{tr}(\rho A). \tag{2.36}$$

The density matrix has the properties $\mathrm{tr}\rho = \sum_i p_i = 1$, as well as $\rho^\dagger = \rho$. Furthermore, for any state $|\Phi\rangle$ we have

$$\langle\Phi|\rho|\Phi\rangle = \sum_i p_i |\langle\Psi_i|\Phi\rangle|^2 \geq 0.$$

A density matrix should be thought of as analogous to a classical probability distribution.

In the context of quantum mechanical ensembles one can define a quantity that is closely analogous to the information entropy for ordinary probability distributions. This quantity is defined as

$$S_{\mathrm{v.N.}}(\rho) = -\mathrm{k_B}\mathrm{tr}(\rho \,\log\rho) = -\mathrm{k}_B \sum_i p_i \log p_i \tag{2.37}$$

and is called the **von Neumann entropy** associated with ρ.

According to the rules of quantum mechanics, the **time evolution** of a state is described by Schrödinger's equation

$$i\hbar \,\frac{d}{dt}\,|\Psi(t)\rangle = H|\Psi(t)\rangle$$

$$\Rightarrow \quad i\hbar \,\frac{d}{dt}\,\rho(t) = \left[H, \rho(t)\right] \equiv H\rho(t) - \rho(t)H.$$

Therefore an ensemble is **stationary** if $[H, \rho] = 0$. In particular, ρ is stationary if it is of the form

$$\rho = f(H) = \sum_i f(E_i)|\Psi_i\rangle\langle\Psi_i|,$$

where $\sum_i f(E_i) = 1$ and $p_i = f(E_i) > 0$ (here, E_i label the eigenvalues of the Hamiltonian H and $|\Psi_i\rangle$ its eigenstates, i.e. $H|\Psi_i\rangle = E_i|\Psi_i\rangle$). The characteristic example is given by

$$f(H) = \frac{1}{Z_\beta} e^{-\beta H}, \tag{2.38}$$

where $Z_\beta = \sum_i e^{-\beta E_i}$. More generally, if $\{Q_\alpha\}$ are operators commuting with H, then another choice is

$$\rho = \frac{1}{Z(\beta, \mu_\alpha)} e^{-\beta H - \sum_\alpha \mu_\alpha Q_\alpha}. \tag{2.39}$$

We will come back to discuss such ensembles below in chapter 4.

One often deals with situations in which a system is comprised of two sub-systems A and B described by Hilbert spaces $\mathcal{H}_A, \mathcal{H}_B$. The total Hilbert space is then $\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B$ ($\otimes$ is the tensor product). If $\{|i\rangle_A\}$ and $\{|j\rangle_B\}$ are orthonormal bases of $\mathcal{H}_A$ and $\mathcal{H}_B$, an orthonormal basis of $\mathcal{H}$ is given by $\{|i,j\rangle = |i\rangle_A \otimes |j\rangle_B\}$.

Consider a (pure) state $|\Psi\rangle$ in $\mathcal{H}$, i.e. a pure state of the total system. It can be expanded as

$$|\Psi\rangle = \sum_{i,j} c_{i,j} |i,j\rangle.$$

We assume that the state is normalized, meaning that

$$\sum_{i,j} \left| c_{i,j} \right|^2 = 1. \tag{2.40}$$

Observables describing measurements of subsystem A consist of operators of the form $\tilde{a} = a \otimes \mathbb{1}_B$, where a is an operator on $\mathcal{H}_A$ and $\mathbb{1}_B$ is the identity operator on $\mathcal{H}_B$ (similarly an observable describing a measurement of system B corresponds to $\tilde{b} = \mathbb{1}_A \otimes b$). For such an operator we can write:

$$\begin{aligned}
\langle \Psi | \tilde{a} | \Psi \rangle &= \sum_{i,j,k,l} \bar{c}_{i,k} c_{j,l} \left\langle i,j | a \otimes \mathbb{1}_B | j,l \right\rangle \\
&= \sum_{i,j,k,l} \bar{c}_{i,k} c_{j,l} \, {}_A\langle i|a|j\rangle_A \underbrace{{}_B\langle k|l\rangle_B}_{\delta_{kl}} \\
&= \sum_{i,j} \underbrace{\left(\sum_k \bar{c}_{i,k} c_{j,k} \right)}_{=:(\rho_A)_{ji}} {}_A\langle i|a|j\rangle_A \\
&= \mathrm{tr}_A \left(a \rho_A \right).
\end{aligned}$$

The operator ρ_A on $\mathcal{H}_A$ by definition satisfies $\rho_A^\dagger = \rho_A$ and by (2.40), it satisfies $\mathrm{tr}\rho_A = 1$. It is also not hard to see that $\langle \Phi | \rho_A | \Phi \rangle \geq 0$. Thus, ρ_A defines a density matrix on the Hilbert space $\mathcal{H}_A$ of system A. One similarly defines ρ_B on $\mathcal{H}_B$.

Definition: The operator ρ_A is called **reduced density matrix** of subsystem A, and ρ_B that of subsystem B.

The reduced density matrix reflects the limited information of an observer only having access to a subsystem. The quantity

$$S_{\text{ent}} := S_{\text{v.N.}}(\rho_A) = -k_B \ \text{tr}\left(\rho_A \log \rho_A\right) \tag{2.41}$$

is called the **entanglement entropy** of subsystem A. One shows that $S_{\text{v.N.}}(\rho_A) = S_{\text{v.N.}}(\rho_B)$, so it does not matter which of the two subsystems we use to define it.

Example: Let $\mathcal{H}_A = \mathbb{C}^2 = \mathcal{H}_B$ with orthonormal basis $\{|\uparrow\rangle, |\downarrow\rangle\}$ for either system A or B. The orthonormal basis of $\mathcal{H}$ is then given by $\{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$.

(i) Let $|\Psi\rangle = |\uparrow\downarrow\rangle$. Then

$$\left\langle \Psi|\tilde{a}|\Psi\right\rangle = \left\langle \uparrow\downarrow |a \otimes \mathbb{1}_B| \uparrow\downarrow\right\rangle = \left\langle \uparrow |a| \uparrow\right\rangle. \tag{2.42}$$

from which it follows that the reduced density matrix of subsystem A is given by

$$\rho_A = |\uparrow\rangle\langle\uparrow|. \tag{2.43}$$

The entanglement entropy is calculated as

$$S_{\text{ent}} = -k_B \ \text{tr}\left(\rho_A \log \rho_A\right) = -k_B \ \left(1 \cdot \log 1\right) = 0. \tag{2.44}$$

(ii) Let $|\Psi\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$. Then

$$\begin{aligned}
\left\langle \Psi|\tilde{a}|\Psi\right\rangle &= \frac{1}{2}\left(\left(\langle\uparrow\downarrow| - \langle\downarrow\uparrow|\right)\left(a \otimes \mathbb{1}_B\right)\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)\right) \\
&= \frac{1}{2}\left(\left\langle\uparrow |a| \uparrow\right\rangle + \left\langle\downarrow |a| \downarrow\right\rangle\right),
\end{aligned} \tag{2.45}$$

from which it follows that the reduced density matrix of subsystem A is given by

$$\rho_A = \frac{1}{2}\left(|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|\right). \tag{2.46}$$

The entanglement entropy is calculated as

$$S_{\text{ent}} = -k_B \ \text{tr}\left(\rho_A \log \rho_A\right) = -k_B \ \left(\frac{1}{2}\log\frac{1}{2} + \frac{1}{2}\log\frac{1}{2}\right) = k_B \log 2. \tag{2.47}$$

3. Time-evolving ensembles

3.1. Boltzmann Equation in Classical Mechanics

In order to understand the dynamical properties of systems in statistical mechanics one has to study non-stationary (i.e. time-dependent) ensembles. A key question, already brought up earlier, is whether systems initially described by a non-stationary ensemble will eventually approach an equilibrium ensemble. An important quantitative tool to understand the approach to equilibrium (e.g. in the case of thin media or weakly coupled systems) is the **Boltzmann equation**, which we discuss here in the case of classical mechanics.

We start with a classical ensemble, described by a probability distribution $\rho(P,Q)$ on phase space. Its time evolution is defined as

$$\rho(P,Q;t) \equiv \rho(P(t),Q(t)) \equiv \rho_t(P,Q), \tag{3.1}$$

where $\big(P(t),Q(t)\big)$ are the phase space trajectories, so

$$\frac{\partial}{\partial t}\rho_t\left(P,Q\right) = \frac{\partial\rho_t(P,Q)}{\partial P}\underbrace{\frac{\partial P}{\partial t}}_{=-\frac{\partial H}{\partial Q}} + \frac{\partial\rho_t(P,Q)}{\partial Q}\underbrace{\frac{\partial Q}{\partial t}}_{=\frac{\partial H}{\partial P}} = \{\rho_t,H\}\left(P,Q\right), \tag{3.2}$$

where $\{\cdot,\cdot\}$ denotes the Poisson bracket. Let us define the 1-particle density f_1 by

$$f_1\left(\vec{p}_1,\vec{x}_1;t\right) \coloneqq \left\langle \sum_i \delta^3\left(\vec{p}_1-\vec{p}_i\right)\delta^3\left(\vec{x}_1-\vec{x}_i\right) \right\rangle$$

$$= N\int \rho_t\left(\vec{p}_1,\vec{x}_1,\vec{p}_2,\vec{x}_2\ldots,\vec{p}_N,\vec{x}_N\right)\prod_{i=2}^{N} d^3x_i d^3p_i. \tag{3.3}$$

Similarly, the two particle density can be computed from ρ via

$$f_2\left(\vec{p}_1,\vec{x}_1,\vec{p}_2,\vec{x}_2;t\right) = N(N-1)\int \rho_t\left(\vec{p}_1,\vec{x}_1,\vec{p}_2,\vec{x}_2\ldots,\vec{p}_N,\vec{x}_N\right)\prod_{i=3}^{N} d^3x_i d^3p_i. \tag{3.4}$$

Analogously, we define the s-particle densities f_s, for $2 < s \leq N$.

The Hamiltonian H_s describing the interaction between s particles can be written as

$$H_s = \sum_{i=1}^{s} \frac{\vec{p}_i^2}{2m} + \sum_{1 \le i < j \le s} \mathcal{V}(\vec{x}_i - \vec{x}_j) + \sum_{i=1}^{s} \mathcal{W}(\vec{x}_i), \qquad (3.5)$$

so that in particular $H_N = H$. One finds the relations

$$\underbrace{\frac{\partial f_s}{\partial t} - \{H_s, f_s\}}_{\text{streaming term}} = \underbrace{\sum_{i=1}^{s} \int d^3 p_{s+1} \ d^3 x_{s+1} \ \frac{\partial \mathcal{V}(\vec{x}_i - \vec{x}_{s+1})}{\partial \vec{x}_i} \cdot \frac{\partial f_{s+1}}{\partial \vec{p}_i}}_{\text{collision term}} . \qquad (3.6)$$

This system of equations is called the **BBGKY hierarchy** (for **B**ogoliubov-**B**orn-**G**reen-**K**irkwood **Y**von hierarchy). The first term ($s = 1$) is given by

$$\left[\frac{\partial}{\partial t} - \underbrace{\frac{\partial \mathcal{W}}{\partial \vec{x}_1}}_{=\vec{F} \ (\text{ext. force})} \cdot \frac{\partial}{\partial \vec{p}_1} + \underbrace{\frac{\vec{p}_1}{m}}_{=\vec{v} \ (\text{velocity})} \cdot \frac{\partial}{\partial \vec{x}_1} \right] f_1 = \int d^3 p_2 \ d^3 x_2 \ \frac{\partial \mathcal{V}(\vec{x}_1 - \vec{x}_2)}{\partial \vec{x}_2} \cdot \underbrace{\frac{\partial f_2}{\partial \vec{p}_1}}_{\text{unknown!}} . $$
$$(3.7)$$

An obvious feature of the BBGKY hierarchy is that the equation for f_1 involves f_2, that for f_2 involves f_3, etc. In this sense the equations for the individual f_i are *not closed*. To get a manageable system, some approximations/truncations are necessary.

In order to derive the Boltzmann equation, the BBGKY-hierarchy is approximated/truncated in the following way:

(a) we set $f_3 \approx 0$.

(b) we assume that $f_2(\vec{p}_1, \vec{x}_1, \vec{p}_2, \vec{x}_2; t) \approx f_1(\vec{p}_1, \vec{x}_1; t) f_1(\vec{p}_2, \vec{x}_2; t)$, which means that the densities are uncorrelated.

Let us discuss the conditions under which such assumptions are (approximately) valid. Basically, one needs to have a sufficiently wide separation of the time-scales of the system. The relevant time scales are described as follows.

(i) Let v be the typical velocity of gas particles $\left(\text{e.g. } v \approx 100 \frac{\text{m}}{\text{s}} \text{ at room temperature and } 1\text{atm}\right)$ and let L be the scale over which $\mathcal{W}(\vec{x})$ varies, i.e. the box size. Then $\tau_v := \frac{L}{v}$ is the extrinsic scale (e.g. $\tau_v \approx 10^{-5}$s for $L \approx 1$mm).

(ii) If d is the range of the interaction $\mathcal{V}(\vec{x})$ (e.g. $d \approx 10^{-10}$m), then $\tau_c := \frac{d}{v}$ is the collision time (e.g. $\tau_c \approx 10^{-12}$s). We should have $\tau_c \ll \tau_v$.

(iii) We can also define the mean free time $\tau_x \approx \frac{\tau_c}{nd^3} \approx \frac{1}{nvd^3}$, $n = \frac{N}{V}$, which is the average time between subsequent collisions. We have $\tau_x \approx 10^{-8}$s $\gg \tau_c$ in our example.

For (a) and (b) to hold, we should have $\tau_v \gg \tau_x \gg \tau_c$.

The Boltzmann equation may now be "derived" by looking at the second equation in the BBGKY hierarchy and neglecting time derivatives. This gives

$$\left[\vec{v}_1 \frac{\partial}{\partial \vec{x}_1} + \vec{v}_2 \frac{\partial}{\partial \vec{x}_2} - \vec{F} \left(\vec{x}_1 - \vec{x}_2 \right) \left(\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2} \right) \right] f_2 = 0, \tag{3.8}$$

The derivation of the Boltzmann equation from this is still rather complicated and we only state the result, which is:

$$\left[\frac{\partial}{\partial t} - \vec{F} \frac{\partial}{\partial \vec{p}_1} + \vec{v}_1 \frac{\partial}{\partial \vec{x}_1} \right] f_1 \left(\vec{p}_1, \vec{x}_1; t \right) =$$

$$- \int d^3 p_2 d^2 \Omega \ \underbrace{\left| \frac{d\sigma}{d\Omega} \right|}_{\text{cross-section}} \cdot \underbrace{\left| \vec{v}_1 - \vec{v}_2 \right|}_{\propto \text{flux}} \cdot \left[f_1 \left(\vec{p}_1, \vec{x}_1; t \right) f_1 \left(\vec{p}_2, \vec{x}_1; t \right) - f_1 \left(\vec{p}_1', \vec{x}_1; t \right) f_1 \left(\vec{p}_2', \vec{x}_1; t \right) \right],$$

$$\tag{3.9}$$

where $\Omega = (\theta, \phi)$ is the solid angle between $\vec{p} = \vec{p}_1 - \vec{p}_2$ and $\vec{p}' = \vec{p}_1' - \vec{p}_2'$, and $d^2\Omega = \sin\theta d\theta d\phi$. The meaning of the differential cross section $|d\sigma/d\Omega|$ is shown in the following picture representing a classical 2-particle scattering process:
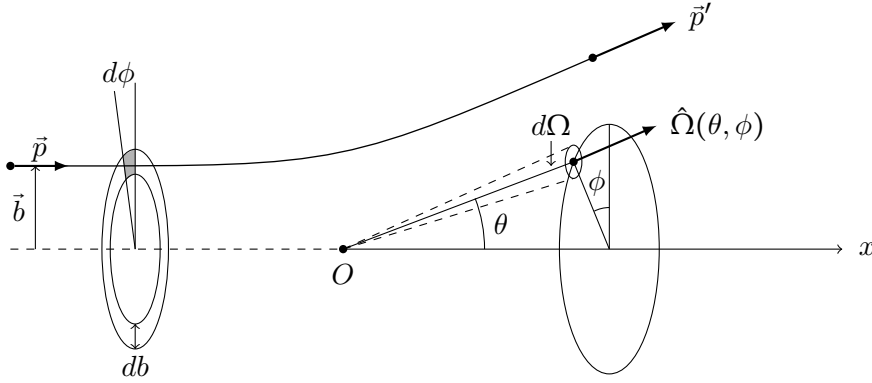
Figure 3.1.: Classical scattering of particles in the "fixed target frame".

The outgoing relative momentum $\vec{p}' = \vec{p}_1' - \vec{p}_2' = \vec{p}' \left(\vec{p}, \vec{b} \right)$ can be viewed as a function of the incoming relative momentum $\vec{p} = \vec{p}_1 - \vec{p}_2$ and the impact vector $\vec{b}$, assuming an elastic collision, i.e. $|\vec{p}| = |\vec{p}'|$. Thus, during the collision, $\vec{p}$ is rotated to a final direction given by the unit vector $\hat{\Omega}(\vec{b})$, indicated by (θ, ϕ). We then define

$$\left| \frac{d\sigma}{d\Omega} \right| := \text{ Jacobian between } \vec{b} \text{ and } \hat{\Omega} = (\theta, \phi) \tag{3.10}$$

$$= \left(\frac{D}{2} \right)^2 \text{ for hard spheres with diameter } D.$$

The integral expression on the right side of the Boltzmann equation (3.9) is called the **collision operator**, and is often denoted as $C[f_1](t, \vec{p}_1, \vec{x}_1)$. It represents the change in the 1-particle distribution due to collisions of particles. The two terms in the brackets [...] under the integral in (3.9) can be viewed as taking into account that new particles with momentum $\vec{p}_1$ can be created or be lost, respectively, when momentum is transferred from other particles in a collision process.

It is important to know whether $f_1(\vec{p}, \vec{x}; t)$ is stationary, i.e. time-independent. Intuitively, this should be the case when the collision term $C[f_1]$ vanishes. This in turn should happen if

$$f_1(\vec{p}_1, \vec{x}; t) f_1(\vec{p}_2, \vec{x}; t) = f_1(\vec{p}_1', \vec{x}; t) f_1(\vec{p}_2', \vec{x}; t). \tag{3.11}$$

As we will now see, one can derive the functional form of the 1-particle density from this condition. Taking the logarithm on both sides of (3.11) gives, with $F_1 = \log f_1$ etc.,

$$F_1 + F_2 = F_{1'} + F_{2'}, \tag{3.12}$$

whence F must be a conserved quantity, i.e. either we have $F = \beta \frac{\vec{p}^2}{2m}$ or $F = \vec{\alpha} \cdot \vec{p}$ or $F = \gamma$. It follows, after renaming constants, that

$$f_1 = c \cdot e^{-\beta \frac{(\vec{p} - \vec{p}_0)^2}{2m}}. \tag{3.13}$$

In principle $c, \beta, \vec{p}_0$ could be functions of $\vec{x}$ and t at this stage, but then the left hand side of the Boltzmann equation does not vanish in general. So (3.13) represents the general *stationary homogeneous* solution to the Boltzmann equation. It is known as the **Maxwell-Boltzmann distribution**. The proper normalization is, from $\int f_1 \, d^3p \, d^3x = N$,

$$c = \frac{N}{V} \left(\frac{\beta}{2\pi m} \right)^{\frac{3}{2}}, \quad \vec{p}_0 = \langle \vec{p} \rangle. \tag{3.14}$$

The mean kinetic energy is found to be $\left\langle \frac{\vec{p}^2}{2m} \right\rangle = \frac{3}{2\beta}$, so $\beta = \frac{1}{k_B T}$ is identified with the inverse **temperature** of the gas.

This interpretation of β is reinforced by considering a gas of N particles confined to a box of volume V. The pressure of the gas results from a force K acting on a wall

element of area A, as depicted in the figure below. The force is equal to:

$$
K = \frac{1}{\Delta t} \int d^3 p \cdot \#\left(\overbrace{\begin{array}{c} \text{particles impacting A} \\ \text{during } \Delta t \text{ with momenta between } \vec{p} \text{ and } \vec{p} + d\vec{p} \end{array}}^{(f_1(\vec{p}) d^3 p) \cdot (A v_x \Delta t)} \right) \times \left(\overbrace{\begin{array}{c} \text{momentum transfer} \\ \text{in } x - \text{direction} \end{array}}^{2 p_x} \right)
$$

$$
= \frac{1}{\Delta t} \int\limits_{-\infty}^{0} dp_x \int\limits_{-\infty}^{\infty} dp_y \int\limits_{-\infty}^{\infty} dp_z \ f_1(\vec{p}) \left(A v_x \Delta t \right) \cdot \left(2 p_x \right).
$$

Note, that the first integral is just over half of the range of p_x, which is due to the fact that only particles moving in the direction of the wall will hit it.

Together with (3.13) it follows that the pressure P is given by

$$
P = \frac{K}{A} = \int d^3 p \ f_1(\vec{p}) \frac{p_x^2}{m} = \frac{n}{\beta}. \tag{3.15}
$$

Comparing with the equation of state for an ideal gas, $PV = N k_B T$, we get $\beta = \frac{1}{k_B T}$.
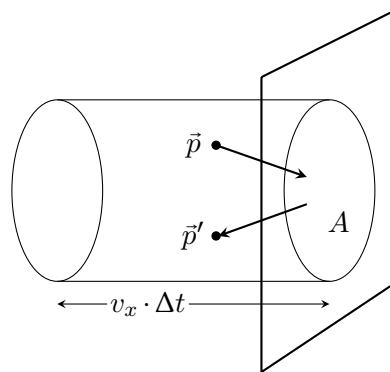

Figure 3.2.: Pressure on the walls due to the impact of particles.

It is noteworthy that, in the presence of external forces, other solutions representing equilibrium (but with a non-vanishing collision term) should also be possible. One only has to think of the following situation, representing a stationary air flow across a wing:
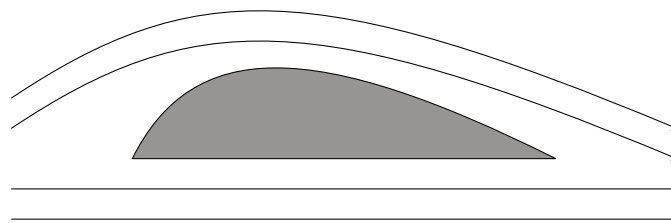
Figure 3.3.: Sketch of the air-flow across a wing.

In this case we have to deal with a much more complicated f_1, not equal to the Maxwell-Boltzmann distribution. As the example of an air-flow suggests, the Boltzmann equation is also closely related to other equations for fluids such as the Euler- or Navier-Stokes equation, which can be seen to arise as approximations of the Boltzmann equation.

The Boltzmann equation can easily be generalized to a gas consisting of several species $\alpha, \beta, \ldots$ which are interacting via the 2-body potentials $\mathcal{V}_{\alpha,\beta}\left(\vec{x}(\alpha) - \vec{x}(\beta)\right)$. As before, we can define the 1-particle density $f_1^{(\alpha)}(\vec{p}, \vec{x}, t)$ for each species. The same derivation leading to the Boltzmann equation now gives the *system of equations*

$$\left[\frac{\partial}{\partial t} - \vec{F}\frac{\partial}{\partial \vec{p}} + \vec{v}\frac{\partial}{\partial \vec{x}}\right] f_1^{(\alpha)} = \sum_\beta C^{(\alpha,\beta)}, \tag{3.16}$$

where the collision term $C^{(\alpha,\beta)}$ is given by

$$\begin{aligned}
C^{(\alpha,\beta)} = & -\int d^3 p_2 d^2\Omega \left|\frac{d\sigma_{\alpha,\beta}}{d\Omega}\right| |\vec{v}_1 - \vec{v}_2| \times \\
& \times \left[f_1^{(\alpha)}\left(\vec{p}_1, \vec{x}_1; t\right) f_1^{(\beta)}\left(\vec{p}_2, \vec{x}_1; t\right) - f_1^{(\alpha)}\left(\vec{p}_1', \vec{x}_1; t\right) f_1^{(\beta)}\left(\vec{p}_2', \vec{x}_1; t\right) \right].
\end{aligned} \tag{3.17}$$

This system of equations has great importance in practice e.g. for the evolution of the *abundances of different particle species in the early universe*. In this case

$$f_1^{(\alpha)}(\vec{p}, \vec{x}; t) \approx f_1^{(\alpha)}(\vec{p}, t) \tag{3.18}$$

are homogeneous distributions and the external force $\vec{F}$ on the left hand side of equations (3.16) is related to the expansion of the universe.

Demanding equilibrium now amounts to

$$f_1^{(\alpha)}(\vec{p}_1; t) f_1^{(\beta)}(\vec{p}_2; t) = f_1^{(\alpha)}(\vec{p}_1'; t) f_1^{(\beta)}(\vec{p}_2'; t), \tag{3.19}$$

and similar arguments as above lead to

$$f_1^{(\alpha)} \propto e^{-\beta \frac{(\vec{p} - \vec{p}_0(\alpha))^2}{2m}}, \tag{3.20}$$

i.e. we have the *same* temperature T for all α. In the context of the early universe it is essential to study deviations from equilibrium in order to explain the observed abundances.

By contrast to the original system of equations (Hamilton's equations or the BBGKY hierarchy), the Boltzmann equation is *irreversible*. This can be seen for example by introducing the function

$$h(t) = -k_B \int d^3 x \; d^3 p \; f_1(\vec{p}, \vec{x}; t) \; \log f_1(\vec{p}, \vec{x}; t) = S_{\inf}(f_1(t)), \tag{3.21}$$

which is called **Boltzmann H-function**. It can be shown (cf. exercises) that $\dot{h}(t) \geq 0$, with equality if

$$f_1(\vec{p}_1, \vec{x}; t) f_1(\vec{p}_2, \vec{x}; t) = f_1(\vec{p}_1', \vec{x}; t) f_1(\vec{p}_2', \vec{x}; t),$$

a result which is known as the **H-theorem**. We just showed this equality holds if and only if f_1 is given by the Maxwell-Boltzmann distribution. Thus, we conclude that $h(t)$ is an increasing function, as long as f_1 is not equal to the Maxwell-Boltzmann distribution. In particular, the evolution of f_1, as described by the Boltzmann equation, is *irreversible.* Since the Boltzmann equation is only an approximation to the full BBGKY hierarchy, which is reversible, there is no mathematical inconsistency. However, it is not clear, a priori, at which stage of the derivation the irreversibility has been allowed to enter. Looking at the approximations (a) and (b) made above, it is clear that the assumption that the 2-particle correlations f_2 are factorized, as in (b), cannot be exactly true, since the outgoing momenta of the particles are correlated. Although this correlation is extremely small after several collisions, it is not exactly zero. Our decision to neglect it can be viewed as one reason for the emergence of irreversibility on a macroscopic scale.

The close analogy between the definition of the Boltzmann H-function and the information entropy S_{inf}, as defined in (2.24), together with the monotonicity of $h(t)$ suggest that h should represent some sort of entropy of the system. The H-theorem is then viewed as a "derivation" of the 2$^{\text{nd}}$ law of thermodynamics (see Chapter 6). However, this point of view is not entirely correct, since $h(t)$ only depends on the 1-particle density f_1 and not on the higher particle densities f_s, which in general should also contribute to the entropy. It is not clear how an entropy with sensible properties has to be defined in a completely general situation, in particular when the above approximations (a) and (b) are not justified.

3.2. Boltzmann Equation, Approach to Equilibrium in Quantum Mechanics

A version of the Boltzmann equation and the H-theorem can also be derived in the quantum mechanical context. The main difference to the classical case is a somewhat modified collision term: the classical differential cross section is replaced by the quantum mechanical differential cross section (in the Born approximation) and the combination

$$f_1(\vec{p}_1, \vec{x}; t) f_1(\vec{p}_2, \vec{x}; t) - f_1(\vec{p}_1', \vec{x}; t) f_1(\vec{p}_2', \vec{x}; t)$$

is somewhat changed in order to accommodate Bose-Einstein resp. Fermi-Dirac statistics (see section 5.1 for an explanation of these terms). This then leads to the corresponding equilibrium distributions in the stationary case. Starting from the quantum Boltzmann

equation, one can again derive a corresponding H-theorem. Rather than explaining the details, we give a simplified "derivation" of the H-theorem, which also will allow us to introduce a simple minded but very useful approximation of the dynamics of probabilities, discussed in more detail in the Appendix.

The basic idea is to ascribe the approach to equilibrium to an incomplete knowledge of the true dynamics due to perturbations. The true Hamiltonian is written as

$$H = H_0 + H_1, \tag{3.22}$$

where H_1 is a tiny perturbation over which we do not have control. For simplicity, we assume that the spectrum of the unperturbed Hamiltonian H_0 is discrete and we write $H_0|n\rangle = E_n|n\rangle$. For a typical eigenstate $|n\rangle$ we then have

$$\frac{\langle n|H_1|n\rangle}{E_n} \ll 1. \tag{3.23}$$

Let p_n be the probability that the system is in the state $|n\rangle$, i.e. we ascribe to the system the density matrix $\rho = \sum_n p_n|n\rangle\langle n|$. For generic perturbations H_1, this ensemble is not stationary with respect to the true dynamics because $[\rho, H] \neq 0$. Consequently, the von Neumann entropy $S_{\text{v.N.}}$ of $\rho(t) = e^{itH}\rho e^{-itH}$ depends upon time. We define this to be the H-function

$$h(t) := S_{\text{v.N.}}(\rho(t)). \tag{3.24}$$

Next, we approximate the dynamics by imagining that our perturbation H_1 will cause jumps from state $|i\rangle$ to state $|j\rangle$ leading to time-dependent probabilities as described by the **master equation**[1]

$$\dot{p}_i(t) = \sum_{j:j\neq i} \left(T_{ij}p_j(t) - T_{ji}p_i(t)\right), \tag{3.25}$$

where T_{ij} is the transition amplitude[2] of going from state $|i\rangle$ to state $|j\rangle$. Thus, the approximated, time-dependent density matrix is $\rho(t) = \sum_n p_n(t)|n\rangle\langle n|$, with $p_n(t)$ obeying the master equation. Under these approximations it is straightforward to calculate that

$$\dot{h}(t) = \frac{1}{2}\text{k}_B \sum_{i,j} T_{ij}[p_i(t) - p_j(t)][\log p_i(t) - \log p_j(t)] \geq 0. \tag{3.26}$$

The latter inequality follows from the fact that both terms in parentheses [...] have the

---

[1] This equation can be viewed as a discretized analog of the Boltzmann equation in the present context. See the Appendix for further discussion of this equation.

[2] According to Fermi's golden rule, the transition amplitude is given by

$$T_{ij} = \frac{2\pi n}{\hbar}|\langle i|H_1|j\rangle|^2 \geq 0,$$

where n is the density of final states.

same sign, just as in the proof of the classical H-theorem (exercises). Note that if we had defined $h(t)$ as the von Neumann entropy, using a density matrix ρ that is diagonal in an eigenbasis of the full Hamiltonian H (rather than the unperturbed Hamiltonian), then we would have obtained $[\rho, H] = 0$ and consequently $\rho(t) = \rho$, i.e. a constant $h(t)$. Thus, in this approach, the H-theorem is viewed as a consequence of our partial ignorance about the system, which prompts us to ascribe to it a density matrix $\rho(t)$ which is diagonal with respect to H_0. In order to justify working with a density matrix ρ that is diagonal with respect to H_0 (and therefore also in order to explain the approach to equilibrium), one may argue very roughly as follows: suppose that we start with a system in a state $|\Psi\rangle = \sum\limits_m \gamma_n|n\rangle$ that is *not* an eigenstate of the true Hamiltonian H. Let us write

$$|\Psi(t)\rangle = \sum_n \gamma_n(t)e^{\frac{iE_n t}{\hbar}}|n\rangle \equiv e^{iHt}|\Psi\rangle.$$

for the time evolved state. If there is no perturbation, i.e. $H_1 = 0$, we get

$$\gamma_n(t) = \gamma_n = \text{const.,}$$

but for $H_1 \neq 0$ this is typically not the case. The time average of an operator (observable) A is given by

$$\lim_{T\to\infty} \frac{1}{T}\int_0^T \langle\Psi(t)|A|\Psi(t)\rangle \, dt = \lim_{T\to\infty} \text{tr}(\rho(T)A), \tag{3.27}$$

with

$$\langle n|\rho(T)|m\rangle = \frac{1}{T}\int_0^T \gamma_n(t)\overline{\gamma_m(t)}e^{\frac{it(E_n - E_m)}{\hbar}} \, dt. \tag{3.28}$$

For $T \to \infty$ the oscillating phase factor $e^{it(E_n - E_m)}$ is expected to cause the integral to vanish for $E_n \neq E_m$, such that $\langle n|\rho(T)|m\rangle \xrightarrow[T\to\infty]{} p_n\delta_{n,m}$. It follows that

$$\lim_{T\to\infty} \frac{1}{T}\int_0^T \langle\Psi(t)|A|\Psi(t)\rangle \, dt = \text{tr}(A\rho), \tag{3.29}$$

where the density matrix ρ is $\rho = \sum_n p_n|n\rangle\langle n|$. Since $[\rho, H_0]$, the ensemble described by ρ is stationary with respect to H_0. The underlying reason is that while $\langle n|H_1|n\rangle$ is $\ll E_n$, it can be large compared to $\Delta E_n = E_n - E_{n+1} = \mathcal{O}(e^{-N})$ (where N is the particle number) and can therefore induce transitions causing the system to equilibrate.

4. Equilibrium Ensembles

4.1. Generalities

In the probabilistic description of a system with a large number of constituents one considers probability distributions (=ensembles) $\rho(P, Q)$ on phase space, rather than individual trajectories. In the previous section, we have given various arguments leading to the expectation that the time evolution of an ensemble will generally lead to an equilibrium ensemble. The study of such ensembles is the subject of equilibrium statistical mechanics. Standard equilibrium ensembles are:

(a) Micro-canonical ensemble (section 4.2).

(b) Canonical ensemble (section 4.3).

(c) Grand canonical (Gibbs) ensemble (section 4.4).

4.2. Micro-Canonical Ensemble

4.2.1. Micro-Canonical Ensemble in Classical Mechanics

Recall that in classical mechanics the phase space Ω of a system consisting of N particles without internal degrees of freedom is given by

$$\Omega = \mathbb{R}^{6N}. \tag{4.1}$$

As before, we define the energy surface Ω_E by

$$\Omega_E = \left\{ (P, Q) \in \Omega : H(P, Q) = E \right\}, \tag{4.2}$$

where H denotes the Hamiltonian of the system. In the micro-canonical ensemble each point of Ω_E is considered to be equally likely. In order to write down the corresponding ensemble, i.e. the density function $\rho(P, Q)$, we define the invariant volume $|\Omega_E|$ of Ω_E by

$$|\Omega_E| := \lim_{\Delta E \to 0} \frac{1}{\Delta E} \int\limits_{E - \Delta E \leq H(P,Q) \leq E} d^{3N} P \, d^{3N} Q, \tag{4.3}$$

which can also be expressed as

$$|\Omega_E| = \frac{\partial \Phi(E)}{\partial E}, \quad \text{with} \ \ \Phi(E) = \int\limits_{H(P,Q) \le E} d^{3N}P \ d^{3N}Q. \tag{4.4}$$

Thus, we can write the probability density of the micro-canonical ensemble as

$$\rho(P,Q) = \frac{1}{|\Omega_E|} \ \delta\left(H(P,Q) - E\right). \tag{4.5}$$

To avoid subtleties coming from the δ-function for sharp energy one sometimes replaces this expression by

$$\rho(P,Q) = \frac{1}{\left|\left\{E - \Delta E \le H(P,Q) \le E\right\}\right|} \cdot \begin{cases} 1, & \text{if } H(P,Q) \in (E - \Delta E, E). \\ 0, & \text{if } H(P,Q) \notin (E - \Delta E, E) \end{cases}. \tag{4.6}$$

Strictly speaking, this depends not only on E but also on ΔE. But in typical cases $|\Omega_E|$ depends exponentially on E, so there is practically no difference between these two expressions for $\rho(P,Q)$ as long as $\Delta E \lesssim E$. We may alternatively write the second definition as:

$$\rho = \frac{1}{W(E)} \left[\Theta(H - E + \Delta E) - \Theta(H - E)\right]. \tag{4.7}$$

Here we have used the Heaviside step function Θ, defined by

$$\Theta(E) = \begin{cases} 1, & \text{for } E > 0 \\ 0, & \text{otherwise.} \end{cases}$$

We have also defined

$$\boxed{W(E) = \left|\left\{E - \Delta E \le H(P,Q) \le E\right\}\right|.} \tag{4.8}$$

Following Boltzmann, we give the following

Definition: The **entropy** of the micro-canonical ensemble is defined by

$$\boxed{S(E) = \mathrm{k_B} \log W(E).} \tag{4.9}$$

As we have already said, in typical cases, changing $W(E)$ in this definition to $\mathrm{k_B} \log |\Omega_E|$ will not significantly change the result. It is not hard to see that we may equivalently write in either case

$$S(E) = -\mathrm{k_B} \int \rho(P,Q) \log \rho(P,Q) \ d^{3N}P d^{3N}Q = S_{\mathrm{inf}}(\rho) \ , \tag{4.10}$$

i.e. Boltzmann's definition of entropy coincides with the definition of the information entropy (2.24) of the microcanonical ensemble ρ. As defined, S is a function of E and implicitly V, N, since these enter the definition of the Hamiltonian and phase space. Sometimes one also specifies other constants of motion or parameters of the system other than E when defining S. Denoting these constants collectively as $\{I_\alpha\}$, one defines W accordingly with respect to E and $\{I_\alpha\}$ by replacing the energy surface with:

$$\Omega_{E,\{I_\alpha\}} := \left\{ (P,Q) \in \Omega : H(P,Q) = E, \ I_\alpha(P,Q) = I_\alpha \right\}. \tag{4.11}$$

In this case $S(E, \{I_\alpha\})$ becomes a function of several variables.

Example:

The ideal gas of N particles in a box has the Hamiltonian $H = \sum_{i=1}^{N} \left(\frac{\vec{p}^2}{2m} + \mathcal{W}(\vec{x}_i) \right)$, where the external potential $\mathcal{W}$ represents the walls of a box of volume V. For a box with hard walls we take, for example,

$$\mathcal{W}(\vec{x}) = \begin{cases} 0 & \text{inside } V \\ \infty & \text{outside } V \end{cases}. \tag{4.12}$$

For the energy surface Ω_E we then find

$$\Omega_E = \{ \ (P,Q) \in \Omega \ | \ \underbrace{\vec{x}_i \text{ inside the box}}_{\to V^N} , \qquad \underbrace{\sum_{i=1}^{N} \vec{p}^2 = 2Em}_{\substack{= \text{ sphere of dimension} \\ 3N-1 \text{ and radius } \sqrt{2Em}}} \ \}, \tag{4.13}$$

from which it follows that

$$|\Omega_E| = V^N \sqrt{2Em}^{3N-1} \underbrace{\text{area} \ (S^{3N-1})}_{= \frac{2\pi^{d/2}}{\Gamma(\frac{d}{2})}} \cdot 2m. \tag{4.14}$$

Here, $\Gamma(x) = (x-1)!$ denotes the Γ-function. The entropy $S(E,V,N)$ is therefore given by

$$S(E,V,N) \approx k_B \left[N \log V + \frac{3N}{2} \log(2\pi m E) - \frac{3N}{2} \log \frac{3N}{2} + \frac{3N}{2} \right], \tag{4.15}$$

where we have used Stirling's approximation:

$$\log x! \approx \sum_{i=1}^{x} \log i \approx \int_{1}^{x} \log y \; dy = x \log x - x + 1$$

$$\Rightarrow \; x! \approx e^{-x} x^x.$$

Thus, we obtain for the entropy of the ideal gas:

$$S(E, V, N) \approx N k_B \log \left[V \left(\frac{4 \pi e m E}{3N} \right)^{3/2} \right]. \tag{4.16}$$

Given the function $S(E, V, N)$ for a system, one can *define* the corresponding temperature, pressure and chemical potential as follows:

Definition: The **empirical temperature** T, **pressure** P and **chemical potential** μ of the microcanonical ensemble are defined as:

$$\boxed{\frac{1}{T} := \frac{\partial S}{\partial E}\bigg|_{V,N} \;, \quad P := T \frac{\partial S}{\partial V}\bigg|_{E,N} \;, \quad \mu := -T \frac{\partial S}{\partial N}\bigg|_{E,V}.} \tag{4.17}$$

For the ideal classical gas this definition, together with (4.16), yields for instance

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{3}{2} \frac{N k_B}{E}, \tag{4.18}$$

which we can rewrite in the more familiar form

$$E = \frac{3}{2} N k_B T. \tag{4.19}$$

This formula states that for the ideal gas we have the equidistribution law

$$\frac{\text{average energy}}{\text{degree of freedom}} = \frac{1}{2} k_B T. \tag{4.20}$$

One can similarly verify that the abstract definition of P in (4.17) above gives

$$PV = k_B N T, \tag{4.21}$$

which is the familiar "equation of state" for an ideal gas.

In order to further motivate the second relation in (4.17), we consider a system comprised of a piston applied to an enclosed gas chamber:
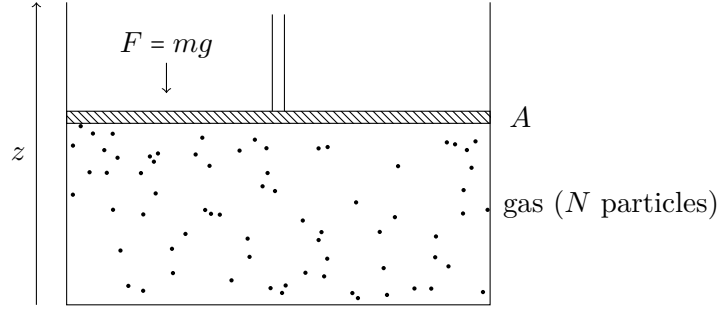
Figure 4.1.: Gas in a piston maintained at pressure P.

Here, we obviously have $PV = mgz$. From the microcanonical ensemble for the combined piston-gas system, the total energy is obtained as

$$H_{\text{total}} = H_{\text{gas}}(P, Q) + H_{\text{piston}}(p, z) \approx H_{\text{gas}}(P, Q) + \underbrace{mgz}_{\text{=pot. energy of piston}}, \tag{4.22}$$

where we have neglected the kinetic energy $p^2/2m$ of the piston (this could be made more rigorous by letting $m \to \infty$, $g \to 0$). Next, we calculate

$$W_{\text{total}}(E_{\text{total}}) = \int_{E_{\text{total}} - \Delta E \ \le \ H_{\text{gas}} + mgz \ \le \ E_{\text{total}}} d^{3N}P \ d^{3N}Q \ dz$$

$$= \int dz \ W_{\text{gas}}(E_{\text{total}} - PV, V, N),$$

with $V = Az$. We evaluate the integral through its value at the maximum, which is located at the point at which

$$0 = \frac{d}{dz} W_{\text{gas}}(E_{\text{total}} - PV, V, N) = \frac{d}{dV} W_{\text{gas}}(E_{\text{total}} - PV, V, N)$$

$$= \frac{\partial W_{\text{gas}}}{\partial E} \cdot (-P) + \frac{\partial W_{\text{gas}}}{\partial V} = \left(-\frac{P}{k_{\text{B}}} \frac{\partial S_{\text{gas}}}{\partial E} + \frac{1}{k_{\text{B}}} \frac{\partial S_{\text{gas}}}{\partial V} \right) e^{\frac{S_{\text{gas}}}{k_{\text{B}}}}.$$

Using $S_{\text{gas}} = k_{\text{B}} \log W_{\text{gas}}$, it follows that

$$\left. \frac{\partial S_{\text{gas}}}{\partial V} \right|_{E,N} = P \frac{\partial S_{\text{gas}}}{\partial E} = \frac{P}{T}, \tag{4.23}$$

which gives the desired relation

$$P = T \left. \frac{\partial S}{\partial V} \right|_{E,N}. \tag{4.24}$$

The quantity $E_{\text{total}} = E_{\text{gas}} + PV$ is also called the **enthalpy**.

It is instructive to compare the definition of the temperature in (4.17) with the parame-

ter β that arose in the Boltzmann-Maxwell distribution (3.13), which we also interpreted as temperature there. We first ask the following question: What is the probability for finding particle number 1 having momentum lying between $\vec{p}_1$ and $\vec{p}_1 + d\vec{p}_1$? The answer is: $W(\vec{p}_1)d^3p_1$, where $W(\vec{p}_1)$ is given by

$$W(\vec{p}_1) = \int \rho(P, Q) \, d^3p_2 \dots d^3p_N \, d^3x_1 \dots d^3x_N. \tag{4.25}$$

We wish to calculate this for the ideal gas. To this end we introduce the Hamiltonian H' and the kinetic energy E' for the remaining atoms:

$$H' = \sum_{i=2}^{N} \left(\frac{\vec{p}_i^2}{2m} + \mathcal{W}(\vec{x}_i) \right), \tag{4.26}$$

$$E' = E - \frac{\vec{p}_1^2}{2m}, \qquad E - H \qquad\qquad = E' - H'. \tag{4.27}$$

From this we get, together with (4.25) and (4.5):

$$W(\vec{p}_1) = \frac{V}{|\Omega_E|} \int \delta(E' - H') \prod_{i=2}^{N} d^3p_i \, d^3x_i = \frac{V \left| \Omega_{E', N-1} \right|}{\left| \Omega_{E,N} \right|}$$

$$= \frac{\left(\frac{3}{2}N - 1 \right)!}{\pi^{\frac{3}{2}} \left(\frac{3}{2}N - \frac{5}{2} \right)! (2mE)^{3/2}} \left(\frac{E'}{E} \right)^{\frac{3N}{2} - \frac{5}{2}}. \tag{4.28}$$

Using now the relations

$$\frac{\left(\frac{3N}{2} + a \right)!}{\left(\frac{3N}{2} + b \right)!} \approx \left(\frac{3N}{2} \right)^{a-b}, \quad \text{for } a, b \ll \frac{3N}{2},$$

we see that for a sufficiently large number of particles (e.g. $N = \mathcal{O}(10^{23})$)

$$W(\vec{p}_1) \approx \left(\frac{3N}{4\pi mE} \right)^{\frac{3}{2}} \left(1 - \frac{\vec{p}_1^2}{2mE} \right)^{\frac{3N}{2} - \frac{5}{2}} \tag{4.29}$$

Using

$$\left(1 - \frac{a}{N} \right)^{bN} \xrightarrow[N \to \infty]{} e^{-ab},$$

and $\beta = \frac{3N}{2E}$ ($\Leftrightarrow E = \frac{3}{2}k_B NT$), we find that

$$\left(1 - \frac{\vec{p}_1^2}{2mE} \right)^{\frac{3N}{2} - \frac{5}{2}} \xrightarrow[N \to \infty]{} e^{-\frac{3N}{2} \frac{\vec{p}_1^2}{2mE}}, \tag{4.30}$$

Consequently, we get exactly the Maxwell-Boltzmann distribution

$$W(\vec{p}_1) = \left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}} e^{-\beta \frac{\vec{p}_1^2}{2m}}, \tag{4.31}$$

which confirms our interpretation of β as $\beta = \frac{1}{k_B T}$.

We can also confirm the interpretation of β by the following consideration: consider two initially isolated systems and put them in thermal contact. The resulting joint probability distribution is given by

$$\rho(P, Q) = \frac{1}{|\Omega_E|} \; \delta \left(\underbrace{H_1(P_1, Q_1)}_{\text{system 1}} + \underbrace{H_2(P_2, Q_2)}_{\text{system 2}} - E \right). \tag{4.32}$$

Since only the overall energy is fixed, we may write for the total allowed phase space volume (exercise):

$$|\Omega_E| = \int dE_1 \; dE_2 \; \underbrace{|\Omega_{E_1}|}_{\text{system 1}} \cdot \underbrace{|\Omega_{E_2}|}_{\text{system 2}} \cdot \delta(E - E_1 - E_2)$$

$$= \int dE_1 \; e^{\frac{S_1(E_1) + S_2(E - E_1)}{k_B}}. \tag{4.33}$$

For typical systems, the integrand is very sharply peaked at the maximum (E_1^*, E_2^*), as depicted in the following figure:

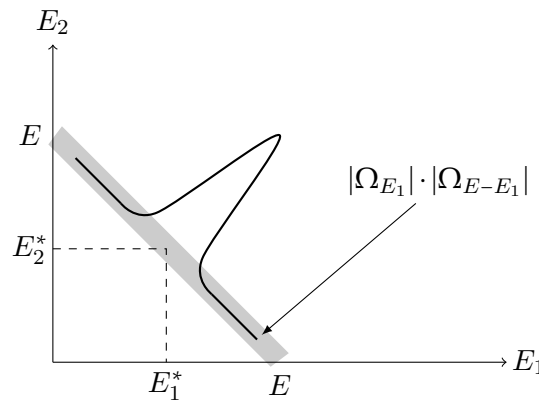Figure 4.2.: The joint number of states for two systems in thermal contact.

At the maximum we have $\frac{\partial S_1}{\partial E}(E_1^*) = \frac{\partial S_2}{\partial E}(E_2^*)$ from which we get the relation:

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{1}{T} \qquad \text{(uniformity of temperature).} \tag{4.34}$$

Since one expects the function to be very sharply peaked at (E_1^*, E_2^*), the integral in

(4.33) can be approximated by

$$S(E) \approx S_1(E_1^*) + S_2(E_2^*),$$

which means that the entropy is (approximately) additive. Note that from the condition of (E_1^*, E_2^*) being a genuine maximum (not just a stationary point), one gets the important **stability condition**

$$\frac{\partial^2 S_1}{\partial E_1^2} + \frac{\partial^2 S_2}{\partial E_2^2} \leq 0, \tag{4.35}$$

implying $\frac{\partial^2 S}{\partial E^2} \leq 0$ if applied to two copies of the same system. We can apply the same considerations if S depends on additional parameters, such as other constants of motion. Denoting the parameters collectively as $X = (X_1, ..., X_n)$, the stability condition becomes

$$\sum_{i,j} \frac{\partial^2 S}{\partial X_i \partial X_j} v_i v_j \leq 0, \tag{4.36}$$

for any choice of displacements v_i (negativity of the Hessian matrix). Thus, in this case, S is a **concave** function of its arguments. Otherwise, if the Hessian matrix has a positive eigenvalue e.g. in the i-th coordinate direction, then the corresponding displacement v_i will drive the system to an inhomogeneous state, i.e. one where the quantity X_i takes different values in different parts of the system (different phases).

4.2.2. Microcanonical Ensemble in Quantum Mechanics

Let H be the Hamiltonian of a system with eigenstates $|n\rangle$ and eigenvalues E_n, i.e. $H|n\rangle = E_n|n\rangle$, and consider the density matrix

$$\rho = \frac{1}{W} \sum_{n:E-\Delta E \leq E_n \leq E} |n\rangle\langle n|, \tag{4.37}$$

where the normalization constant W is chosen such that $\text{tr}\rho = 1$. The density matrix ρ is analogous to the distribution function $\rho(P, Q)$ in the classical microcanonical ensemble, eq. (4.6), since it effectively amounts to giving equal probability to all eigenstates with energies lying between E and $E - \Delta E$. By analogy with the classical case we get

$$\boxed{W = \text{number of states between } E - \Delta E \text{ and } E,} \tag{4.38}$$

and we define the corresponding entropy $S(E)$ again by

$$\boxed{S(E) = k_B \log W(E)}. \tag{4.39}$$

Since $W(E)$ is equal to the number of states with energies lying between $E - \Delta E$ and E, it also depends, strictly speaking, on ΔE. But for $\Delta E \lesssim E$ and large N, this dependency can be neglected (cf. Homework 3). Note that

$$S_{\text{v.N.}}(\rho) = -k_B \, \text{tr}\left(\rho \log \rho\right) = -k_B \cdot \sum_{n:E-\Delta E \leq E_n \leq E} \frac{1}{W} \, \log \frac{1}{W} \, ,$$

$$= k_B \log W \cdot \frac{1}{W} \sum_{n:E-\Delta E \leq E_n \leq E} 1$$

$$= k_B \log W,$$

so $S = k_B \log W$ is equal to the von Neumann entropy for the statistical operator ρ, defined in (4.37) above. Let us illustrate this definition in an

Example: Free atom in a cube

We consider a free particle ($N = 1$) in a cube of side lengths $\left(L_x, L_y, L_z\right)$. The Hamiltonian is given by $H = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$. We impose boundary conditions such that the normalized wave function Ψ vanishes at the boundary of the cube. This yields the eigenstates

$$\Psi(x, y, z) = \sqrt{\frac{8}{V}} \sin(k_x \cdot x) \sin(k_y \cdot y) \sin(k_z \cdot z), \tag{4.40}$$

where $k_x = \frac{\pi n_x}{L_x}, \, \ldots,$ with $n_x = 1, 2, 3, \ldots$.
The corresponding energy eigenvalues are given by

$$E_n = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right), \tag{4.41}$$

since $p_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$, etc. Recall that W was defined by

$$W = \text{ number of states } |n_x, n_y, n_z\rangle \text{ with } E - \Delta E \leq E_n \leq E.$$

The following figure gives a sketch of this situation (with $k_z = 0$):
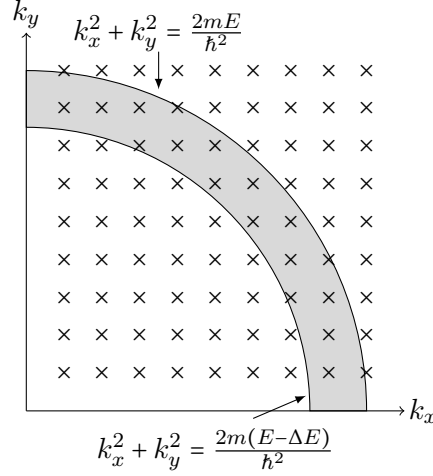
Figure 4.3.: Number of states with energies lying between $E - \Delta E$ and E.

In the continuum approximation we have (recalling that $\hbar = \frac{h}{2\pi}$):

$$
\begin{aligned}
W \quad &= \quad \sum_{E-\Delta E \leq E_n \leq E} 1 \qquad \approx \int_{E-\Delta E \leq E_n \leq E} d^3 n \\[2ex]
&= \int_{\{E-\Delta E \leq \frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right) \leq E\}} \frac{L_x L_y L_z}{\pi^3} d^3 k \\[2ex]
&= \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \frac{V}{\pi^3} \int_{E-\Delta E} E'^2 \, dE' \int_{1/8 \text{ of } S^2} d^2\Omega \\[2ex]
&= \frac{4\pi}{3} \frac{V}{(2\pi)^3} \left(\frac{2mE}{\hbar^2}\right)^{\frac{3}{2}} \Bigg|_{E-\Delta E}^{E} \\[2ex]
&\approx \frac{4\pi}{3} V \frac{(2mE)^{\frac{3}{2}}}{h^3}, \qquad \text{for } \Delta E \approx E.
\end{aligned}
\tag{4.42}
$$

If we compute W according to the definition in classical mechanics, we would get

$$
\begin{aligned}
W &= \int_{\{E-\Delta E \leq H \leq E\}} d^3 p \, d^3 x \;=\; V \int_{\{E-\Delta E \leq \frac{\vec{p}^2}{2m} \leq E\}} d^3 p \\[2ex]
&= V (2m)^{\frac{3}{2}} \int_{\{E-\Delta E \leq E' \leq E\}} E'^2 \, dE' \int_{S^2} d^2\Omega \\[2ex]
&= \frac{4\pi}{3} V (2mE)^{\frac{3}{2}} \Bigg|_{E-\Delta E}^{E} .
\end{aligned}
$$

This is just h^3 times the quantum mechanical result. For the case of N particles, this suggests the following relation[1] :

$$W_N^{\text{qm}} \approx \frac{1}{h^{3N}} \ W_N^{\text{cl}}. \tag{4.44}$$

This can be understood intuitively by recalling the uncertainty relation $\Delta p \ \Delta x \gtrsim h$, together with $p \sim \frac{\pi n \hbar}{V^{\frac{1}{3}}}, n \in \mathbb{N}$.

4.2.3. Mixing entropy of the ideal gas

A puzzle concerning the definition of entropy in the micro-canonical ensemble (e.g. for an ideal gas) is revealed if we consider the following situation of two chambers, each of which is filled with an ideal gas:
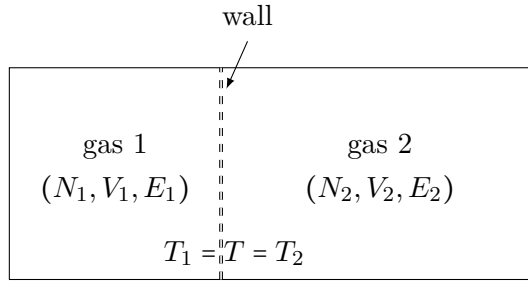
Figure 4.4.: Two gases separated by a removable wall.

The total volume is given by $V = V_1 + V_2$, the total particle number by $N = N_1 + N_2$ and the total energy by $E = E_1 + E_2$. Both gases are at the same temperature T. Using the expression (4.16) for the *classical* ideal gas, the entropies $S_i(N_i, V_i, E_i)$ are calculated as

$$S_i(N_i, V_i, E_i) = N_i \ \text{k}_\text{B} \ \log\left[V_i\left(\frac{4\pi e m_i E_i}{3N_i}\right)^{\frac{3}{2}}\right]. \tag{4.45}$$

The wall is now removed and the gases can mix. The temperature of the resulting ideal gas is determined by

$$\frac{3}{2}\text{k}_\text{B}T = \frac{E_1 + E_2}{N_1 + N_2} = \frac{E_i}{N_i}. \tag{4.46}$$

---

[1]The quantity W^{cl} is for this reason often *defined* by

$$W^{\text{cl}}(E, N) \coloneqq h^{-3N}\left|\Omega_{E,N}\right|. \tag{4.43}$$

Also, one often includes further combinatorial factors to include the distinction between distinguishable and indistinguishable particles, cf. (4.49).

The total entropy S is now found as (we assume $m_1 = m_2 \equiv m$ for simplicity):

$$S = N\ k_{\mathrm{B}}\ \log\left[V\,(2\pi m k_{\mathrm{B}}T)^{\frac{3}{2}}\right]$$

$$= \underbrace{N\ k_{\mathrm{B}}\log V - N_1\ k_{\mathrm{B}}\ \log V_1 - N_2\ k_{\mathrm{B}}\ \log V_2}_{\Delta S} + S_1 + S_2, \qquad (4.47)$$

From this it follows that the **mixing entropy** ΔS is given by

$$\Delta S = N_1\ k_{\mathrm{B}}\ \log\frac{V}{V_1} - N_2\ k_{\mathrm{B}}\ \log\frac{V}{V_2}$$

$$= -N\ k_{\mathrm{B}}\ \sum_i c_i \log v_i, \qquad (4.48)$$

with $c_i = \frac{N_i}{N}$ and $v_i = \frac{V_i}{V}$. This holds also for an arbitrary number of components and raises the following *paradox*: if both gases are *identical* with the same density $\frac{N_1}{N} = \frac{N_2}{N}$, from a macroscopic viewpoint clearly "nothing happens" as the wall is removed. Yet, $\Delta S \neq 0$. The resolution of this paradox is that the particles have been treated as **distinguishable**, i.e. the states
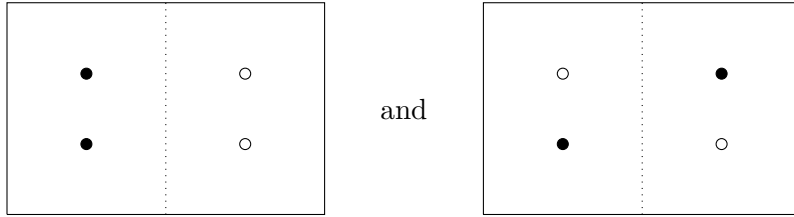
have been counted as microscopically different. However, if both gases are the same, they ought to be treated as **indistinguishable**. This change results in a different definition of W in both cases. Namely, depending on the case considered, the correct definition of W should be:

$$W(E,V,\{N_i\}) := \begin{cases} \left|\Omega(E,V,\{N_i\})\right| & \text{if distinguishable} \\ \frac{1}{\prod\limits_i N_i!}\left|\Omega(E,V,\{N_i\})\right| & \text{if indistinguishable,} \end{cases} \qquad (4.49)$$

where N_i is the number of particles of species i. Thus, the second definition is the physically correct one in our case. With this change (which in turn results in a different definition of the entropy S), the mixing entropy of two identical gases is now $\Delta S = 0$. In quantum mechanics the symmetry factor $\frac{1}{N!}$ in W^{qm} (for each species of indistinguishable particles) is automatically included due to the Bose/Fermi alternative, which we shall discuss later, leading to an automatic resolution of the paradox.

The non-zero mixing entropy of two identical gases is seen to be unphysical also at

the classical level because the entropy should be an *extensive* quantity. Indeed, the arguments of the previous subsection suggest that for $V_1 = V_2 = \frac{1}{2}V$ and $N_1 = N_2 = \frac{1}{2}N$ we have

$$\left| \Omega(E, V, N) \right| = \int dE' \left| \Omega\left(E - E', \frac{V}{2}, \frac{N}{2} \right) \right| \left| \Omega\left(E', \frac{V}{2}, \frac{N}{2} \right) \right|$$

$$\approx \left| \Omega\left(\frac{1}{2}E, \frac{1}{2}V, \frac{1}{2}N \right) \right|^2$$

(the maximum of the integrand above should be sharply peaked at $E' = \frac{E}{2}$). It follows for the entropy that, approximately,

$$S(E, N, V) = 2S\left(\frac{E}{2}, \frac{N}{2}, \frac{V}{2} \right). \tag{4.50}$$

The same consideration can be repeated for ν subsystems and yields

$$S(E, N, V) = \nu S\left(\frac{E}{\nu}, \frac{N}{\nu}, \frac{V}{\nu} \right), \tag{4.51}$$

and thus

$$S(E, N, V) = N \cdot \sigma(\epsilon, n), \tag{4.52}$$

for some function σ in two variables, where $\epsilon = \frac{E}{N}$ is the average energy per particle and $n = \frac{N}{V}$ is the particle density. Hence S is an **extensive quantity**, i.e. S is proportional to N. A non-zero mixing entropy would contradict the extensivity property of S.

4.3. Canonical Ensemble

4.3.1. Canonical Ensemble in Quantum Mechanics

We consider a system (system A) in thermal contact with an (infinitely large) heat reservoir (system B):
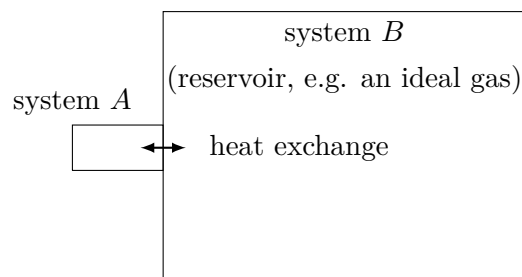
Figure 4.5.: A small system in contact with a large heat reservoir.

The overall energy $E = E_A + E_B$ of the combined system is fixed, as are the particle numbers N_A, N_B of the subsystems. We think of N_B as much larger than N_A; in fact we shall let $N_B \to \infty$ at the end of our derivation. We accordingly describe the total Hilbert space of the system by a tensor product, $\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B$. The total Hamiltonian of the combined system is

$$H = \underbrace{H_A}_{\text{system A}} + \underbrace{H_B}_{\text{system B}} + \underbrace{H_{AB}}_{\text{interaction (neglected)}}, \tag{4.53}$$

where the interaction is needed in order that the subsystems can interact with each other. Its precise form is not needed, as we shall assume that the interaction strength is arbitrarily small. The Hamiltonians H_A and H_B of the subsystems A and B act on the Hilbert spaces $\mathcal{H}_A$ and $\mathcal{H}_B$, and we choose bases so that:

$$H_A |n\rangle_A = E_n^{(A)} |n\rangle_A,$$
$$H_B |m\rangle_B = E_m^{(B)} |m\rangle_B,$$
$$|n, m\rangle = |n\rangle_A \otimes |m\rangle_B.$$

Since E is conserved, the quantum mechanical statistical operator of the combined system is given by the micro canonical ensemble with density matrix

$$\rho = \frac{1}{W} \cdot \sum_{\substack{n,m: \\ E - \Delta E \le E_n^{(A)} + E_m^{(B)} \le E}} |n, m\rangle\langle n, m|. \tag{4.54}$$

The reduced density matrix for sub system A is calculated as

$$\rho_A = \frac{1}{W} \sum_n \left(\overbrace{\sum_{m: E - E_n^{(A)} - \Delta E \le E_m^{(A)} \le E - E_n^{(A)}} 1}^{=W_B\left(E - E_n^{(A)}\right)} \right) |n\rangle_A \otimes {}_A\langle n|.$$

Now, using the extensively of the entropy S_B of system B we find (with $n_B = N_B/V_B$

the particle density and σ_B the entropy per particle of system B)

$$\log W_B\left(E - E_n^{(A)}\right) = \frac{1}{k_B} S_B\left(E - E_n^{(A)}\right)$$

$$= \frac{N_B}{k_B}\sigma_B\left(\frac{E}{N_B}, n_B\right) - \frac{N_B}{k_B}\frac{E_n^{(A)}}{N_B}\frac{\partial\sigma_B}{\partial\epsilon}\left(\frac{E}{N_B}, n_B\right)$$

$$+ \underbrace{\frac{N_B}{k_B}\left(\frac{E_n^{(A)}}{N_B}\right)^2\frac{\partial^2\sigma_B}{\partial\epsilon^2}\left(\frac{E}{N_B}, n_B\right) + \dots}_{=\mathcal{O}\left(\frac{1}{N_B}\right)\to 0 \text{ (as } N_B\to\infty, \text{ i.e., reservoir } \infty\text{-large!)}} \quad .$$

Thus, using $\beta = \frac{1}{k_B T}$ and $\frac{1}{T} = \frac{\partial S}{\partial E}$, we have for an infinite reservoir

$$\log W_B\left(E - E_n^{(A)}\right) = \log W_B(E) - E_n^{(A)}\beta, \tag{4.55}$$

which means

$$W_B\left(E - E_n^{(A)}\right) = \frac{1}{Z}\,e^{-\beta E_n^{(A)}}. \tag{4.56}$$

Therefore, we find the following expression for the reduced density matrix for system A:

$$\rho_A = \frac{1}{Z}\sum_n e^{-\beta E_n^{(A)}}|n\rangle_A \otimes {}_A\langle n|, \tag{4.57}$$

where $Z = Z(\beta, N_A, V_A)$ is called **canonical partition function**. Explicitly:

$$\boxed{Z(N, \beta, V) = \text{tr}\left[e^{-\beta H(V,N)}\right] = \sum_n e^{-\beta E_n}}\ . \tag{4.58}$$

Here we have dropped the subscripts "A" referring to our sub system since we can at this point forget about the role of the reservoir B (so $H = H_A, V = V_A$ etc. in this formula). This finally leads to the **statistical operator of the canonical ensemble**:

$$\boxed{\rho = \frac{1}{Z(\beta, N, V)}e^{-\beta H(N,V)}}\ . \tag{4.59}$$

Particular, the only quantity characterizing the reservoir entering the formula is the temperature T.

4.3.2. Canonical Ensemble in Classical Mechanics

In the classical case we can make similar considerations as in the quantum mechanical case. Consider the same situation as above. The phase space of the combined system is

$$(P, Q) = (\underbrace{P_A, Q_A}_{\text{system A}}, \underbrace{P_B, Q_B}_{\text{system B}}).$$

The Hamiltonian of the total system is written as

$$H(P, Q) = H_A(P_A, Q_A) + H_B(P_B, Q_B) + H_{AB}(P, Q). \tag{4.60}$$

H_{AB} accounts for the interaction between the particles from both systems and is neglected in the following. By analogy with the quantum mechanical case we get a reduced probability distribution ρ_A for sub system A:

$$\rho_A(P_A, Q_A) = \int d^{3N_B} P_B \; d^{3N_B} Q_B \; \rho(P_A, Q_A, P_B, Q_B),$$

with

$$\rho = \frac{1}{W} \cdot \begin{cases} 1 & \text{if } E - \Delta E \leq H(P, Q) \leq E \\ 0 & \text{otherwise.} \end{cases}$$

From this it follows that

$$\rho_A(P_A, Q_A) = \frac{1}{W} \int\limits_{\{E - \Delta E \leq H_A + H_B \leq E\}} d^{3N_B} P_B \; d^{3N_B} Q_B$$

$$= \frac{1}{W} \int\limits_{\{E - H_A(P_A, Q_A) - \Delta E \leq H_B(P_B, Q_B) \leq E + H_A(P_A, Q_A)\}} d^{3N_B} P_B \; d^{3N_B} Q_B$$

$$= \frac{1}{W(E)} \; W_2(E - H_1(P_1, Q_1))$$

It is then demonstrated precisely as in the quantum mechanical case that the reduced density matrix $\rho \equiv \rho_A$ for system A is given by (for an infinitely large system B):

$$\boxed{\rho(P, Q) = \frac{1}{Z} e^{-\beta H(P, Q)}}, \tag{4.61}$$

where $P = P_A, Q = Q_A, H = H_A$ in this formula. The **classical canonical partition function** $Z = Z(\beta, N, V)$ for N **indistinguishable** particles is conventionally fixed by $(h^{3N} N!)^{-1} \int \rho_1 d^{3N} P d^{3N} Q = 1$, which, for an external square well potential confining the

system to a box of volume V, leads to

$$
\begin{aligned}
Z &:= \left(\frac{1}{N!h^{3N}}\right) \int d^{3N}P \ d^{3N}Q \ e^{-\beta H(P,Q)} \\
&= \frac{1}{N!h^{3N}} \left(\frac{2\pi m}{\beta}\right)^{3N/2} \int_{V^N} d^{3N}Q \ e^{-\beta \mathcal{V}_N(Q)}
\end{aligned}
\tag{4.62}
$$

The quantity $\lambda := \frac{h}{\sqrt{2\pi m k_B T}}$ is sometimes called the "**thermal deBroglie wavelength**". As a rule of thumb, quantum effects start being significant if λ exceeds the typical dimensions of the system, such as the mean free path length or system size. Using this definition, we can write

$$
\boxed{Z(\beta, N, V) = \frac{1}{N!\lambda^{3N}} \int_{V^N} d^{3N}Q \ e^{-\beta \mathcal{V}_N(Q)}} \ .
\tag{4.63}
$$

Of course, this form of the partition function applies to classical, not quantum, systems. The unconventional factor of h^{3N} is nevertheless put in by analogy with the quantum mechanical case because one imagines that the "unit" of phase space for N particles (i.e. the phase space measure) is given by $d^{3N}Pd^{3N}Q/(N!h^{3N})$, inspired by the uncertainty principle $\Delta Q \Delta P \sim h$, see e.g. our discussion of the atom in a cube for why the normalized classical partition function then approximates the quantum partition function. The motivation of the factor $N!$ is due to the fact that we want to treat the particles as indistinguishable. Therefore, a permuted phase space configuration should be viewed as equivalent to the unpermuted one, and since there are $N!$ permutations, the factor $1/N!$ effectively compensates a corresponding overcounting (here we implicitly assume that $\mathcal{V}_N$ is symmetric under permutations). For the discussion of the $N!$-factor, see also our discussion on mixing entropy. In practice, these factors often do not play a major role because the quantities most directly related to thermodynamics are derivatives of

$$
\boxed{F := -\beta^{-1} \log Z(\beta, N, V)} \ ,
\tag{4.64}
$$

for instance $P = -\partial F/\partial V|_{T,N}$, see chapter 6.5 for a detailed discussion of such relations. F is also called the **free energy**.

Example:
One may use the formula (4.63) to obtain the **barometric formula** for the *average particle density* at a position $\vec{x}$ in a given external potential. In this case the Hamiltonian H is given by

$$
H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + \sum_{i=1}^{N} \underbrace{\mathcal{W}(\vec{x}_i)}_{\substack{\text{external potential,} \\ \text{no interaction} \\ \text{between the particles}}} \ ,
$$

which yields the probability distribution

$$\rho(P,Q) = \frac{1}{Z}e^{-\beta H(P,Q)} = \frac{1}{Z}\prod_{i=1}^{N}e^{-\beta\left(\frac{\vec{p}_i^2}{2m}+\mathcal{W}(\vec{x}_i)\right)}. \tag{4.65}$$

The particle density $n(\vec{x})$ is given by

$$n(\vec{x}) = \left\langle \sum_{i=1}^{N}\delta^3(\vec{x}_i - \vec{x})\right\rangle = N\int d^3p\ \frac{1}{Z_1}e^{-\beta\left(\frac{\vec{p}^2}{2m}+\mathcal{W}(\vec{x})\right)}, \tag{4.66}$$

where

$$Z_1 = \int d^3p\ d^3x\ e^{-\beta\left(\frac{\vec{p}^2}{2m}+\mathcal{W}(\vec{x})\right)} = \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}}\int d^3x\ e^{-\beta(\mathcal{W}(\vec{x}))}. \tag{4.67}$$

From this we obtain the barometric formula

$$n(\vec{x}) = n_0 e^{-\beta\mathcal{W}(\vec{x})}, \tag{4.68}$$

with n_0 given by

$$n_0 = \frac{N}{\int d^3x\ e^{-\beta\mathcal{W}(\vec{x})}}. \tag{4.69}$$

In particular, for the gravitational potential, $\mathcal{W}(x,y,z) = -mgz$, we find

$$n(z) = n_0\ e^{z\frac{mg}{k_B T}}. \tag{4.70}$$

To double-check with our intuition we provide an alternative derivation of this formula: let $P(\vec{x})$ be the pressure at $\vec{x}$ and $\vec{F}(\vec{x}) = -\vec{\nabla}\mathcal{W}(\vec{x})$ the force acting on one particle. For the *average force density* $\vec{f}(\vec{x})$ in equilibrium we thus obtain

$$\vec{f}(\vec{x}) = \vec{n}(\vec{x})\vec{F}(\vec{x}) = -\vec{n}(\vec{x})\ \vec{\nabla}\mathcal{W}(\vec{x}) = \vec{\nabla}P(\vec{x}). \tag{4.71}$$

Together with $P(\vec{x}) = n(\vec{x})k_B T$ it follows that

$$k_B T\ \vec{\nabla}n(\vec{x}) = -n(\vec{x})\vec{\nabla}\mathcal{W}(\vec{x}) \tag{4.72}$$

and thus

$$k_B T\ \vec{\nabla}\log n(\vec{x}) = -\vec{\nabla}\mathcal{W}(\vec{x}), \tag{4.73}$$

which again yields the barometric formula

$$n(\vec{x}) = n_0 e^{-\beta\mathcal{W}(\vec{x})}. \tag{4.74}$$

4.3.3. Equidistribution Law and Virial Theorem in the Canonical Ensemble

We first derive the equidistribution law for classical systems with a Hamiltonian of the form

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m_i} + \mathcal{V}(Q), \quad Q = (\vec{x}_1, \ldots, \vec{x}_N). \tag{4.75}$$

We take as the probability distribution the canonical ensemble as discussed in the previous subsection, with probability distribution given by

$$\rho(P, Q) = \frac{1}{Z} e^{-\beta H(P,Q)}. \tag{4.76}$$

Then we have for any observable $A(P, Q)$:

$$\begin{aligned}
0 &= \int d^{3N}P \, d^{3N}Q \frac{\partial}{\partial p_{i\alpha}} \left(A(P,Q) \, \rho(P,Q) \right) \\
&= \int d^{3N}P \, d^{3N}Q \left(\frac{\partial A}{\partial p_{i\alpha}} - \beta A \frac{\partial H}{\partial p_{i\alpha}} \right) \rho(P,Q) \\
&= \left\langle \frac{\partial A}{\partial p_{i\alpha}} \right\rangle - \beta \left\langle A \frac{\partial H}{\partial p_{i\alpha}} \right\rangle, \qquad i = 1, \ldots, N, \ \alpha = 1, 2, 3.
\end{aligned} \tag{4.77}$$

From this we obtain the relation

$$k_B T \left\langle \frac{\partial A}{\partial p_{i\alpha}} \right\rangle = \left\langle A \frac{\partial H}{\partial p_{i\alpha}} \right\rangle, \tag{4.78}$$

and similarly

$$k_B T \left\langle \frac{\partial A}{\partial x_{i\alpha}} \right\rangle = \left\langle A \frac{\partial H}{\partial x_{i\alpha}} \right\rangle. \tag{4.79}$$

The function A should be chosen such that that the integrand falls of sufficiently rapidly. For $A(P, Q) = p_{i\alpha}$ and $A(P, Q) = x_{i\alpha}$, respectively, we find

$$\left\langle p_{i\alpha} \frac{\partial H}{\partial p_{i\alpha}} \right\rangle = \left\langle \frac{p_{i\alpha}^2}{m_i} \right\rangle = k_B T \tag{4.80}$$

$$\left\langle x_{i\alpha} \frac{\partial H}{\partial x_{i\alpha}} \right\rangle = \left\langle x_{i\alpha} \frac{\partial \mathcal{V}}{\partial x_{i\alpha}} \right\rangle = k_B T. \tag{4.81}$$

The first of these equations is called **equipartition** or **equidistribution law**.

We split up the potential $\mathcal{V}$ into a part coming from the interactions of the particles and

a part describing an external potential, i.e.

$$\mathcal{V}(Q) = \underbrace{\sum_{i<j} \mathcal{V}(\vec{x}_i - \vec{x}_j)}_{\text{interactions}} + \underbrace{\sum_{i} \mathcal{W}(\vec{x}_i,)}_{\text{external potential}} \quad . \qquad (4.82)$$

$$= \frac{1}{2} \sum_{i,j} \mathcal{V}(\vec{x}_i - \vec{x}_j)$$

Writing $\vec{x}_{kl} \equiv \vec{x}_k - \vec{x}_l$ for the relative distance between the k-th and the l-th particle, we find by a lengthy calculation:

$$\sum_{i,\alpha} \left\langle x_{i\alpha} \frac{\partial \mathcal{V}(Q)}{\partial x_{i\alpha}} \right\rangle = \frac{1}{2} \sum_{i,\alpha} \sum_{k,l} \left\langle x_{i\alpha} \frac{\partial}{\partial x_{i\alpha}} \mathcal{V}(\vec{x}_k - \vec{x}_l) \right\rangle + \sum_{i,\alpha} \sum_{k} \left\langle x_{i\alpha} \frac{\partial \mathcal{W}}{\partial x_{i\alpha}} (\vec{x}_k) \right\rangle$$

$$= \frac{1}{2} \sum_{i,\alpha,k,\beta,l} \left\langle x_{i\alpha} \left(\frac{\partial \mathcal{V}}{\partial x_\beta} \right) (\vec{x}_k - \vec{x}_l) \right\rangle (\delta_{ik} - \delta_{il}) \delta_{\alpha\beta} + \int d^3x \left\langle \sum_{k} \delta^3(\vec{x} - \vec{x}_k) \right\rangle \vec{x} \cdot \vec{\nabla} \mathcal{W}(\vec{x})$$

$$= \frac{1}{2} \sum_{k,l} \left\langle (\vec{x}_k - \vec{x}_l) \vec{\nabla} \mathcal{V} (\vec{x}_k - \vec{x}_l) \right\rangle + \int d^3x \underbrace{n(\vec{x}) \vec{F}(\vec{x})}_{\substack{\text{force density} = -\frac{\partial p}{\partial \vec{x}}, \\ p = \text{ pressure density}}} \cdot \vec{x}$$

$$= \frac{1}{2} \sum_{k,l} \left\langle \vec{x}_{kl} \frac{\partial \mathcal{V}}{\partial \vec{x}_{kl}} \right\rangle - \underbrace{\int d^3x \ \vec{x} \cdot \frac{\partial p}{\partial \vec{x}}}_{\text{partial integral}} = \frac{1}{2} \sum_{k,l} \left\langle \vec{x}_{kl} \frac{\partial \mathcal{V}}{\partial \vec{x}_{kl}} \right\rangle + \int d^3x \ \underbrace{\vec{\nabla} \vec{x}}_{=3} \cdot p$$

$$= \frac{1}{2} \sum_{k,l} \left\langle \vec{x}_{kl} \frac{\partial \mathcal{V}}{\partial \vec{x}_{kl}} \right\rangle + 3PV,$$

since $P = \int d^3x \, p$. According to the equipartition law we have $\sum_{i\alpha} \left\langle x_{i\alpha} \frac{\partial \mathcal{V}}{\partial x_{i\alpha}} \right\rangle = 3N k_B T$ and therefore obtain the **virial law** for classical systems

$$PV = N k_B T - \underbrace{\frac{1}{6} \sum_{k,l} \left\langle \vec{x}_{kl} \frac{\partial \mathcal{V}}{\partial \vec{x}_{kl}} \right\rangle}_{=0 \text{ for ideal gas}}. \qquad (4.83)$$

Thus, interactions tend to increase P when they are repulsive, and tend to decrease P when they are attractive. This is of course consistent with our intuition.

A well-known application of the virial law is the following example:

Example: estimation of the mass of distant galaxies:
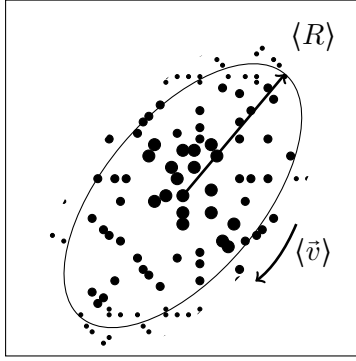
Figure 4.6.: Distribution and velocity of stars in a galaxy.

We use the relations (4.80) we found above,

$$\left\langle \frac{\vec{p}_1^2}{m_1} \right\rangle = \left\langle \frac{\partial \mathcal{V}}{\partial \vec{x}_1} \vec{x}_1 \right\rangle = 3k_{\mathrm{B}}T,$$

assuming that the stars in the outer region have reached thermal equilibrium, so that they can be described by the canonical ensemble. We put $\vec{v} = \vec{p}_1/m_1$, $v = |\vec{v}|$ and $R = |\vec{x}_1|$, and assume that $\langle \vec{v}^2 \rangle \approx \langle v \rangle^2$ as well as

$$\left\langle \frac{\partial \mathcal{V}}{\partial \vec{x}_1} \vec{x}_1 \right\rangle = m_1 G \sum_{j \neq 1} \left\langle \frac{m_j}{\left| \vec{x}_1 - \vec{x}_j \right|} \right\rangle \approx m_1 M G \left\langle \frac{1}{R} \right\rangle \approx m_1 M G \frac{1}{\langle R \rangle}, \qquad (4.84)$$

supposing that the potential felt by star 1 is dominated by the Newton potential created by the core of the galaxy containing most of the mass $M \approx \sum_j m_j$. Under these approximations, we conclude that

$$\frac{M}{\langle R \rangle} \approx \frac{\langle v \rangle^2}{G}. \qquad (4.85)$$

This relation is useful for estimating M because $\langle R \rangle$ and $\langle v \rangle$ can be measured or estimated. Typically $\langle v \rangle = \mathcal{O}\left(10^2 \frac{\mathrm{km}}{\mathrm{s}}\right)$.

Continuing with the general discussion, if the potential attains a minimum at $Q = Q_0$ we have $\frac{\partial \mathcal{V}}{\partial x_{i\alpha}}(Q_0) = 0$, as sketched in the following figure:
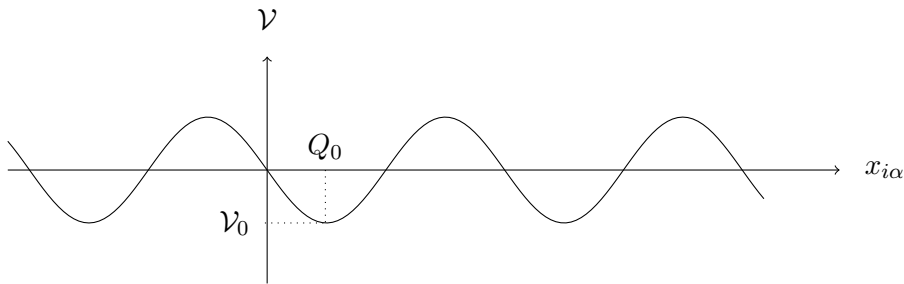
Figure 4.7.: Sketch of a potential $\mathcal{V}$ of a lattice with a minimum at Q_0.

Setting $\mathcal{V}(Q_0) \equiv \mathcal{V}_0$, we can Taylor expand around Q_0:

$$\mathcal{V}(Q) = \mathcal{V}_0 + \frac{1}{2} \sum \underbrace{\frac{\partial^2 \mathcal{V}}{\partial x_{i\alpha} \partial x_{j\beta}}(Q_0)}_{=f_{i\alpha j\beta}} \Delta x_{i\alpha} \Delta x_{j\beta} + \dots, \tag{4.86}$$

where $\Delta Q = Q - Q_0$. In this approximation ($|\Delta Q| \ll 1$, i.e. for small oscillations around the minimum) we have

$$\sum_{i,\alpha} \left\langle x_{i\alpha} \frac{\partial \mathcal{V}}{\partial x_{i\alpha}} \right\rangle \approx 2 \langle \mathcal{V} \rangle = \sum_{i,\alpha} k_B T = 3N\ k_B T, \tag{4.87}$$

$$\sum_{i,\alpha} \left\langle \frac{p_{i\alpha}^2}{m_i} \right\rangle = 2 \left\langle \sum_i \frac{\vec{p}_i^2}{2m_i} \right\rangle = 3N\ k_B T. \tag{4.88}$$

It follows that the mean energy $\langle H \rangle$ of the system is given by

$$\langle H \rangle = 3N k_B T. \tag{4.89}$$

This relation is called the **Dulong-Petit law**. For real lattice systems there are deviations from this law at low temperature T through quantum effects and at high temperature T through non-linear effects, which are not captured by the approximation (4.86).

Our discussion for classical systems can be adapted to the quantum mechanical context, but there are some changes. Consider the canonical ensemble with statistical operator $\rho = \frac{1}{Z} e^{-\beta H}$. From this it immediately follows that

$$[\rho, H] = 0, \tag{4.90}$$

which in turn implies that for any observable A we have

$$\langle [H, A] \rangle = \operatorname{tr}\left(\rho\,[A, H]\right) = -\operatorname{tr}\left([\rho, H]\,A\right) = 0. \tag{4.91}$$

Now let $A = \sum_i \vec{x}_i \cdot \vec{p}_i$ and assume, as before, that

$$H = \sum_i \frac{\vec{p}_i^2}{2m_i} + \mathcal{V}_N(Q). \tag{4.92}$$

By using $[a, bc] = [a, b] c + b [a, c]$ and $\vec{p}_j = \frac{\hbar}{i} \frac{\partial}{\partial \vec{x}_j}$ we obtain

$$[H, A] = \sum_{i,j} \left[\frac{\vec{p}_i^2}{2m_i}, \vec{x}_j \right] \cdot \vec{p}_j + \sum_j \vec{x}_j \left[\mathcal{V}(Q), \vec{p}_j \right]$$

$$= \frac{\hbar}{i} \sum_j \frac{\vec{p}_j^2}{m_j} + i\hbar \sum_j \vec{x}_j \partial_{\vec{x}_j} \mathcal{V}(Q),$$

which gives

$$\sum_j \left\langle \vec{x}_j \frac{\partial \mathcal{V}}{\partial \vec{x}_j} \right\rangle = 2 \left\langle H_{\text{kin}} \right\rangle \quad (\hbar \text{ cancels out}). \tag{4.93}$$

Applying now the same arguments as in the classical case to evaluate the left hand side leads to

$$PV = \underbrace{\frac{2}{3} \left\langle H_{\text{kin}} \right\rangle}_{\substack{\neq N k_{\text{B}} T \text{ for ideal gas} \\ \Rightarrow \text{ quantum effects!}}} - \frac{1}{6} \sum_{k,l} \left\langle \vec{x}_{kl} \frac{\partial \mathcal{V}}{\partial \vec{x}_{kl}} \right\rangle. \tag{4.94}$$

For an ideal gas the contribution from the potential is by definition absent, but the contribution from the kinetic piece does not give the same formula as in the classical case, as we will discuss in more detail below in chapter 5. Thus, even for an *ideal* quantum gas ($\mathcal{V} = 0$), the classical formula $PV = N k_{\text{B}} T$ receives corrections!

4.4. Grand Canonical Ensemble

This ensemble describes the following physical situation: a small system (system A) is coupled to a large reservoir (system B). Energy *and* particle exchange between A and B are possible.
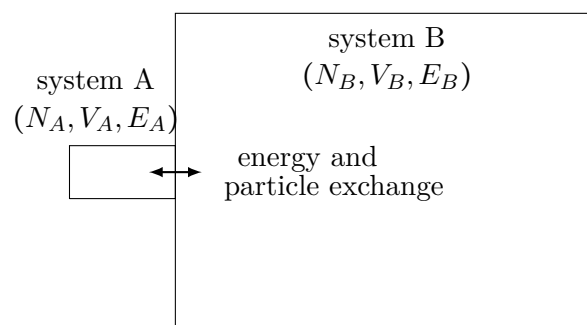

Figure 4.8.: A small system coupled to a large heat and particle reservoir.

The treatment of this ensemble is similar to that of the canonical ensemble. For definiteness, we consider the quantum mechanical case. We have $E = E_A + E_B$ for the total energy, and $N = N_A + N_B$ for the total particle number. The *total* system A+B is

described by the *microcanonical ensemble*, since E and N are conserved. The Hilbert space for the total system is again a tensor product, and the statistical operator ρ of the total system is accordingly given by

$$\rho = \frac{1}{W} \cdot \sum_{\substack{E - \Delta E \leq E_n^{(A)} + E_m^{(B)} \leq E \\ N_n^{(A)} + N_m^{(B)} = N}} \left|n, m\right\rangle\left\langle n, m\right|, \tag{4.95}$$

where the total Hamiltonian of the combined system is

$$H = \underbrace{H_A}_{\text{system A}} + \underbrace{H_B}_{\text{system B}} + \underbrace{H_{AB}}_{\text{interaction (neglected)}}, \tag{4.96}$$

We are using notations similar to the canonical ensemble such as $|n, m\rangle = |n\rangle_A |m\rangle_B$ and

$$H_{A/B} |n\rangle_{A/B} = E_n^{(A/B)} |n\rangle_{A/B}, \tag{4.97}$$

$$\hat{N}_{A/B} |n\rangle_{A/B} = N_n^{(A/B)} |n\rangle_{A/B}. \tag{4.98}$$

Note that the particle numbers of the individual subsystems fluctuate, so we describe them by number *operators* $\hat{N}_A, \hat{N}_B$ acting on $\mathcal{H}_A, \mathcal{H}_B$.

The statistical operator for system A is described by the reduced density matrix ρ_A for this system, namely by

$$\rho_A = \frac{1}{W} \sum_n W_B\left(E - E_n^{(A)}, N - N_n^{(A)}, V_B\right) |n\rangle_A \otimes {}_A\langle n|. \tag{4.99}$$

As before, in the canonical ensemble, we use that the entropy is an extensive quantity to write

$$\log W_B\left(E_B, N_B, V_B\right) = \frac{1}{k_B} S_B\left(E_B, N_B, V_B\right)$$
$$= \frac{1}{k_B} V_B\, \sigma_B\left(\frac{E_B}{V_B}, \frac{N_B}{V_B}\right),$$

for some function σ in two variables. Now we let $V_B \to \infty$, but keeping $\frac{E}{V_B}$ and $\frac{N}{V_B}$ constant. Arguing precisely as in the case of the canonical ensemble, and using now also the definition of the chemical potential in (4.17), we find

$$\log W_B\left(E - E_n^{(A)}, N - N_n^{(A)}, V_B\right) = \log W_2\left(E, N, V_B\right) - \beta E_n^{(A)} + \beta \mu N_n^{(A)} \tag{4.100}$$

for $N_B, V_B \to \infty$. By the same arguments as for the temperature in the canonical ensemble the chemical potential μ is the same for both systems in equilibrium. We

obtain for the reduced density matrix of system A:

$$\rho_A = \frac{1}{Y} \sum_n e^{-\beta\left(E_n^{(A)} - \mu N_n^{(A)}\right)} |n\rangle_A \otimes {}_A\langle n| \tag{4.101}$$

Thus, only the quantities β and μ characterizing the reservoir (system B) have an influence on system B. Dropping from now on the reference to "A", we can write the statistical operator of the grand canonical ensemble as

$$\boxed{\rho = \frac{1}{Y} e^{-\beta\left(H(V) - \mu \hat{N}(V)\right)}}, \tag{4.102}$$

where H and $\hat{N}$ are now **operators**. The constant $Y = Y(\mu, \beta, V)$ is determined by $\mathrm{tr}\rho_1 = 1$ and is called the **grand canonical partition function**. Explicitly:

$$\boxed{Y(\mu, \beta, V) = \mathrm{tr}\left[e^{-\beta\left(H(V) - \mu\hat{N}\right)}\right] = \sum_n e^{-\beta(E_n - \mu N_n)}}. \tag{4.103}$$

The analog of the free energy for the grand canonical ensemble is the **Gibbs free energy**. It is defined by

$$\boxed{G := -\beta^{-1} \log Y(\beta, \mu, V)}. \tag{4.104}$$

The grand canonical partition function can be related to the canonical partition function. The Hilbert space of our system (i.e., system A) can be decomposed

$$\mathcal{H} = \underbrace{\mathbb{C}}_{\text{vacuum}} \oplus \underbrace{\mathcal{H}_1}_{\text{1 particle}} \oplus \underbrace{\mathcal{H}_2}_{\text{2 particles}} \oplus \underbrace{\mathcal{H}_3}_{\text{3 particles}} \oplus \dots, \tag{4.105}$$

with $\mathcal{H}_N$ the Hilbert space for a fixed number N of particles[2], and that the total Hamiltonian is given by

$$H = H_1 + H_2 + H_3 + \dots$$

$$H_N = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + \mathcal{V}_N\left(\vec{x}_1, \dots, \vec{x}_N\right).$$

Then $\left[H, \hat{N}\right] = 0$ ($\hat{N}$ has eigenvalue N on $\mathcal{H}_N$), and H and $\hat{N}$ are simultaneously diagonalized, with (assuming a discrete spectrum of H)

$$H |\alpha, N\rangle = E_{\alpha, N} |\alpha, N\rangle \quad \text{and} \quad \hat{N} |\alpha, N\rangle = N |\alpha, N\rangle. \tag{4.106}$$

---

[2]For distinguishable particles, this would be $\mathcal{H}_N = L^2(\mathbb{R}^N)$. However, in real life, quantum mechanical particles are either bosons or fermions, and the corresponding definition of the N-particle Hilbert space has to take this into account, see Ch. 5.

From this we get:

$$Y(\beta, \mu, V) = \sum_{\alpha, N} e^{-\beta(E_{\alpha,N} - \mu N)} = \sum_N e^{+\beta \mu N} \sum_\alpha e^{-\beta E_{\alpha,N}}$$

$$= \sum_N \underbrace{Z(N, \beta, V)}_{\text{canonical partition function!}} e^{\beta \mu N}, \qquad (4.107)$$

which is the desired relation between the canonical and the grand canonical partition function.

We also note that for a potential of the standard form

$$\mathcal{V}_N = \sum_{1 \le i < j \le N} \mathcal{V}(\vec{x}_i - \vec{x}_j) + \sum_{1 \le i \le N} \mathcal{W}(\vec{x}_i)$$

we may think of replacing $H_N \to H_N - \mu N$ as being due to $\mathcal{W} \to \mathcal{W} - \mu$. Therefore, for variable particle number N, there is no arbitrary additive constant in the 1-particle potential $\mathcal{W}$, but it is determined by the chemical potential μ. A larger μ gives greater statistical weight in Y to states with larger N, just as larger T (smaller β) gives greater weight to states with larger E.

4.5. Summary of different equilibrium ensembles

Let us summarize the equilibrium ensembles we have discussed in this chapter in a table:

Ensemble	Defining property	Partition function	Statistical operator
Microcanonical ensemble	no energy exchange no particle exchange	$W(E, N, V)$	$\rho = \frac{1}{W} \left[\Theta(H - E + \Delta E) - \Theta(H - E) \right]$
Canonical ensemble	energy exchange no particle exchange	$Z(\beta, N, V)$	$\rho = \frac{1}{Z} e^{-\beta H}$
Grand canonical ensemble	energy exchange particle exchange	$Y(\beta, \mu, V)$	$\rho = \frac{1}{Y} e^{-\beta(H - \mu \hat{N})}$

Table 4.1.: Properties of the different equilibrium ensembles.

The relationship between the partition functions W, Z, Y and the corresponding natural termodynamic "potentials" is summarized in the following table:

Further explanations regarding the various thermodynamic potentials are given below

Ensemble	Name of potential	Symbol	Relation with partion function
Microcanonical ensemble	Entropy	$S(E, N, V)$	$S = k_B \log W$
Canonical ensemble	Free energy	$F(\beta, N, V)$	$F = -\beta^{-1} \log Z$
Grand canonical ensemble	Gibbs free energy	$G(\beta, \mu, V)$	$G = -\beta^{-1} \log Y$

Table 4.2.: Relationship to different thermodynamic potentials.

in section 6.7.

4.6. Approximation methods

For interacting systems, it is normally impossible to calculate thermodynamic quantities exactly. In these cases, approximations or numerical methods must be used. In the appendix, we present the Monte-Carlo algorithm, which can be turned into an efficient method for numerically evaluating quantities like partition functions. Here we present an example of an expansion technique.

For simplicity, we consider a classical system in a box of volume V, with N-particle Hamiltonian H_N given by

$$H_N = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + \underbrace{\sum_{1 \leq i < j \leq N} \mathcal{V}_{ij}}_{\substack{=\mathcal{V}_N \\ \text{= interaction}}} + \underbrace{\sum_{j=1}^{N} \mathcal{W}_j}_{\substack{=\mathcal{W}_N \\ \text{= external potential,} \\ \text{due to box of volume } V}}, \tag{4.108}$$

where $\mathcal{V}_{ij} = \mathcal{V}(\vec{x}_i - \vec{x}_j)$ is the two-particle interaction between the i-th and the j-th particle. The partition function for the grand canonical ensemble is (see (4.103)):

$$\begin{aligned} Y(\mu, \beta, V) &= \sum_{N=0}^{\infty} e^{\beta \mu N} Z(\beta, V, N) \\ &= \sum_{N=0}^{\infty} e^{\beta \mu N} \cdot \frac{1}{N! \lambda^{3N}} \cdot \int_{V^N} d^{3N} Q \ e^{-\beta \mathcal{V}_N(Q)}. \end{aligned} \tag{4.109}$$

Here, $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$ is the thermal deBroglie wavelength. To compute the remaining integral over $Q = (\vec{x}_1, \ldots, \vec{x}_N)$ is generally impossible, but one can derive an expansion of which the first few terms may often be evaluated exactly. For this we write the

integrand as

$$e^{-\beta \mathcal{V}_N} = \exp\left(-\beta \sum_{i<j} \mathcal{V}_{ij}\right) = \prod_{i<j} e^{-\beta \mathcal{V}_{ij}} \equiv \prod_{i<j} (1 + f_{ij}), \qquad (4.110)$$

where we have set $f_{ij} \equiv f(\vec{x}_i - \vec{x}_j) = 1 - e^{-\beta \mathcal{V}_{ij}}$. The idea is that we can think of $|f_{ij}|$ as small in some situations of interest, e.g. when the gas is dilute (such that $|\mathcal{V}_{ij}| \ll 1$ in "most of phase space"), or when β is small (i.e. for large temperature T). With this in mind, we expand the above product as

$$e^{-\beta \mathcal{V}_N} = 1 + \sum f_{ij} + \sum f_{ij} f_{kl} + \dots, \qquad (4.111)$$

and substitute the result into the integral $\int_{V^N} d^{3N}Q \, e^{-\beta \mathcal{V}_N(Q)}$. The general form of the resulting integrals that we need to evaluate is suggested by the following representative example for $N = 6$ particles:

$$\int d^4 x_1 \dots d^3 x_6 \; f_{12} f_{35} f_{45} f_{36} = \qquad (4.112)$$

To keep track of all the integrals that come up, we introduced the following convenient graphical notation. In our example, this graphical notation amounts to the following. Each circle corresponds to an an integration, e.g.

$$(4.114)$$

and each line corresponds to an f_{ij} in the integrand, e.g.

$$(4.115)$$

The connected parts of a diagram are called "clusters". Obviously, the integral associated with a graph factorizes into the corresponding integrals for the clusters. Therefore, the "cluster integrals" are the building blocks, and we define

$$b_l(V, \beta) = \frac{1}{l! \lambda^{3l-3} V} \cdot (\text{sum of all } l - \text{cluster integrals}). \qquad (4.116)$$

The main result in this context, known as the **linked cluster theorem**[3], is that

$$\frac{1}{V} \log Y(\mu, V, \beta) = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} b_l(V, \beta) z^l, \qquad (4.117)$$

---

[3]The proof of the linked cluster theorem is very similar to that of the formula (2.10) for the cumulants $\langle x^n \rangle_c$, see section 2.1.

where $z = e^{\beta\mu}$ is sometimes called the **fugacity**. If the f_{ij} are sufficiently small, the first few terms $(b_1, b_2, b_3, \ldots)$ will give a good approximation. Explicitly, one finds (exercise):
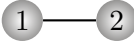
$$b_1 = \frac{1}{1!\lambda^0 V} \int_V d^3x = 1, \tag{4.118}$$
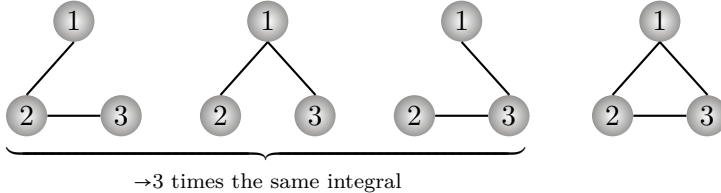
$$b_2 = \frac{1}{2!\lambda^3 V} \int_{V^2} d^3x_1 d^3x_2 f_{12}, \tag{4.119}$$

$$b_3 = \frac{1}{3!\lambda^6 V} \int_{V^3} d^3x_1 d^3x_2 d^3x_3 (\underbrace{f_{12}f_{23} + f_{13}f_{12} + f_{13}f_{23}}_{\to 3 \text{ times the same integral}} + f_{12}f_{13}f_{23}), \tag{4.120}$$

since the possible 1-,2- and 3-clusters are given by:

1-clusters (b_1):

2-clusters (b_2):

3-clusters (b_3):

$\to$3 times the same integral

As exemplified by the first 3 terms in b_3, topologically identical clusters (i.e. ones that differ only by a permutation of the particles) give the same cluster integral. Thus, we only need to evaluate the cluster integrals for topologically distinct clusters.

Given an approximation for $\frac{1}{V} \log Y$, one obtains approximations for the equations of state etc. by the general methods described in more detail in section 6.5.

5. The Ideal Quantum Gas

5.1. Hilbert Spaces, Canonical and Grand Canonical Formulations

When discussing the mixing entropy of classical ideal gases in section 4.2.3, we noted that Gibbs' paradox could resolved by treating the particles of the same gas species as **indistinguishable**. How to treat indistinguishable particles In quantum mechanics? If we have N particles, the state vectors Ψ are elements of a Hilbert space, such as $\mathcal{H}_N = L^2\left(V \times \ldots \times V, d^3x_1 \ldots d^3x_N\right)$ for particles in a box $V \subset \mathbb{R}^3$ without additional quantum numbers. The probability of finding the N particles at prescribed positions $\vec{x}_1, \ldots, \vec{x}_N$ is given by $\left|\Psi\left(\vec{x}_1, \ldots, \vec{x}_N\right)\right|^2$. For identical particles, this should be the same as $\left|\Psi\left(\vec{x}_{\sigma(1)}, \ldots, \vec{x}_{\sigma(N)}\right)\right|^2$ for any permutation

$$
\sigma : \begin{pmatrix} 1 & 2 & 3 & \ldots & N-1 & N \\ \sigma(1) & \sigma(2) & \sigma(3) & \ldots & \sigma(N-1) & \sigma(N) \end{pmatrix}.
$$

Thus, the map $\mathcal{U}_\sigma : \Psi\left(\vec{x}_1, \ldots, \vec{x}_N\right) \mapsto \Psi\left(\vec{x}_{\sigma(1)}, \ldots, \vec{x}_{\sigma(N)}\right)$ should be represented by a phase, i.e.

$$
\mathcal{U}_\sigma \Psi = \eta_\sigma \Psi, \qquad |\eta_\sigma| = 1.
$$

From $\mathcal{U}_\sigma^2 = \mathbb{1}$ it then follows that $\eta_\sigma^2 = 1$, hence $\eta_\sigma \in \{\pm 1\}$ and from $\mathcal{U}_\sigma \mathcal{U}_{\sigma'} = \mathcal{U}_{\sigma\sigma'}$ it follows that $\eta_\sigma \eta_{\sigma'} = \eta_{\sigma\sigma'}$. The only possible constant assignments for η_σ are therefore given by

$$
\eta_\sigma = \begin{cases} 1 & \forall \sigma \quad \text{(Bosons)} \\ \mathrm{sgn}(\sigma) & \forall \sigma \quad \text{(Fermions)}. \end{cases} \tag{5.1}
$$

Here the signum of σ is defined as

$$
\mathrm{sgn}(\sigma) = (-1)^{\#\{\text{transpositions in } \sigma\}} = (-1)^{\left(\#\{\text{``crossings'' in } \sigma\}\right)}. \tag{5.2}
$$

The second characterization also makes plausible the fact that $\mathrm{sgn}(\sigma)$ is an invariant satisfying $\mathrm{sgn}(\sigma)\mathrm{sgn}(\sigma') = \mathrm{sgn}(\sigma\sigma')$.

Example:

Consider the following permutation:
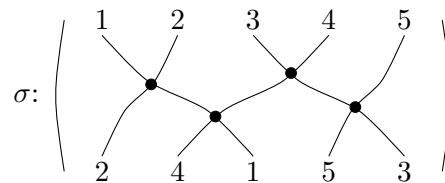
In this example we have $\text{sgn}(\sigma) = +1 = (-1)^4$.

In order to go from the Hilbert space $\mathcal{H}_N$ of distinguishable particles such as

$$\mathcal{H}_N = \underbrace{\mathcal{H}_1 \otimes \ldots \otimes \mathcal{H}_1}_{N \text{ factors}}$$

$$\mathcal{H}_N \ni |\Psi\rangle = |i_1\rangle \otimes \ldots \otimes |i_N\rangle \equiv |i_1 \ldots i_N\rangle$$

$$H|i\rangle = E_i|i\rangle \quad \text{1-particle Hamiltonian on } \mathcal{H}_1$$

to the Hilbert space for Bosons/Fermions one can apply the projection operators

$$\mathcal{P}_+ = \frac{1}{N!} \sum_{\sigma \in S_N} \mathcal{U}_\sigma$$

$$\mathcal{P}_- = \frac{1}{N!} \sum_{\sigma \in S_N} \text{sgn}(\sigma) \mathcal{U}_\sigma.$$

As projectors the operators $\mathcal{P}_\pm$ fulfill the following relations:

$$\mathcal{P}_\pm^2 = \mathcal{P}_\pm, \quad \mathcal{P}_\pm^\dagger = \mathcal{P}_\pm, \quad \mathcal{P}_+\mathcal{P}_- = \mathcal{P}_-\mathcal{P}_+ = 0.$$

The Hilbert spaces for Bosons/Fermions, respectively, are then given by

$$\mathcal{H}_N^\pm = \begin{cases} \mathcal{P}_+\mathcal{H}_N & \text{for Bosons} \\ \mathcal{P}_-\mathcal{H}_N & \text{for Fermions.} \end{cases} \tag{5.3}$$

In the following, we consider N non-interacting, non-relativistic particles of mass m in a box with volume $V = L^3$, together with Dirichlet boundary conditions. The Hamiltonian of the system in either case is given by

$$H_N = \sum_{i=1}^N \frac{\vec{p}_i^{\,2}}{2m} = \sum_{i=1}^N -\frac{\hbar^2}{2m} \partial_{\vec{x}_i}^2. \tag{5.4}$$

The eigenstates for a *single* particle are given by the wave functions

$$\Psi_{\vec{k}}(\vec{x}) = \sqrt{\frac{8}{V}} \sin(k_x x) \sin(k_y y) \sin(k_z z), \tag{5.5}$$

where $k_x = \frac{\pi n_x}{L}, \ldots$, with $n_x = 1, 2, 3, \ldots$, and similarly for the y, z-components. The product wave functions $\Psi_{\vec{k}_1}(\vec{x}_1) \cdots \Psi_{\vec{k}_N}(\vec{x}_N)$ do *not* satisfy the symmetry requirements for Bosons/Fermions. To obtain these we have to apply the projectors $\mathcal{P}_\pm$ to the states $|k_1\rangle \otimes \cdots \otimes |k_N\rangle \in \mathcal{H}_N$. We define:

$$|\vec{k}_1, \ldots, \vec{k}_N\rangle_\pm := \frac{N!}{\sqrt{c_\pm}} \mathcal{P}_\pm \Big(\underbrace{|k_1\rangle \otimes \ldots \otimes |k_N\rangle}_{|k_1,\ldots,k_N\rangle} \Big), \tag{5.6}$$

where $c_\pm$ is a normalization constant, defined by demanding that $_\pm\langle \vec{k}_1, \ldots, \vec{k}_N | \vec{k}_1, \ldots, \vec{k}_N\rangle_\pm = 1$. (We have used the Dirac notation $\langle x | \vec{k}\rangle \equiv \Psi_{\vec{k}}(\vec{x})$.) Explicitly, we have:

$$|\vec{k}_1, \ldots, \vec{k}_N\rangle_+ = \frac{1}{\sqrt{c_+}} \sum_{\sigma \in S_N} |\vec{k}_{\sigma(1)}, \ldots, \vec{k}_{\sigma(N)}\rangle \quad \text{for Bosons,} \tag{5.7}$$

$$|\vec{k}_1, \ldots, \vec{k}_N\rangle_- = \frac{1}{\sqrt{c_-}} \sum_{\sigma \in S_N} \text{sgn}(\sigma) |\vec{k}_{\sigma(1)}, \ldots, \vec{k}_{\sigma(N)}\rangle \quad \text{for Fermions.} \tag{5.8}$$

Note, that the factor $\frac{1}{N!}$ coming from $\mathcal{P}_\pm$ has been absorbed into $c_\pm$.

Examples:

(a) *Fermions with $N = 2$:* A normalized two-particle fermion state is given by

$$|\vec{k}_1, \vec{k}_2\rangle_- = \frac{1}{\sqrt{2}} \Big(|\vec{k}_1, \vec{k}_2\rangle - |\vec{k}_2, \vec{k}_1\rangle \Big),$$

with $|\vec{k}_1, \vec{k}_2\rangle_- = 0$ if $\vec{k}_1 = \vec{k}_2$. This implements the **Pauli principle**.
More generally, for an N-particle fermion state we have

$$|\ldots, \vec{k}_i, \ldots, \vec{k}_j, \ldots\rangle_- = 0 \quad \text{whenever } \vec{k}_i = \vec{k}_j. \tag{5.9}$$

(b) *Bosons with $N = 2$:* A normalized two-particle boson state is given by

$$|\vec{k}_1, \vec{k}_2\rangle_+ = \frac{1}{\sqrt{2}} \Big(|\vec{k}_1 \vec{k}_2\rangle + |\vec{k}_2 \vec{k}_1\rangle \Big). \tag{5.10}$$

(c) *Bosons with $N = 3$:* A normalized three-particle boson state with $\vec{k}_1 = \vec{k}$, $\vec{k}_2 = \vec{k}_3 = \vec{p}$ is given by

$$|\vec{k}, \vec{p}, \vec{p}\rangle_+ = \frac{1}{\sqrt{3}} \Big(|\vec{p}, \vec{p}, \vec{k}\rangle + |\vec{p}, \vec{k}, \vec{p}\rangle + |\vec{k}, \vec{p}, \vec{p}\rangle \Big). \tag{5.11}$$

The normalization factors c_+, c_- are given in general as follows:

(a) *Bosons:* Let $n_{\vec{k}}$ be the number of appearances of the mode $\vec{k}$ in $|\vec{k}_1, \ldots, \vec{k}_N\rangle_+$, i.e. $n_{\vec{k}} = \sum_i \delta_{\vec{k}, \vec{k}_i}$. Then c_+ is given by

$$c_+ = N! \prod_{\vec{k}} n_{\vec{k}}. \tag{5.12}$$

In example (c) above we have $n_{\vec{k}} = 1$, $n_{\vec{p}} = 2$ and thus

$$c_+ = 3!2!1! = 12.$$

Note, that this is correct since

$$|\vec{k}, \vec{p}, \vec{p}\rangle_+ = \frac{1}{\sqrt{12}} \left(|\vec{p}, \vec{p}, \vec{k}\rangle + |\vec{p}, \vec{k}, \vec{p}\rangle + |\vec{k}, \vec{p}, \vec{p}\rangle + |\vec{p}, \vec{p}, \vec{k}\rangle + |\vec{p}, \vec{k}, \vec{p}\rangle + |\vec{k}, \vec{p}, \vec{p}\rangle, \right)$$

because there are $3! = 6$ permutations in S_3.

(b) *Fermions:* In this case we have $c_- = N!$. To check this, we note that

$$\left\langle \{\vec{k}\} \,\middle|\, \{\vec{k}\} \right\rangle_- = \sum_{\sigma, \sigma' \in S_N} \frac{1}{c_-} \left\langle \vec{k}_{\sigma(1)}, \ldots, \vec{k}_{\sigma(N)} \,\middle|\, \vec{k}_{\sigma'(1)}, \ldots, \vec{k}_{\sigma'(N)} \right\rangle$$

$$= \frac{N!}{c_-} \sum_{\sigma \in S_N} \left\langle \vec{k}_1, \ldots, \vec{k}_N \,\middle|\, \vec{k}_{\sigma(1)}, \ldots, \vec{k}_{\sigma(N)} \right\rangle$$

$$= \frac{N! \, n_{\vec{k}_1}! n_{\vec{k}_2}! \ldots n_{\vec{k}_N}!}{c_-} = \frac{N!}{c_-} = 1,$$

because the term under the second sum is zero unless the permuted $\{\vec{k}\}$'s are identical (this happens $\prod_{\vec{k}} n_{\vec{k}}!$ times for either bosons or fermions), and because for fermions, the occupation numbers $n_{\vec{k}}$ can be either zero or one.

The **canonical partition function** $Z^\pm$ is now defined as:

$$\boxed{Z^\pm(N, V, \beta) := \mathrm{tr}_{\mathcal{H}_N^\pm}\left(e^{-\beta H}\right)}. \tag{5.13}$$

In general the partition function is difficult to calculate. It is easier to momentarily move onto the **grand canonical ensemble**, where the particle number N is variable, i.e. it is given by a particle number operator $\hat{N}$ with eigenvalues $N = 0, 1, 2, \ldots$. The Hilbert space is then given by the bosonic $(+)$ or fermionic $(-)$ **Fock space**

$$\mathcal{H}^\pm = \bigoplus_{N \geq 0} \mathcal{H}_N^\pm = \mathbb{C} \oplus \mathcal{H}_1^\pm \oplus \ldots \tag{5.14}$$

On $\mathcal{H}_N^\pm$ the particle number operator $\hat{N}$ has eigenvalue N. The **grand canonical partition function** $Y^\pm$ is then defined as before as (cf. (4.103) and (4.107)):

$$Y^\pm(\mu, V, \beta) := \mathrm{tr}_{\mathcal{H}^\pm}\left(e^{-\beta(H - \mu\hat{N})}\right) = \sum_{N=0}^{\infty} e^{+\mu\beta N} Z^\pm(N, V, \beta) \tag{5.15}$$

Another representation of the states in $\mathcal{H}^\pm$ is the one based on the **occupation numbers** $n_{\vec{k}}$:

(a) $\left|\{n_{\vec{k}}\}\right\rangle_+, \qquad n_{\vec{k}} = 0, 1, 2, 3, \ldots$ for Bosons,

(b) $\left|\{n_{\vec{k}}\}\right\rangle_-, \qquad n_{\vec{k}} = 0, 1$ for Fermions.

The **creation/destruction operators** may then be defined as

$$a_{\vec{k}}^\dagger\left|\ldots, n_{\vec{k}}, \ldots\right\rangle_\pm = \sqrt{n_{\vec{k}} + 1}\left|\ldots, n_{\vec{k}} + 1, \ldots\right\rangle_\pm, \tag{5.16}$$

$$a_{\vec{k}}\left|\ldots, n_{\vec{k}}, \ldots\right\rangle_\pm = \sqrt{n_{\vec{k}}}\left|\ldots, n_{\vec{k}} - 1, \ldots\right\rangle_\pm, \tag{5.17}$$

in either case. Those operators fulfill the following commutation/anticommutation relations:

(a) Bosons:

$$\left[a_{\vec{k}}, a_{\vec{p}}^\dagger\right] = \delta_{\vec{k}, \vec{p}}$$
$$\left[a_{\vec{k}}, a_{\vec{p}}\right] = \left[a_{\vec{k}}^\dagger, a_{\vec{p}}^\dagger\right] = 0$$

(b) Fermions:

$$\left\{a_{\vec{k}}^\dagger, a_{\vec{p}}\right\} = \delta_{\vec{k}, \vec{p}}$$
$$\left\{a_{\vec{k}}, a_{\vec{p}}\right\} = \left\{a_{\vec{k}}^\dagger, a_{\vec{p}}^\dagger\right\} = 0,$$

where $[A, B] = AB - BA$ denotes the commutator and $\{A, B\} = AB + BA$ denotes the anticommutator of two operators.

We denote by $\hat{N}_{\vec{k}}$ the particle number operator $\hat{N}_{\vec{k}} = a_{\vec{k}}^\dagger a_{\vec{k}}$ with eigenvalues $n_{\vec{k}}$. The Hamiltonian may then be written as

$$H = \sum_{\vec{k}} \epsilon(\vec{k})\hat{N}_{\vec{k}} = \sum_{\vec{k}} \epsilon(\vec{k})a_{\vec{k}}^\dagger a_{\vec{k}} \tag{5.18}$$

where $\epsilon(\vec{k}) = \frac{\hbar^2 \vec{k}^2}{2m}$ for *non-relativistic* particles. With the formalism of creation and destruction operators at hand, the grand canonical partition function for bosons and fermions, respectively, may now be calculated as follows:

(a) *Bosons ("+")*:

$$Y^+(\mu, V, \beta) = \sum_{\{n_{\vec{k}}\}^+} \left\langle \{n_{\vec{k}}\} | e^{-\beta(H-\mu\hat{N})} | \{n_{\vec{k}}\} \right\rangle_+$$

$$= \sum_{\{n_{\vec{k}}\}} e^{-\beta \sum_{\vec{k}} n_{\vec{k}}\left(\epsilon(\vec{k})-\mu\right)}$$

$$= \prod_{\vec{k}} \left(\sum_{n=0}^{\infty} e^{-\beta\left(\epsilon(\vec{k})-\mu\right)n} \right)$$

$$= \prod_{\vec{k}} \left(1 - e^{-\beta\left(\epsilon(\vec{k})-\mu\right)} \right)^{-1}. \tag{5.19}$$

(b) *Fermions ("-")*:

$$Y^-(\mu, V, \beta) = \sum_{\{n_{\vec{k}}\}^-} \left\langle \{n_{\vec{k}}\} | e^{-\beta(H-\mu\hat{N})} | \{n_{\vec{k}}\} \right\rangle_-$$

$$= \prod_{\vec{k}} \left(1 + e^{-\beta(\epsilon(\vec{k})-\mu)} \right)^{1}. \tag{5.20}$$

The **expected number densities** $\bar{n}_{\vec{k}}$, which are defined as

$$\bar{n}_{\vec{k}} := \left\langle \hat{N}_{\vec{k}} \right\rangle_{\pm} = \mathrm{tr}_{\mathcal{H}^{\pm}} \left(\frac{\hat{N}_{\vec{k}}}{Y^{\pm}} e^{-\beta(H-\mu\hat{N})} \right), \tag{5.21}$$

can be calculated by means of a trick. Let us consider the bosonic case ("+"). From the above commutation relations we obtain

$$\hat{N}_{\vec{k}} a_{\vec{p}}^{\dagger} = a_{\vec{p}}^{\dagger} \left(\hat{N}_{\vec{k}} + \delta_{\vec{k},\vec{p}} \right) \quad \text{and} \quad a_{\vec{p}} \hat{N}_{\vec{k}} = \left(\hat{N}_{\vec{k}} + \delta_{\vec{k},\vec{p}} \right) a_{\vec{p}}. \tag{5.22}$$

From this it follows by a straightforward calculation that

$$\bar{n}_{\vec{k}} = \mathrm{tr}_{\mathcal{H}^+} \left(\frac{1}{Y^+} a_{\vec{k}}^{\dagger} a_{\vec{k}} e^{-\beta(H-\mu\hat{N})} \right) = \mathrm{tr}_{\mathcal{H}^+} \left(\frac{1}{Y^+} a_{\vec{k}}^{\dagger} a_{\vec{k}} e^{-\sum_{\vec{p}} \beta(\epsilon(\vec{p})-\mu)\hat{N}_{\vec{p}}} \right)$$

$$= \mathrm{tr}_{\mathcal{H}^+} \left(\frac{1}{Y^+} a_{\vec{k}}^{\dagger} e^{-\sum_{\vec{p}} \beta(\epsilon(\vec{p})-\mu)(\hat{N}_{\vec{p}}+\delta_{\vec{k},\vec{p}})} a_{\vec{k}} \right)$$

$$= \mathrm{tr}_{\mathcal{H}^+} \left(\frac{1}{Y^+} a_{\vec{k}} a_{\vec{k}}^{\dagger} e^{-\sum_{\vec{p}} \beta(\epsilon(\vec{p})-\mu)(\hat{N}_{\vec{p}}+\delta_{\vec{k},\vec{p}})} \right)$$

$$= e^{-\beta(\epsilon(\vec{k})-\mu)} \mathrm{tr}_{\mathcal{H}^+} \frac{1}{Y^+} \underbrace{a_{\vec{k}} a_{\vec{k}}^{\dagger}}_{1+\hat{N}_{\vec{k}}} e^{-\sum_{\vec{p}} \beta(\epsilon(\vec{p})-\mu)\hat{N}_{\vec{p}}}$$

$$= e^{-\beta(\epsilon(\vec{k})-\mu)} \left(1 + \bar{n}_{\vec{k}} \right).$$

Applying similar arguments in the fermionic case we find for the expected number densities:

$$\bar{n}_{\vec{k}} = \frac{1}{e^{\beta(\epsilon(\vec{k}) - \mu)} - 1}, \qquad \text{for bosons,} \tag{5.23}$$

$$\bar{n}_{\vec{k}} = \frac{1}{e^{\beta(\epsilon(\vec{k}) - \mu)} + 1}, \qquad \text{for fermions.} \tag{5.24}$$

These distributions are called **Bose-Einstein distribution** and **Fermi-Dirac distribution**, respectively. Note, that the particular form of $\epsilon(\vec{k})$ was not important in the derivation. In particular, (5.23) and (5.24) also hold for relativistic particles (see section 5.3). The classical distribution $\bar{n}_{\vec{k}} \propto e^{-\beta\epsilon(\vec{k})}$ is obtained in the limit $\beta\epsilon(\vec{k}) \gg 1$ i.e. $\epsilon(\vec{k}) \gg k_B T$, consistent with our experience that quantum effects are usually only important for energies that are small compared to the temperature.

The **mean energy** $E_\pm$ is given by

$$E_\pm = \langle H \rangle_\pm = \sum_{\vec{k}} \left\langle \epsilon(\vec{k}) \hat{N}_{\vec{k}} \right\rangle_\pm = \sum_{\vec{k}} \epsilon(\vec{k}) \bar{n}_{\vec{k}}^\pm. \tag{5.25}$$

5.2. Degeneracy pressure for free fermions

Let us now go back to the **canonical ensemble**, with density matrix $\rho^\pm$ given by

$$\rho^\pm = \frac{1}{Z_N^\pm} \mathcal{P}_\pm e^{-\beta H_N}. \tag{5.26}$$

Let $|\{\vec{x}\}\rangle_\pm$ be an eigenbasis of the position operators. Then, with $\eta \in \{+, -\}$:

$$_\eta\left\langle \{\vec{x}'\} \mid \rho \mid \{\vec{x}\} \right\rangle_\eta = {\sum_{\{\vec{k}\}}}' \sum_{\sigma, \sigma' \in S_N} \frac{1}{c_\eta} \eta_\sigma \eta_{\sigma'} \frac{1}{Z_N} e^{-\beta \sum\limits_{i=1}^{N} \frac{\hbar^2 \vec{k}_i^2}{2m}} \Psi^+_{\sigma\{\vec{k}\}}(\{\vec{x}'\}) \underbrace{\Psi_{\sigma'\{\vec{k}\}}(\{\vec{x}\})}_{\equiv \prod\limits_{i=1}^{N} \Psi_{\vec{k}\sigma(i)}(\vec{x}_i)}, \tag{5.27}$$

where $\Psi_{\vec{k}}(\vec{x}) \in \mathcal{H}_1$ are the 1-particle wave functions and

$$\eta_\sigma = \begin{cases} 1 & \text{for bosons} \\ \text{sgn}(\sigma) & \text{for fermions.} \end{cases} \tag{5.28}$$

The sum $\sum'_{\{\vec{k}_1, \dots, \vec{k}_N\}}$ is restricted in order to ensure that each identical particle state appears only once. We may equivalently work in terms of the occupation number rep-

resentation $|\{n_{\vec{k}}\}\rangle_{\pm}$. It is then clear that

$$\sum_{\{\vec{k}\}}{}' = \sum_{\{\vec{k}\}} \frac{\Pi_{\{\vec{k}\}}\, n_{\vec{k}}!}{N!},$$ (5.29)

where the factor in the *unrestricted* sum compensates the over-counting. This gives with the formulas for c_η derived above

$$_\eta\left\langle\{\vec{x}'\}\,|\,\rho\,|\,\{\vec{x}\}\right\rangle_\eta = \sum_{\{\vec{k}\}} \frac{\Pi_{\vec{k}}\, n_{\vec{k}}!}{N!} \frac{1}{\Pi_{\vec{k}}\, n_{\vec{k}}!N!} \sum_{\sigma,\sigma'\in S_N} \frac{\eta_\sigma\eta_{\sigma'}}{Z_N} e^{-\beta\sum_i \frac{\hbar^2\vec{k}_i^2}{2m}}\, \Psi^+_{\sigma'\{\vec{k}\}}(\{\vec{x}'\})\, \Psi_{\sigma\{\vec{k}\}}(\{\vec{x}\}).$$ (5.30)

For $V \to \infty$ we may replace the sum $\sum\limits_{\vec{k}}$ by $\frac{V}{(2\pi)^3}\int d^3k$, which yields

$$_\eta\left\langle\{\vec{x}'\}\,|\,\rho\,|\,\{\vec{x}\}\right\rangle_\eta = \frac{1}{Z_N N!^2} \frac{V^N}{(2\pi)^{3N}} \sum_{\sigma,\sigma'} \eta_\sigma\eta_{\sigma'} \int \frac{1}{V^N} d^{3N}k\; e^{-\beta\sum\limits_{i=1}^{N} \frac{\hbar^2\vec{k}_i^2}{2m}}\, e^{-i\sum\limits_{j=1}^{N}(\vec{k}_{\sigma j}\vec{x}_j - \vec{k}_{\sigma' j}\vec{x}'_j)}$$

$$= \frac{1}{Z_N N!^2} \sum_{\sigma,\sigma'} \eta_\sigma\eta_{\sigma'} \prod_j \int \frac{d^3k}{(2\pi)^3} e^{-i\vec{k}(\vec{x}_{\sigma j}-\vec{x}'_{\sigma' j})}\, e^{-\beta\frac{\vec{k}^2\hbar^2}{2m}}.$$

The Gaussian integrals can be explicitly performed, giving the result

$$\frac{1}{\lambda^3} e^{-\frac{\pi}{\lambda^2}\left(\vec{x}_{\sigma j}-\vec{x}'_{\sigma' j}\right)^2}$$

with the thermal deBroglie wavelength $\lambda = \frac{h}{\sqrt{2\pi m k_\mathrm{B}T}}$. Relabeling the summation indices then results in

$$_\eta\left\langle\{\vec{x}'\}\,|\,\rho\,|\,\{\vec{x}\}\right\rangle_\eta = \frac{1}{Z_N \lambda^{3N} N!} \sum_\sigma \eta_\sigma e^{-\frac{\pi}{\lambda^2}\sum_j(\vec{x}_j - \vec{x}_{\sigma j})}$$ (5.31)

Setting $\vec{x}' = \vec{x}$, taking $\int d^{3N}x$ on both sides gives, and using tr $\rho \stackrel{!}{=} 1$ gives:

$$Z_N = \frac{1}{N!\lambda^{3N}} \int d^{3N}x \sum_{\sigma\in S_N} \eta_\sigma e^{-\frac{\pi}{\lambda^2}\sum_j(\vec{x}_j - \vec{x}_{\sigma j})^2}.$$ (5.32)

The terms with $\sigma \neq \mathrm{id}$ are suppressed for $\lambda \to 0$ (i.e. for $h \to 0$ or $T \to \infty$), so the leading order contribution comes from $\sigma = \mathrm{id}$. The next-to leading order corrections come from those σ having precisely 1 transposition (there are $\frac{N(N-1)}{2}$ of them). A permutation with precisely one transposition corresponds to an exchange of two particles. Neglecting

next-to-next-to leading order corrections, the canonical partition function is given by

$$Z_N = \frac{1}{N!\lambda^{3N}} \int d^{3N}x \left[1 + \frac{N}{2}(N-1)\,\eta\,e^{-\frac{2\pi}{\lambda^2}(\vec{x}_1 - \vec{x}_2)^2} + \dots\right]$$

$$\underset{\int d^3x = V}{=} \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N \left[1 + \frac{N(N-1)}{2V}\,\eta\,\int d^3r\,e^{-\frac{2\pi}{\lambda^2}\vec{r}^2} + \dots\right] \tag{5.33}$$

$$= \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N \left[1 + \frac{N(N-1)}{2V}\,\eta\,\left(\frac{2\pi\lambda^2}{4\pi}\right)^{\frac{3}{2}} + \dots\right].$$

The **free energy** $F := -\mathrm{k_B}T\log Z_N$ is now calculated as

$$F = \underbrace{-N\mathrm{k_B}T\log\left[\frac{e}{\lambda^3}\cdot\frac{V}{N}\right]}_{\text{using } N! \approx N^N e^{-N}} - \underbrace{\frac{\mathrm{k_B}TN^2}{2V}}_{\text{using } \log(1+\epsilon)\approx\epsilon}\frac{\lambda^3}{2^{\frac{3}{2}}}\eta + \dots \tag{5.34}$$

Together with the following relation for the pressure (cf. (4.17)),

$$P = -\left.\frac{\partial F}{\partial V}\right|_T, \tag{5.35}$$

it follows that

$$P = n\mathrm{k_B}T\left(1 - \eta\,n\,\frac{\lambda^3}{2^{\frac{5}{2}}} + \dots\right), \tag{5.36}$$

where $n = \frac{N}{V}$ is the particle density. Comparing to the classical ideal gas, where we had $P = n\mathrm{k_B}T$, we see that when $n\lambda^3$ is of order 1, quantum effects significantly increase the pressure for fermions ($\eta = -1$) while they decrease the pressure for bosons ($\eta = +1$). As we can see comparing the expression (5.33) with the leading order term in the cluster expansion of the classical gas (see chapter 4.6), this effect is also present for a *classical* gas to leading order if we include a 2-body potential $\mathcal{V}(\vec{r})$, such that

$$e^{-\beta\mathcal{V}(\vec{r})} - 1 = \eta e^{\frac{-2\pi\vec{r}^2}{\lambda^2}} \quad \text{(from (5.33))}. \tag{5.37}$$

It follows that for the potential $\mathcal{V}(\vec{r})$ it holds

$$\mathcal{V}(\vec{r}) = -\mathrm{k_B}T\log\left[1 + \eta e^{-\frac{2\pi\vec{r}^2}{\lambda^2}}\right] \approx -\mathrm{k_B}T\eta e^{-\frac{2\pi\vec{r}^2}{\lambda^2}}, \qquad \text{for } r \gtrsim \lambda. \tag{5.38}$$

A sketch of $\mathcal{V}(\vec{r})$ is given in the following picture:
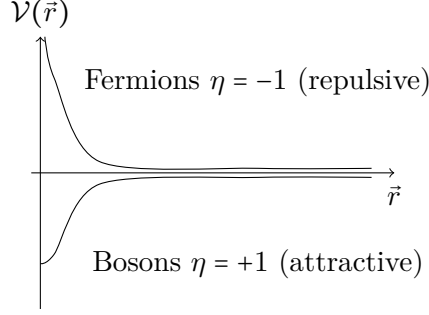
Figure 5.1.: The potential $\mathcal{V}(\vec{r})$ ocurring in (5.38).

Thus, we can say that quantum effects lead to an effective potential. For fermions the resulting coorection to the pressure P in (5.36) is called **degeneracy pressure**. Note that according to (5.36) the degeneracy pressure is proportional to $k_B T n^2 \lambda^3$ for fermions, which increases strongly for increasing density n. It provides a mechanism to support very dense objects against gravitational collapse, e.g. in neutron stars.

5.3. Spin Degeneracy

For particles with spin the energy levels have a corresponding g-fold degeneracy. Since different spin states have the same energy the Hamiltonian is now given by

$$H = \sum_{\vec{k},s} \epsilon(\vec{k}) a^{\dagger}_{\vec{k},s} a_{\vec{k},s}, \qquad s = 1, \ldots, g = 2S+1, \tag{5.39}$$

where the creation/destruction operators $a^{\dagger}_{\vec{k},s}$ and $a_{\vec{k},s}$ fulfill the commutation relations

$$\left[a^{\dagger}_{\vec{k},s}, a_{\vec{k}',s'} \right] = \delta_{\vec{k},\vec{k}'} \delta_{s,s'}. \tag{5.40}$$

For the grand canonical ensemble the Hilbert space of particles with spin is given by

$$\mathcal{H}^{\pm} = \bigoplus_{N \geq 0} \mathcal{H}^{\pm}_N, \quad \mathcal{H}_1 = L^2(V, d^3x) \otimes \mathbb{C}^g. \tag{5.41}$$

It is easy to see that for the grand canonical ensemble this results in the following expressions for the expected number densities $\bar{n}_{\vec{k}}$ and the mean energy $E_{\pm}$:

$$\bar{n}^{\pm}_{\vec{k}} = \left\langle \hat{N}_{\vec{k}} \right\rangle_{\pm} = \frac{g}{e^{\beta(\epsilon(\vec{k})-\mu)} \mp 1} \tag{5.42}$$

$$E = \left\langle H \right\rangle_{\pm} = g \sum_{\vec{k}} \frac{\epsilon(\vec{k})}{e^{\beta(\epsilon(\vec{k})-\mu)} \mp 1}. \tag{5.43}$$

In the canonical ensemble we find similar expressions. For a non-relativistic gas we get, with $\sum\limits_{\vec{k}} \to V \int \frac{d^3k}{(2\pi)^3}$ for $V \to \infty$:

$$\epsilon_\pm := \frac{E_\pm}{V} = g \int \frac{d^3k}{(2\pi)^3} \frac{\hbar^2 k^2}{2m} \frac{1}{e^{\beta(\frac{\hbar^2 k^2}{2m} - \mu)} \mp 1}. \tag{5.44}$$

Setting $x = \frac{\hbar^2 k^2}{2mk_BT}$ or equivalently $k = \frac{2\pi^{\frac{1}{2}}}{\lambda} x^{\frac{1}{2}}$ and defining the fugacity $z := e^{\beta\mu}$, we find

$$\frac{\epsilon^\pm}{k_BT} = \frac{g}{\lambda^3} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{dx \, x^{\frac{3}{2}}}{z^{-1}e^x \mp 1}. \tag{5.45}$$

or similarly

$$\bar{n}^\pm = \frac{\langle \hat{N} \rangle_\pm}{V} = \frac{g}{\lambda^3} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{dx \, x^{\frac{1}{2}}}{z^{-1}e^x \mp 1}. \tag{5.46}$$

Furthermore, we also have the following relation for the pressure $P_\pm$ and the grand canonical potential $G_\pm = -k_BT \log Y^\pm$ (cf. section 4.4):

$$P_\pm = -\frac{\partial G^\pm}{\partial V}\bigg|_{T,\mu}. \tag{5.47}$$

From (5.46) it follows that in the case of spin degeneracy the grand canonical partition function $Y^\pm$ is given by

$$Y^\pm = \left[\prod_{\vec{k}} \left(1 \mp z e^{-\beta\epsilon(\vec{k})} \right) \right]^{\mp g}. \tag{5.48}$$

Taking the logarithm on both sides and taking a large volume $V \to \infty$ to approximate the sum by an integral as before yields

$$\frac{P_\pm}{k_BT} = \mp g \int \frac{d^3k}{(2\pi)^3} \log \left[1 \mp z e^{-\frac{\hbar^2 k^2}{2mk_BT}} \right]$$

$$= \frac{g}{\lambda^3} \frac{4}{3} \sqrt{\pi}^{-1} \int_0^\infty \frac{dx \, x^{\frac{3}{2}}}{z^{-1}e^x \mp 1}. \tag{5.49}$$

To go to the last line, we used a partial integration in x. For $z \ll 1$, i.e. $\mu\beta = \frac{\mu}{k_BT} \ll 0$ one can expand $\bar{n}^\pm$ in z around $z = 0$. Using the relation

$$\int \frac{dx \, x^{m-1}}{z^{-1}e^x - \eta} = \eta(m-1)! \sum_{n=1}^\infty \frac{(\eta z)^n}{n^m},$$

(which for $\eta z = 1$ yields the Riemann ζ-function), one finds that

$$\frac{\bar{n}_\pm \lambda^3}{g} = z \pm \frac{z^2}{2^{\frac{3}{2}}} + \frac{z^3}{3^{\frac{3}{2}}} \pm \frac{z^4}{4^{\frac{3}{2}}} + \dots \tag{5.50}$$

$$\frac{\beta P_\pm \lambda^3}{g} = z \pm \frac{z^2}{2^{\frac{5}{2}}} + \frac{z^3}{3^{\frac{5}{2}}} \pm \frac{z^4}{4^{\frac{5}{2}}} + \dots \tag{5.51}$$

Solving (5.50) for z and substituting into (5.51) gives

$$P_\pm = \bar{n}_\pm k_B T \left[1 \mp \frac{1}{2^{\frac{5}{2}}} \left(\frac{\bar{n}_\pm \lambda^3}{g} \right) + \dots \right], \tag{5.52}$$

which for $g = 1$ gives the same result for the degeneracy pressure we obtained previously in (5.36). Note again the "+" sign for fermions.

5.4. Black Body Radiation

We know that the dispersion relation for photons is given by (note that the momentum is $\vec{p} = \hbar \vec{k}$):

$$\epsilon(\vec{k}) = \hbar c \left| \vec{k} \right|. \tag{5.53}$$

There are two possibilities for the helicity ("spin") of a photon which is either parallel or anti-parallel to $\vec{p}$, corresponding to the polarization of the light. Hence, the degeneracy factor for photons is $g = 2$ and the Hamiltonian is given by

$$H = \sum_{\vec{p},s=\pm 1} \epsilon(\vec{p}) a^+_{\vec{p},s} a_{\vec{p},s} + \underbrace{\dots}_{\text{interaction}} \quad (\vec{p} \neq 0). \tag{5.54}$$

Under normal circumstances there is practically no interaction beween the photons, so the interaction terms indicated by "..." can be neglected in the previous formula. The following picture is a sketch of a 4-photon interaction, where σ denotes the cross section for the corresponding 2-2 scattering process obtained from the computational rules of quantum electrodynamics:
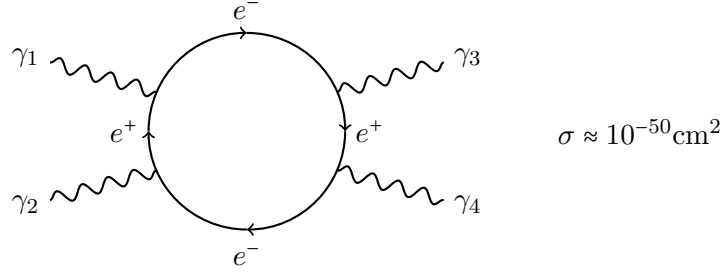
Figure 5.2.: Lowest-order Feynman diagram for photon-photon scattering in Quantum Electrodynamics.

The mean collision time of the photons is given by

$$\frac{1}{\tau} = \frac{c\sigma N}{V} = c\sigma n \approx 10^{-44} \times n \frac{\text{cm}^3}{\text{s}}, \qquad (5.55)$$

where $N = \langle \hat{N} \rangle$ is the average number of photons inside V and $n = N/V$ their density. Even in extreme places like the interior sun, where $T \approx 10^7 \text{K}$, this leads to a mean collision time of 10^{18}s. This is more than the age of the universe, which is approximately 10^{17}s. From this we conclude that *we can safely treat the photons as an ideal gas*!

By the methods of the previous subsection we find for the grand canonical partition function, with $\mu = 0$:

$$Y = \text{tr}\left(e^{-\beta H}\right) = \left[\prod_{\vec{p} \neq 0} \frac{1}{1 - e^{-\beta \epsilon(\vec{p})}}\right]^2, \qquad (5.56)$$

since the degeneracy factor is $g = 2$ and photons are bosons. For the Gibbs free energy (in the limit $V \to \infty$) we get[1]

$$G = -k_B T \log Y = \frac{2V}{\beta} \int \frac{d^3 p}{(2\pi\hbar)^3} \log\left(1 - e^{-\beta cp}\right) = \frac{V(k_B T)^4}{\pi^2 (\hbar c)^3} \int_0^\infty dx\, x^2 \log(1 - e^{-x})$$

$$= \frac{V(k_B T)^4}{\pi^2 (\hbar c)^3} \left(-\frac{1}{3}\right) \underbrace{\int_0^\infty \frac{dx\, x^3}{e^x - 1}}_{=-2\zeta(4)=-\frac{\pi^4}{45}} = -\frac{V(k_B T)^4}{(\hbar c)^3} \frac{\pi^2}{45}.$$

$$\Rightarrow \boxed{G = -\frac{4\sigma}{3c} V T^4}. \qquad (5.58)$$

Here, $\sigma = 5.67 \times 10^{-8} \frac{\text{J}}{\text{s m}^2 \text{K}^4}$ is the **Stefan-Boltzmann constant**.

The **entropy** was defined as $S := -k_B \text{tr}\left(\rho \log \rho\right)$ with $\rho = \frac{1}{Y} e^{-\beta H}$. One easily finds

---

[1]Here, we make use of the **Riemann zeta function**, which is defined by

$$\zeta(s) = \sum_{n \geq 1} n^{-s}, \quad \text{for Re}(s) > 1. \qquad (5.57)$$

the relation

$$S = -\left.\frac{\partial G}{\partial T}\right|_{V,\mu=0} = \left.\frac{\partial}{\partial T}\left(k_B T \ \log Y\right)\right|_{V,\mu=0}, \tag{5.59}$$

(see chapter 6.5 for a systematic review of such formulas) or

$$\Rightarrow \quad \boxed{S = \frac{16\sigma}{3c}VT^3} \tag{5.60}$$

The **mean energy E** is found as

$$E = \langle H \rangle = 2\sum_{\vec{p}\neq 0}\epsilon(\vec{p})\frac{1}{e^{\beta\epsilon(\vec{p})}-1} = 2V\int\frac{d^3p}{(2\pi\hbar)^3}\frac{|\vec{p}|}{e^{\beta c|\vec{p}|}-1}.$$

$$\Rightarrow \quad \boxed{E = \frac{4\sigma}{c}VT^4} \tag{5.61}$$

Finally, the pressure P can be calculated as

$$P = -\left.\frac{\partial G}{\partial V}\right|_{T,\mu=0} = \left.\frac{\partial}{\partial V}\left(k_B T \ \log Y\right)\right|_{T,\mu=0}, \tag{5.62}$$

see again chapter 6.5 for systematic review of such formulas. This gives

$$\Rightarrow \quad \boxed{P = \frac{4\sigma}{3c}T^4} \tag{5.63}$$

As an example, for the sun, with $T_{sun} = 10^7$K, the pressure is $P = 2,500,000$ atm and for a H-bomb, with $T_{bomb} = 10^5$K, the pressure is $P = 0.25$ atm.

Note that for photons we have

$$\boxed{P = \frac{1}{3}\frac{E}{V} \quad \Leftrightarrow \quad E = 3PV}. \tag{5.64}$$

This is also known as the **Stefan-Boltzmann law**.

Photons in a cavity: Consider now a setup where photons can leave a cavity through a small hole:
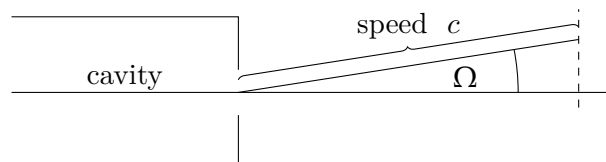
Figure 5.3.: Photons leaving a cavity.

The intensity of the radiation which goes through the opening is given by

$$\mathrm{I}(\nu, T) = \int \underbrace{\frac{cu(\nu)\, d\Omega}{4\pi}}_{\substack{\text{radiation into} \\ \text{solid angle } d\Omega}} = \frac{1}{4\pi} \int\limits_0^{2\pi} d\phi \int\limits_0^1 d\cos\vartheta\; cu(\nu) = \frac{c}{4} u(\nu),$$

where c is the speed of light, and where $u(\nu)d\nu$ is the average number of emitted particles in frequency range $\nu \dots \nu + d\nu$ per unit volume. We thus have

$$\mathrm{I}_{\text{total}} = \int\limits_0^\infty d\nu\; \mathrm{I}(\nu, T) = \sigma T^4. \tag{5.65}$$

We now find $u(\nu)$. For the **mean particle number** $\langle N_{\vec{p}} \rangle$ we first find

$$\left\langle \hat{N}_{\vec{p}} \right\rangle = \frac{2}{e^{\beta c |\vec{p}|} - 1} \qquad \text{for momentum } \vec{p} = \hbar\vec{k}. \tag{5.66}$$

The number of occupied states in a "volume" d^3p is hence on average given by

$$\frac{2}{e^{\beta c|\vec{p}|} - 1} V \frac{d^3p}{(2\pi\hbar)^3},$$

hence the number per interval $p \dots p + dp$ is given by

$$\frac{V}{\pi^2 \hbar^3} p^2 \frac{dp}{e^{\beta c p} - 1}.$$

The average number of emitted particles in frequency range $\nu \dots \nu + d\nu$ per volume $u(\nu)d\nu$ is p times this number divided by V, which together with $E_{\text{photon}} = pc = h\nu$ gives

$$\boxed{u(\nu) = \frac{h}{\pi c^3} \frac{\nu^3}{e^{\frac{h\nu}{k_B T}} - 1}}. \tag{5.67}$$

This is the famous law found by Planck in 1900 which lead to the development of quantum theory! The Planck distribution looks as follows:
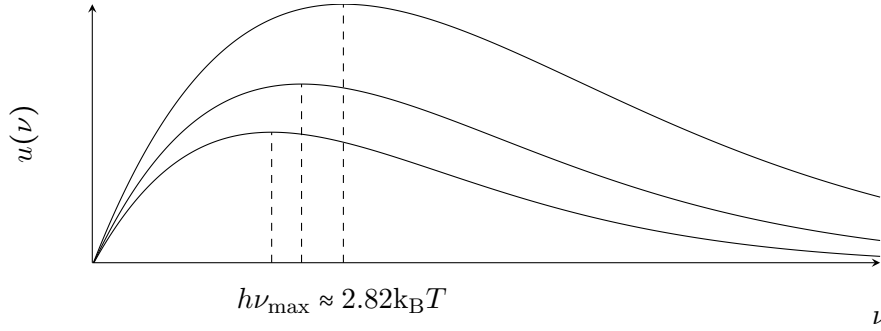
Figure 5.4.: Sketch of the Planck distribution for different temperatures.

Solving $u'(\nu_{\max}) = 0$ one finds that the maximum of $u(\nu)$ lies at $h\nu_{\max} \approx 2.82 k_B T$, a relation also known as **Wien's law**. The following *limiting cases* are noteworthy:

(i) $h\nu \ll k_B T$:

In this case we have

$$u(\nu) \approx \frac{k_B T \nu^2}{\pi c^3} \tag{5.68}$$

This formula is valid in particular for $h \to 0$, i.e. it represents the classical limit. It was known *before* the Planck formula. It is not only inaccurate for larger frequencies but also fundamentally problematic since it suggests $\langle H \rangle = E \propto \int d\nu \, u(\nu) = \infty$, which indicates an instability not seen in reality.

(ii) $h\nu \gg k_B T$:

In this case we have

$$u(\nu) \approx \frac{h\nu^3}{\pi c^3} e^{\frac{-h\nu}{k_B T}} \tag{5.69}$$

This formula had been found empirically by Wien without proper interpretation of the constants (and in particular without identifying h).

We can also calculate the **mean total particle number**:

$$\langle \hat{N} \rangle = \sum_{\vec{p} \neq 0} \frac{2}{e^{\beta c |\vec{p}|} - 1} \approx 2V \int \frac{d^3 p}{(2\pi\hbar)^3} \frac{1}{e^{\beta c |\vec{p}|} - 1}$$

$$= \frac{2\zeta(3)}{\pi^2} V \left(\frac{k_B T}{\hbar c} \right)^3 \tag{5.70}$$

Combining this formula with that for the entropy S, eq. (5.60), gives the relation

$$S = \frac{8\pi^4}{3\zeta(3)} k_B N \approx 3.6 N k_B. \tag{5.71}$$

where $N \equiv \langle \hat{N} \rangle$ is the mean total particle number from above. Thus, for an ideal photon

gas we have $S = \mathcal{O}(1)\mathrm{k_B}N$, i.e. each photon contributes one unit to $\frac{S}{\mathrm{k_B}}$ on average (see the problem sheets for a striking application of this elementary relation).

5.5. Degenerate Bose Gas

Ideal quantum gases of bosonic particles show a particular behavior for low temperature T and large particle number densities $n = \frac{\langle \hat{N} \rangle}{V}$. We first discuss the ideal Bose gas in a *finite* volume. In this case, the expected particle density was given by

$$n = \frac{\langle \hat{N} \rangle}{V} = \frac{g}{V} \sum_{\vec{k}} \frac{1}{e^{\beta\left(\epsilon(\vec{k})-\mu\right)} - 1}. \tag{5.72}$$

The sum is calculated for sufficiently large volumes again by replacing $\sum_{\vec{k}}$ by $V \int \frac{d^3k}{(2\pi)^3}$, which yields

$$\begin{aligned} n &\approx g \int \frac{d^3k}{(2\pi)^3} \frac{1}{e^{\beta\left(\epsilon(\vec{k})-\mu\right)} - 1} \\ &= \frac{g}{2\pi^2} \int dk \frac{k^2}{e^{\beta\left(\epsilon(\vec{k})-\mu\right)} - 1} \end{aligned} \tag{5.73}$$

The particle density is clearly maximal for $\mu \to 0$ and its maximal value is given by n_c where, with $\epsilon(k) = \frac{\hbar^2 k^2}{2m}$,

$$\begin{aligned} n_c &= \frac{g}{2\pi^2} \int dk \frac{k^2}{e^{\beta\epsilon(\vec{k})} - 1} \\ &= \frac{g}{2\pi^2} \left(\frac{2m}{\beta\hbar^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{dx\ x^2}{e^{x^2} - 1} \\ &= \frac{g}{2\pi^2} \left(\frac{2m}{\beta\hbar^2}\right)^{\frac{3}{2}} \sum_{n=1}^\infty \int_0^\infty dx\ x^2 e^{-nx^2} \\ &= \frac{g}{\lambda^3} \zeta\left(\frac{3}{2}\right), \end{aligned}$$

and where $\lambda = \sqrt{\frac{h^2}{2\pi m \mathrm{k_B}T}}$ is the thermal deBroglie wavelength. From this wee see that $n \le n_c$, and the limiting density is achieved for the limiting temperature

$$T_c = \frac{h^2}{2\pi m \mathrm{k_B}} \left(\frac{n}{g\zeta\left(\frac{3}{2}\right)}\right)^{\frac{2}{3}}. \tag{5.74}$$

Equilibrium states with higher densities $n > n_c$ are not possible at finite volume. A new phenomenon happens, however, for infinite volume, i.e. in the thermodynamic limit, $V \to \infty$. Here, we must be careful because density matrices are only formal

(e.g. the partition function $Y \to \infty$), so it is better to characterize equilibrium states by the so-called **KMS condition** (for **K**ubo-**M**artin-**S**chwinger) for equilibrium states. As we will see, new interesting equilibrium states that can be found in this way in the thermodynamic limit. They correspond to a **Bose-condensate**, or a gas in a **superfluid state**.

To motivate the KMS condition, recall that in the case of no spin ($g = 1$) we had the commutation relations $\left[a_{\vec{k}}, a_{\vec{p}}^{+}\right] = \delta_{\vec{k}, \vec{p}}$ for the creation/destruction operators. From this it follows that for a Gibbs state $\langle \ldots \rangle$ we have

$$\boxed{\left\langle a_{\vec{p}}^{\dagger} a_{\vec{k}} \right\rangle = e^{-\beta \left(\epsilon(\vec{k}) - \mu \right)} \left\langle a_{\vec{k}} a_{\vec{p}}^{\dagger} \right\rangle} , \tag{5.75}$$

and therefore

$$\left(1 - e^{-\beta \left(\epsilon(\vec{k}) - \mu \right)} \right) \left\langle a_{\vec{p}}^{\dagger} a_{\vec{k}} \right\rangle = e^{-\beta \left(\epsilon(\vec{k}) - \mu \right)} \delta_{\vec{k}, \vec{p}}. \tag{5.76}$$

In the thermodynamic limit (*infinite* volume), $V \to \infty$, we should make the replacements

$$\text{finite volume:} \quad \vec{k} \in \left(\frac{\pi}{L} \mathbb{Z} \right)^3 \quad \text{and} \quad \begin{cases} a_{\vec{k}} \\ \delta_{\vec{k}, \vec{p}} \end{cases} \longrightarrow \text{infinite volume:} \quad \vec{k} \in \mathbb{R}^3 \quad \text{and} \quad \begin{cases} a(\vec{k}) \\ \delta^3(\vec{k} - \vec{p}) \end{cases}$$

Thus, we expect that in the thermodynamic limit:

$$\left(1 - e^{-\beta \left(\frac{\hbar^2 \vec{k}^2}{2m} - \mu \right)} \right) \left\langle a^{\dagger}(\vec{p}) a(\vec{k}) \right\rangle = e^{-\beta \left(\frac{\vec{k}^2 \hbar^2}{2m} - \mu \right)} \delta^3(\vec{p} - \vec{k}). \tag{5.77}$$

In that limit, the statistical operator ρ of the grand canonical ensemble does not make mathematical sense, because $e^{-\beta H + \beta \mu \hat{N}}$ does not have a finite trace (i.e. $Y = \infty$). Nevertheless, the condition (5.77), called the "KMS condition" in this context, still makes sense. We view it as the appropriate substitute for the notion of Gibbs state in the thermodynamic limit.

What are the solutions of the KMS-condition? For $\mu < 0$ the unique solution is the usual Bose-Einstein distribution:

$$\left\langle a^{\dagger}(\vec{k}) a(\vec{p}) \right\rangle = \frac{\delta^3(\vec{p} - \vec{k})}{e^{\beta \left(\frac{\hbar^2 k^2}{2m} - \mu \right)} - 1}.$$

The point is that for $\mu = 0$ other solutions are also possible, for instance

$$\left\langle a^{+}(\vec{p}) a(\vec{k}) \right\rangle = \frac{\delta^3(\vec{p} - \vec{k})}{e^{\beta \frac{\hbar^2 \vec{k}^2}{2m}} - 1} + (2\pi)^3 n_0 \, \delta^3(\vec{k}) \delta^3(\vec{p})$$

for some $n_0 \geq 0$ (this follows from $\langle A^{+} A \rangle \geq 0$ for operators A in any state). The particle number density in the thermodynamic limit ($V \to \infty$) is best expressed in terms of the

creation operators at sharp position $\vec{x}$:

$$a(\vec{p}) = \frac{1}{(2\pi)^{\frac{3}{2}}} \int d^3x \; e^{-i\vec{p}\vec{x}} a(\vec{x}). \tag{5.78}$$

The particle number density at the point $\vec{x}$ is then defined as $\hat{N}(\vec{x}) := a^\dagger(\vec{x})a(\vec{x})$ and therefore we have, for $\mu = 0$:

$$n = \left\langle \hat{N}(\vec{x}) \right\rangle = \frac{1}{(2\pi)^3} \int d^3p \; d^3k \left\langle a^\dagger(\vec{p})a(\vec{k}) \right\rangle e^{-i(\vec{p}-\vec{k})\vec{x}} = n_c + n_0. \tag{5.79}$$

Thus, in this equilibrium state we have a macroscopically large occupation number n_0 of the zero mode causing a different particle density at $\mu = 0$. The fraction of zero modes, that is, that of the modes in the "condensate", can be written using our definition of T_c as

$$n_0 = n \left(1 - \left(\frac{T}{T_c} \right)^{3/2} \right), \tag{5.80}$$

for T below T_c, and $n_0 = 0$ above T_c. The formation of the condensate can thereby be seen as a phase transition at $T = T_c$.

We can also write down more general solutions to the KMS-condition, for example:

$$\left\langle a^\dagger(\vec{x})a(\vec{y}) \right\rangle = \int \frac{d^3k}{(2\pi)^3} \frac{e^{i\vec{k}(\vec{x}-\vec{y})}}{e^{\beta \frac{\hbar^2 k^2}{2m}} - 1} + \overline{f(\vec{x})} f(\vec{y}), \tag{5.81}$$

where f is *any* harmonic function, i.e. a function such that $\vec{\nabla}^2 f = 0$. To understand the physical meaning of these states, we define the **particle current** operator $\vec{j}(\vec{x})$ as

$$\vec{j}(\vec{x}) := \frac{-i}{2m} \left(a^\dagger(\vec{x})\vec{\nabla}a(\vec{x}) - a(\vec{x})\vec{\nabla}a^\dagger(\vec{x}) \right). \tag{5.82}$$

An example of a harmonic function is $f(\vec{x}) = 1 + im\vec{v} \cdot \vec{x}$, and in this case one finds the expectation value

$$\left\langle \vec{j}(\vec{x}) \right\rangle = \frac{-i}{2m} \left(\overline{f(\vec{x})}\vec{\nabla}f(\vec{x}) - f(\vec{x})\vec{\nabla}\overline{f(\vec{x})} \right) = \vec{v} \tag{5.83}$$

This means that the condensate flows in the direction of $\vec{v}$ without leaving equilibrium. Another solution is $f(\vec{x}) = f(x, y, z) = x + iy$. In this case one finds

$$\left\langle \vec{j}(x, y, z) \right\rangle = (-y, x, 0)$$

describing a circular motion around the origin (vortex). The condensate can hence flow or form vortices without leaving equilibrium. This phenomenon goes under the name of **superfluidity**.

6. The Laws of Thermodynamics

The laws of thermodynamics predate the ideas and techniques from statistical mechanics, and are, to some extent, simply consequences of more fundamental ideas derived in statistical mechanics. However, they are still in use today, mainly because:

(i) they are easy to remember.

(ii) they are to some extent universal and model-independent.

(iii) microscopic descriptions are sometimes not known (e.g. black hole thermodynamics) or are not well-developed (non-equilibrium situations).

(iv) they are *useful*!

The laws of thermodynamics are based on:

(i) The empirical evidence that, for a very large class of macroscopic systems, equilibrium states can generally be characterized by very few parameters. These thermodynamic parameters, often called $X_1, ..., X_n$ in the following, can hence be viewed as "coordinates" on the space of equilibrium systems.

(ii) The idea to perform mechanical work on a system, or to bring equilibrium systems into "thermal contact" with reservoirs in order to produce new equilibrium states in a controlled way. The key idea here is that these changes (e.g. by "heating up a system" through contact with a reservoir system) should be extremely gentle so that the system is not pushed out of equilibrium too much. One thereby imagines that one can describe such a gradual change of the system by a succession of equilibrium states, i.e. a curve in the space of coordinates $X_1, ..., X_n$ characterizing the different equilibrium states. This idealized notion of an infinitely gentle/slow change is often referred to as "quasi-static".

(iii) Given the notions of quasi-static changes in the space of equilibrium states, one can then postulate certain rules guided by empirical evidence that tell us which kind of changes should be possible, and which ones should not. These are, in essence, the laws of thermodynamics. For example, one knows that if one has access to equilibrium systems at different temperature, then one system can perform work on the other system. The first and second law state more precise conditions about

such processes and imply, respectively, the existence of an energy- and entropy function on equilibrium states. The zeroth law just states that being in thermal equilibrium with each other is an equivalence relation for systems, i.e. in particular transitive. It implies the existence of a temperature function labelling the different equivalence classes.

6.1. The Zeroth Law

0th law of thermodynamics: *If two subsystems I,II are separately in thermal contact with a third system, III, then they are in thermal equilibrium with each other.*

The 0th law implies the existence of a function

$$\Theta : \{\text{equilibrium systems}\} \to \mathbb{R},$$

such that Θ is equal for systems in thermal equilibrium with each other. To see this, let us imagine that the equilibrium states of the systems I,II and III are parametrized by some coordinates $\{A_1, A_2, \ldots\}, \{B_1, B_2, \ldots\}$ and $\{C_1, C_2, \ldots\}$. Since a change in I implies a corresponding change in III, there must be a constraint[1]

$$f_{\text{I,III}}\left(\{A_1, A_2, \ldots; C_1, C_2, \ldots\}\right) = 0 \tag{6.1}$$

and a similar constraint

$$f_{\text{II,III}}\left(\{B_1, B_2, \ldots; C_1, C_2, \ldots\}\right) = 0, \tag{6.2}$$

which we can write as

$$C_1 = \tilde{f}_{\text{I,III}}\left(\{A_1, A_2, \ldots; C_2, C_3, \ldots\}\right) = \tilde{f}_{\text{II,III}}\left(\{B_1, B_2, \ldots; C_2, C_3, \ldots\}\right). \tag{6.3}$$

Since, according to the 0th law, we also must have the constraint

$$f_{\text{I,II}}\left(\{A_1, A_2, \ldots, B_1, B_2, \ldots\}\right) = 0, \tag{6.4}$$

we can proceed by noting that for $\{A_1, A_2, \ldots, B_1, B_2, \ldots\}$ which satisfy the last equation, (6.3) must be satisfied for *any* $\{C_2, C_3, \ldots\}$! Thus, we let III be our reference system and set $\{C_2, C_3, \ldots\}$ to *any* convenient but fixed value. This reduces the condition (6.4)

---

[1] This is how one could actually mathematically implement the idea of "thermal contact"

for equilibrium between I and II to:

$$\Theta\left(\{A_1, A_2, \ldots\}\right) := \tilde{f}_{\mathrm{I,III}}\left(\{A_1, A_2, \ldots, C_2, C_3, \ldots\}\right)$$

$$= \tilde{f}_{\mathrm{II,III}}\left(\{B_1, B_2, \ldots, C_2, C_3, \ldots\}\right) = \Theta\left(\{B_1, B_2, \ldots\}\right). \qquad (6.5)$$

This means that equilibrium is characterized by some function Θ of thermodynamic coordinates, which has the properties of a *temperature*.

We may choose as our reference system III an **ideal gas**, with

$$\frac{PV}{Nk_{\mathrm{B}}} = \text{ const. } = T[\mathrm{K}] =: \Theta. \qquad (6.6)$$

By bringing this system (for $V \to \infty$) in contact with any other system, we can measure the (absolute) temperature of the latter. For example, one can define the triple point of the system **water-ice-vapor** to be at 273.16 K. Together with the definition of $k_{\mathrm{B}} = 1.4 \times 10^{-23} \frac{\mathrm{J}}{\mathrm{K}}$) this then defines, in principle, the Kelvin temperature scale. Of course in practice the situation is more complicated because ideal gases do not exist.
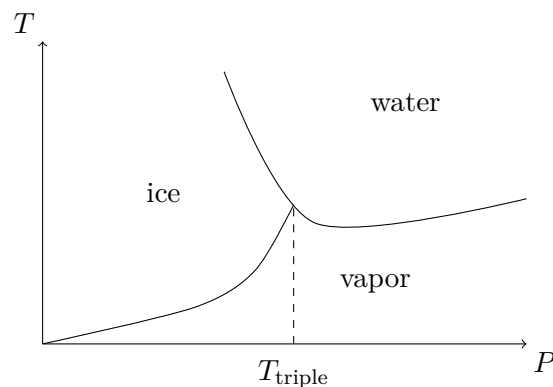
Figure 6.1.: The triple point of ice water and vapor in the (P, T) phase diagram

The Zeroth Law implies in particular: *The temperature of a system in equilibrium is constant throughout the system.* This has to be the case since subsystems obtained by imaginary walls are in equilibrium with each other, see the following figure:
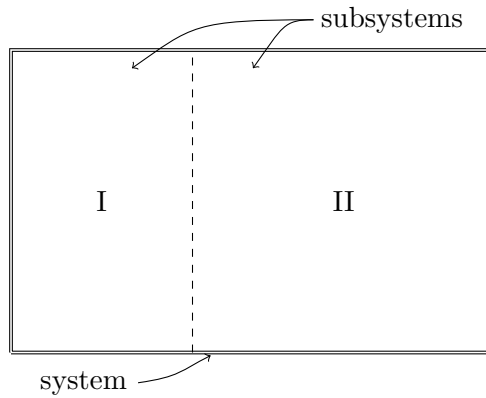
Figure 6.2.: A large system divided into subsystems I and II by an imaginary wall.

6.2. The First Law

1$^{\text{st}}$ law of thermodynamics: *The amount of work required to change adiabatically a thermally isolated system from an initial state i to a final state f depends only on i and f, not on the path of the process.*
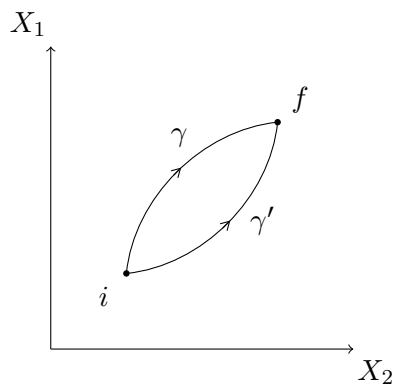
Figure 6.3.: Change of system from initial state i to final state f along two different paths.

Here, by an 'adiabatic change", one means a change without heat exchange. Consider a particle moving in a potential. By fixing an arbitrary reference point X_0, we can define an energy landscape

$$E(X) = \int_{X_0}^{X} \delta W, \tag{6.7}$$

where the integral is along any path connecting X_0 with X, and where X_0 is a reference point corresponding to the zero of energy. δW is the infinitesimal change of work done along the path. In order to define more properly the notion of such integrals of "infinitesimals", we will now make a short mathematical digression on differential forms.

Differentials ("differential forms")

A **1-form** (or **differential**) is an expression of the form

$$\alpha = \sum_{i=1}^{N} \alpha_i(X_1, \ldots, X_N) \, \mathrm{d}X_i. \tag{6.8}$$

We define

$$\int_\gamma \alpha := \int_0^1 \sum_{i=1}^{N} \alpha_i(X_1(t), \ldots, X_N(t)) \underbrace{\frac{dX_i(t)}{dt} dt}_{\text{``=}dX_i\text{''}}, \tag{6.9}$$

which in general is γ-dependent. Given a function $f(X_1, \ldots, X_N)$ on $\mathbb{R}^N$, we write

$$\mathrm{d}f(X_1, \ldots, X_N) = \frac{\partial f}{\partial X_1}(X_1, \ldots, X_N) \, \mathrm{d}X_1 + \ldots + \frac{\partial f}{\partial X_N}(X_1, \ldots, X_N) \, \mathrm{d}X_N. \tag{6.10}$$

$\mathrm{d}f$ is called an "exact" 1-form. From the definition of the path integral along γ it is obvious that

$$\int_\gamma \mathrm{d}f = \int_0^1 \frac{d}{dt} \left\{ f(X_1(t), \ldots, X_N(t)) \right\} dt = f\big(\gamma(1)\big) - f\big(\gamma(0)\big), \tag{6.11}$$

so the integral of an exact 1-form only depends on the beginning and endpoint of the path. An example of a curve $\gamma : [0,1] \to \mathbb{R}^2$ is given in the following figure:

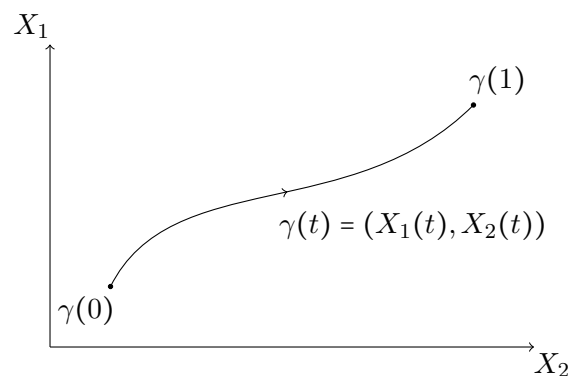
Figure 6.4.: A curve $\gamma : [0,1] \to \mathbb{R}^2$.

The converse is also true: The integral is independent of the path γ if and only if there exists a function f on $\mathbb{R}^N$, such that $\mathrm{d}f = \alpha$, or equivalently, if and only if $\alpha_i = \frac{\partial f}{\partial X_i}$.

The notion of a p-form generalizes that of a 1-form. It is an expression of the form

$$\alpha = \sum_{i_1,\ldots,i_p} \alpha_{i_1\ldots i_p} dX_{i_1} \ldots dX_{i_p}, \tag{6.12}$$

where $\alpha_{i_1\ldots i_p}$ are (smooth) functions of the coordinates X_i. We declare the dX_i to anti-commute,

$$dX_i dX_j = -dX_j dX_i. \tag{6.13}$$

Then we may think of the coefficient tensors as totally anti-symmetric, i.e. we can assume without loss of generality that

$$\alpha_{i_{\sigma(1)}\ldots i_{\sigma(p)}} = \text{sgn}(\sigma)\, \alpha_{i_1\ldots i_p}, \tag{6.14}$$

where σ is any permutation of p elements and sgn is its signum (see the discussion of fermions in the chapter on the ideal quantum gas). We may now introduce an operator d with the following properties:

(i) $d(fg) = dfg + (-1)^p f dg$,

(ii) $df = \sum_i \frac{\partial f}{\partial X_i} dX_i$ for 1-forms f,

(iii) $d^2 X_i = 0$,

where in (i), (iii) f is any p form and g is any q form. On scalars (i.e. 0-forms) the operator is defined (ii) as before, and the remaining rules (i), (iii) then determine it for any p-form. The relation (**??**) can be interpreted as saying that we should think of the differentials $dX_i, i = 1, \ldots, N$ as "fermionic-" or "anti-commuting variables".[2] For instance, we then get for a 1-form α:

$$d\alpha = \sum_{i,j} \frac{\partial \alpha_i}{\partial X_j} \underbrace{dX_j dX_i}_{=-dX_i dX_j} \tag{6.15}$$

$$= \frac{1}{2} \sum_{i,j} \left(\frac{\partial \alpha_i}{\partial X_j} - \frac{\partial \alpha_j}{\partial X_i} \right) dX_j dX_i . \tag{6.16}$$

The expression for $d\alpha$ of a p-form follows similarly by applying the rules (i)-(iv). The rules imply the most important relation for p forms,

$$d^2\alpha = d(d\alpha) = 0 . \tag{6.17}$$

Conversely, it can be shown that for any $p + 1$ form f on $\mathbb{R}^N$ such that $df = 0$ we must have $f = d\alpha$ for some p-form α. This result is often referred to as the **Poincaré lemma**.

---

[2]Mathematically, the differentials dX_i are the generators of a Grassmann algebra of dimension N.

An important and familiar example for this from field theory is provided by force fields $\vec{f}$ on $\mathbb{R}^3$. The components f_i of the force field may be identified with the components of a 1-form called $F = \sum f_i \mathrm{d}X_i$. The condition $\mathrm{d}F = 0$ is seen to be equivalent to $\vec{\nabla} \times \vec{f} = 0$, i.e. we have a conservative force field. Poincaré's lemma implies the existence of a potenial $-\mathcal{W}$, such that $F = -\mathrm{d}\mathcal{W}$; in vector notation, $\vec{f} = -\vec{\nabla}\mathcal{W}$. A similar statement is shown to hold for p-forms

Just as a 1-form can be integrated over oriented curves (1-dimensional surfaces), a p form can be integrated over an oriented p-dimensional surface Σ. If that surface is parameterized by N functions $X_i(t_1, ..., t_p)$ of p parameters $(t_1, \ldots, t_p) \in U \subset \mathbb{R}^p$ (the ordering of which defines an orientation of the surface), we define the corresponding integral as

$$\int_\Sigma \alpha = \int_U dt_1 ... dt_p \sum_{i_1, ..., i_p} \alpha_{i_1 ... i_p}(X(t_1, ..., t_p)) \frac{\partial X_{i_1}}{\partial t_1} ... \frac{\partial X_{i_p}}{\partial t_p} \ . \tag{6.18}$$

The value of this integral is independent of the chosen parameterization up to a sign which corresponds to our choice of orientation. The most important fact pertaining to integrals of differential forms is Gauss' theorem (also called Stokes' theorem in this context):

$$\int_\Sigma \mathrm{d}\alpha = \int_{\partial \Sigma} \alpha \ . \tag{6.19}$$

In particular, the integral of a form $\mathrm{d}\alpha$ vanishes if the boundary $\partial \Sigma$ of Σ is empty.

Using the language of differentials, the 1st law of thermodynamics may also be stated as saying that, in the absence of heat exchange, the infinitesimal work is an exact 1-form,

$$\mathrm{d}E = \delta W \ , \tag{6.20}$$

or alternatively,

$$\mathrm{d}\delta W = 0 \ . \tag{6.21}$$

We can break up the infinitesimal work change into the various forms of possible work such as in

$$\mathrm{d}E = \delta W = \sum_i \underbrace{J_i}_{\text{force}} \underbrace{\mathrm{d}X_i}_{\text{displacement}} = -P\mathrm{d}V + \mu\mathrm{d}N + \{\text{other types of work, see table}\} \ ,$$

$$\tag{6.22}$$

if the change of state is **adiabatic** (no heat transfer!). If there is heat transfer, then the

1$^{\text{st}}$ law gets replaced by

$$\boxed{\mathrm{d}E = \delta Q + \sum_i \underbrace{J_i}_{\text{force}} \underbrace{\mathrm{d}X_i}_{\text{displacement}} .} \qquad (6.23)$$

This relation is best viewed as the definition of the infinitesimal heat change δQ. Thus, we could say that the first law is just energy conservation, where energy can consist of either mechanical work or heat. We may then write

$$\delta Q = \mathrm{d}E - \sum_i \underbrace{J_i}_{\text{force}} \underbrace{\mathrm{d}X_i}_{\text{displacement}} \qquad (6.24)$$
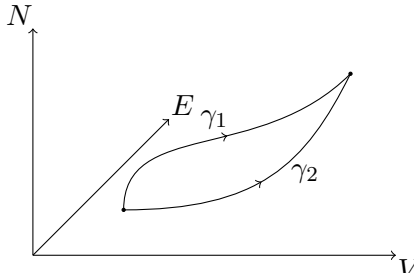
from which it can be seen that δQ is a 1-form depending on the variables $(E, X_1, ..., X_n)$.

An overview over several thermodynamic forces and displacements is given in the following table:

System	Force J_i	Displacement X_i
wire	tension F	length L
film	surface tension τ	area A
fluid/gas	pressure P	volume V
magnet	magnetic field $\vec{B}$	magnetization $\vec{M}$
electricity	electric field $\vec{E}$	polarization $\vec{\Pi}$
	stat. potential ϕ	charge q
chemical	chemical potential μ	particle number N

Table 6.1.: Some thermodynamic forces and displacements for various types of systems.

Since δQ is not an exact differential (in particular $\mathrm{d}\delta Q \neq 0$) we have

$$\Delta Q_1 = \int_{\gamma_1} \delta Q \neq \int_{\gamma_2} \delta Q = \Delta Q_2$$

So, there does *not* exist a function $Q = Q(V, A, N, \dots)$ such that $\delta Q = \mathrm{d}Q$! Traditionally, one refers to processes where $\delta Q \neq 0$ as "non-adiabatic", i.e. heat is transferred.

6.3. The Second Law

2ⁿᵈ law of thermodynamics (Kelvin): *There are no processes in which heat goes over from a reservoir, is **completely** converted to other forms of energy, and nothing else happens.*

One important consequence of the 2nd law is the existence of a state function S, called *entropy*. As before, we denote the n "displacement variables" generically by $X_i \in \{V, N, \ldots\}$ and the "forces" by $J_i \in \{-P, \mu, \ldots\}$, and consider equilibrium states labeled by $(E, \{X_i\})$ in an $n + 1$-dimensional space. We consider within this space the " adiabatic" submanifold $\mathcal{A}$ of all states that can be reached from a given state $(E^*, \{X_i^*\})$ by means of a **reversible** and **quasi-static** (i.e. sufficiently slowly performed) process. On this submanifold we must have

$$\mathrm{d}E - \sum_{i=1}^{n} J_i \mathrm{d}X_i = 0, \tag{6.25}$$

since otherwise there would exist processes disturbing the energy balance (through the exchange of heat), and we could then choose a sign of δQ such that work is performed on a system by converting heat energy into work, which is impossible by the 2nd law.

We choose a (not uniquely defined) function S labeling different submanifolds $\mathcal{A}$:
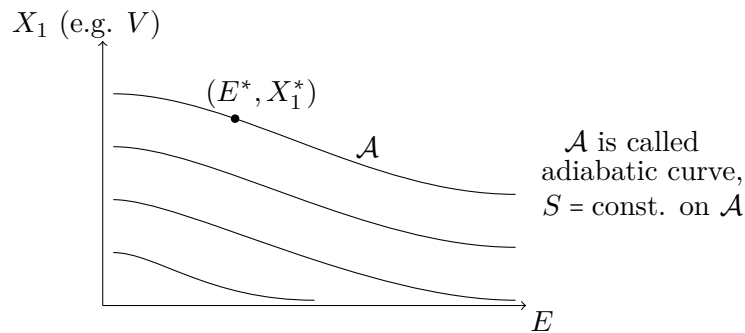
Figure 6.5.: Sketch of the submanifolds $\mathcal{A}$.

This means that $\mathrm{d}S$ is proportional to $\mathrm{d}E - \sum_{i=1}^{n} J_i \, \mathrm{d}X_i$. Thus, at each point $(E, \{X_i\})$ there is a function $\Theta(E, X_1, \ldots, X_n)$ such that

$$\Theta \mathrm{d}S = \mathrm{d}E - \sum_{i=1}^{n} J_i \mathrm{d}X_i \tag{6.26}$$

Θ can be identified with the temperature $T[\text{K}]$ for suitable choice of $S = S(E, X_1, \ldots, X_n)$,

which then uniquely defines S. This is seen for instance by comparing the coefficients in

$$T\mathrm{d}S = T\left(\frac{\partial S}{\partial E}\mathrm{d}E + \sum_{i=1}^{n}\frac{\partial S}{\partial X_i}\mathrm{d}X_i\right) = \mathrm{d}E - \sum_{i=1}^{n}J_i \ \mathrm{d}X_i, \tag{6.27}$$

which yields

$$0 = \underbrace{\left(T\frac{\partial S}{\partial E} - 1\right)}_{=0}\mathrm{d}E + \sum_{i=1}^{n}\underbrace{\left(\frac{\partial S}{\partial X_i} + J_i\right)}_{=0}\mathrm{d}X_i \tag{6.28}$$

Therefore, the following relations hold:

$$\frac{1}{T} = \frac{\partial S}{\partial E} \qquad \text{and} \qquad J_i = -\frac{\partial S}{\partial X_i}. \tag{6.29}$$

We recognize the first of those relations as the defining relation for temperature which was stated in the microcanocical ensemble (cf. section 4.2.1.). We can now rewrite (6.26) as

$$\boxed{\mathrm{d}E = T\mathrm{d}S + \sum_{i=1}^{n}J_i \ \mathrm{d}X_i = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N + \ldots} \tag{6.30}$$

By comparing this formula with that for energy conservation for a process **without** heat transfer, we identify

$$\delta Q = \text{heat transfer} = T\mathrm{d}S \quad \Rightarrow \quad \boxed{\mathrm{d}S = \frac{\delta Q}{T}} \quad (\text{noting that } d(\delta Q) \neq 0!). \tag{6.31}$$

Equation (6.30), which was derived for **quasi-static** processes, is the most important equation in thermodynamics.

Example: As an illustration, we calculate the **adiabatic curves $\mathcal{A}$ for an ideal gas**. The defining relation is, with $n = 1$ and $X_1 = V$ in this case

$$0 = \mathrm{d}E + P\mathrm{d}V.$$

Since $PV = Nk_{\mathrm{B}}T$ and $E = \frac{3}{2}Nk_{\mathrm{B}}T$ for the ideal gas, we find

$$P = P(E, V) = \frac{2}{3}\frac{E}{V}, \tag{6.32}$$

and therefore

$$0 = \mathrm{d}E + \frac{2}{3}\frac{E}{V}\mathrm{d}V. \tag{6.33}$$

Thus, we can parametrize the adiabatic $\mathcal{A}$ by $E = E(V)$, such that $\mathrm{d}E = \frac{\partial E(V)}{\partial V}\mathrm{d}V$ on

$\mathcal{A}$. We then obtain

$$0 = \underbrace{\left(\frac{\partial E}{\partial V} + \frac{2}{3}\frac{E}{V}\right)}_{=0}\mathrm{d}V$$

$$\Rightarrow \quad E(V) = E^*\left(\frac{V^*}{V}\right)^{2/3}$$
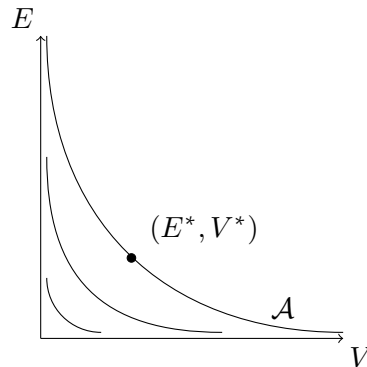
Figure 6.6.: Adiabatics of the ideal gas

Of course, we may also switch to other thermodynamic variables, like (S,V), such that E now becomes a function of (S,V):

$$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V = \left(\frac{\partial E}{\partial V}\right)\mathrm{d}V + \left(\frac{\partial E}{\partial S}\right)\mathrm{d}S \tag{6.34}$$

The defining relation for the adiabatics then reads

$$0 = \underbrace{\left(\frac{\partial E}{\partial V} + P\right)}_{=0}\mathrm{d}V + \underbrace{\left(\frac{\partial E}{\partial S} - T\right)}_{=0}\mathrm{d}S \tag{6.35}$$

from which it follows that

$$T = \left.\frac{\partial E}{\partial S}\right|_V \quad \text{and} \quad P = -\left.\frac{\partial E}{\partial V}\right|_S, \tag{6.36}$$

which hold generally (cf. section 4.2.1, eq. (4.17)). For an ideal gas ($PV = Nk_\mathrm{B}T$ and $E = \frac{3}{2}Nk_\mathrm{B}T$) we thus find

$$-\frac{\partial E}{\partial V}V = k_\mathrm{B}N\frac{\partial E}{\partial S},$$

$$E = \frac{3}{2}k_\mathrm{B}N\frac{\partial E}{\partial S}$$

which we can solve as

$$E(S,V) = E(S^*,V)e^{\frac{2}{3}\frac{S-S^*}{k_B N}}.$$ (6.37)

Since we also have

$$\frac{1}{E}\frac{\partial E}{\partial V} = -\frac{2}{3}\frac{1}{V},$$ (6.38)

we find for the function $E(S,V)$:

$$E(S,V) = E(S^*,V^*)\left(\frac{V^*}{V}\right)^{\frac{2}{3}} e^{\frac{2}{3}\frac{S-S^*}{k_B N}}.$$ (6.39)

Solving this relation for S, we obtain the relation

$$S = k_B N \log(c^* E^{\frac{3}{2}} V), \qquad (c^* \text{ involves } E^*, S^*, V^*).$$ (6.40)

This coincides with the expression (4.16), found in section 4.2.1 with the help of classical statistical mechanics provided we set $c^* = (4\pi m)^{\frac{3}{2}}\left(\frac{e}{N}\right)^{\frac{5}{2}}$. Indeed, we find in that case

$$S = Nk_B \log\left[\frac{V}{N}\left(\frac{4\pi em}{3}\frac{E}{N}\right)^{\frac{3}{2}}\right]$$ (6.41)

This coincides with the formula found before in the context of the micro canonical ensemble. (Note the we must treat the particles there as indistinguishable and include the $\frac{1}{N!}$ into the definition of the microcanonical partition function $W(E,N,V)$ for indistinguishable particles, cf. section 4.2.3).

6.4. Cyclic processes

6.4.1. The Carnot Engine

We next discuss the **Carnot engine** for an **ideal** (mono atomic) gas. As discussed in section 4.2., the ideal gas is characterized by the relations:

$$E = \frac{3}{2}Nk_B T = \frac{3}{2}PV.$$ (6.42)

We consider the cyclic process consisting of the following steps:

I → II: isothermal expansion at $T = T_H$,

II → III: adiabatic expansion $(\delta Q = 0)$,

III → IV: isothermal compression at $T = T_C$,

IV → I: adiabatic compression

where we assume $T_H > T_C$.

We want to work out the **efficiency** η, which is defined as

$$\eta := \frac{\Delta W}{\Delta Q_{\text{in}}} \tag{6.43}$$

where

$$\Delta Q_{\text{in}} = \int_I^{II} \delta Q$$

is the total heat added to the system (analogously, $\Delta Q_{\text{out}} = \int_{III}^{IV} \delta Q$ is the total heat given off by system into a colder reservoir), and where

$$\Delta W = \oint \delta W = \left(\int_I^{II} + \int_{II}^{III} + \int_{III}^{IV} + \int_{IV}^{I} \right) \delta W$$

is the total work done by the system. We may also write $\delta Q = T \mathrm{d}S$ and $\delta W = P \mathrm{d}V$ (or more generally $\delta W = -\sum_{i=1}^{n} J_i dX_i$ if other types of mechanical/ chemical work are performed by the system). By definition no heat exchange takes place during II $\to$ III and IV $\to$ I.

We now wish to calculate η_{Carnot}. We can for instance take P and V as the variables to describe the process. We have $PV = \text{const.}$ for isothermal processes by (6.42). To calculate the adiabatics, we could use the results from above and change the variables from $(E, V) \to (P, V)$ using (6.42), but it is just as easy to do this from scratch: We start with $\delta Q = 0$ for an adiabatic process. From this follows that

$$0 = \mathrm{d}E + P \mathrm{d}V \tag{6.44}$$

Since on adiabatics we may take $P = P(V)$, this yields

$$\mathrm{d}E = \frac{3}{2} \mathrm{d}(PV) = \frac{3}{2} \left(V \frac{\partial P}{\partial V} + P \right) \mathrm{d}V, \tag{6.45}$$

and therefore

$$0 = \frac{3}{2} \mathrm{d}(PV) + P \mathrm{d}V = \underbrace{\left(\frac{3}{2} V \frac{\partial P}{\partial V} + \frac{5}{2} P \right)}_{=0} \mathrm{d}V. \tag{6.46}$$

This yields the following relation:

$$V \frac{\partial P}{\partial V} = -\frac{5}{3} P, \quad \Rightarrow \quad PV^{\gamma} = \text{const.}, \quad \gamma = \frac{5}{3} \tag{6.47}$$

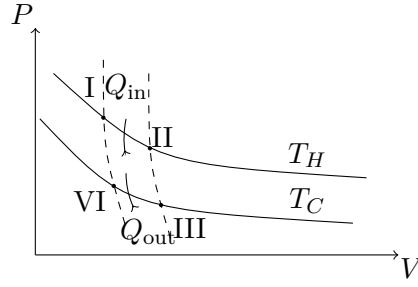So in a (P, V)-diagram the Carnot process looks as follows:

Figure 6.7.: Carnot cycle for an ideal gas. The solid lines indicate isotherms and the dashed lines indicate adiabatics.

From $E = \frac{3}{2}PV$, which gives $\mathrm{d}E = 0$ on isotherms, it follows that the total heat added to the system is given by

$$\Delta Q_{\mathrm{in}} = \int_I^{II} \underbrace{(\mathrm{d}E + P\mathrm{d}V)}_{\substack{\text{1}^{\text{st}}\text{ law} \\ \delta Q = \mathrm{d}E + P\mathrm{d}V}} = \int_I^{II} \underbrace{P\mathrm{d}V}_{\substack{\text{from } \mathrm{d}E=0 \\ \text{on isotherms}}}$$

$$= N k_B T_H \underbrace{\int_I^{II} V^{-1}\mathrm{d}V}_{PV = Nk_B T_H \text{ on isotherm}}$$

$$= N k_B T_H \log \frac{V_{II}}{V_I}. \tag{6.48}$$

Using this result together with $P\mathrm{d}V = -\mathrm{d}E$ on adiabatics we find for the total mechanical work done by the system:

$$\Delta W = \int_I^{II} P\mathrm{d}V + \int_{II}^{III} P\mathrm{d}V + \int_{III}^{IV} P\mathrm{d}V + \int_{IV}^{I} P\mathrm{d}V$$

$$= N k_B T_H \log \frac{V_{II}}{V_I} - \int_{II}^{III} \mathrm{d}E - N k_B T_C \log \frac{V_{III}}{V_{IV}} - \int_{IV}^{I} \mathrm{d}E$$

$$= E_{II} - E_{III} + E_{IV} - E_I + N k_B \left(T_H \log \frac{V_{II}}{V_I} - T_C \log \frac{V_{III}}{V_{IV}} \right).$$

By conservation of energy, $\oint \mathrm{d}E = 0$, we get

$$E_{II} - E_{III} + E_{IV} - E_I = E_{II} - E_I + E_{IV} - E_{III}$$

$$= \int_I^{II} \mathrm{d}E \quad + \quad \int_{III}^{IV} \mathrm{d}E = 0,$$

since $dE = d\left(\frac{3}{2}Nk_BT\right) = 0$ on isotherms. From this it follows that

$$\Delta W = Nk_B\left(T_H \log\frac{V_{II}}{V_I} - T_C \log\frac{V_{III}}{V_{IV}}\right). \qquad (6.49)$$

We can now use (6.48) and (6.49) to find

$$\eta_{\text{Carnot}} = \frac{\Delta W}{\Delta Q_{\text{in}}} = 1 - \frac{T_C}{T_H}\frac{\log V_{III}/V_{IV}}{\log V_{II}/V_I} \qquad (6.50)$$

The relation (6.47) for the adiabatics, together with the ideal gas condition (6.42) implies

$$P_{II}V_{II}^{\gamma} = P_{III}V_{III}^{\gamma} \;\Rightarrow\; T_H V_{II}^{\gamma-1} = T_C V_{III}^{\gamma-1},$$

$$P_I V_I^{\gamma} = P_{IV}V_{IV}^{\gamma} \;\Rightarrow\; T_H V_I^{\gamma-1} = T_C V_{IV}^{\gamma-1},$$

$$\Rightarrow \frac{V_{II}}{V_I} = \frac{V_{III}}{V_{IV}}.$$

We thus find for the efficiency of the Carnot cycle

$$\boxed{\eta = 1 - \frac{T_C}{T_H}} \qquad (6.51)$$

This fundamental relation for the efficiency of a Carnot cycle can be derived also using the variables (T,S) instead of (P,V), which also reveals the distinguished role played by this process. As $dT = 0$ for isotherms and $dS = 0$ for adiabatic processes, the Carnot cycle is just a rectangle in the T-S-diagram:
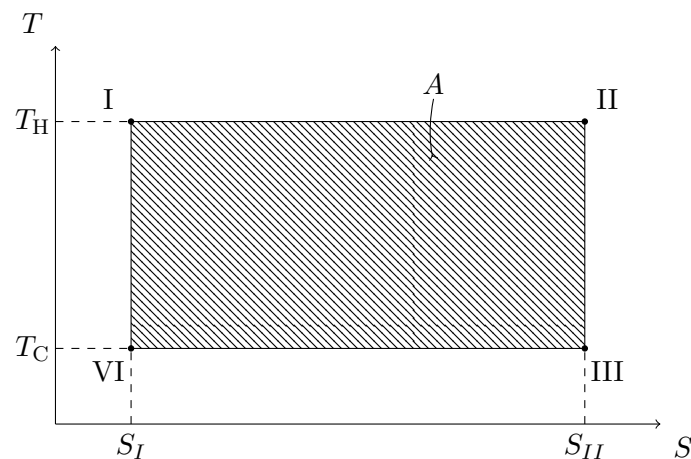

Figure 6.8.: The Carnot cycle in the (T,S)-diagram.

We evidently have for the total heat added to the system:

$$\Delta Q_{\text{in}} = \int_I^{II} \delta Q = \int_I^{II} TdS = T_H(S_{II} - S_I). \tag{6.52}$$

To compute ΔW, the total mechanical work done by the system, we observe that (as $\oint \mathrm{d}E = 0$)

$$\begin{aligned} \Delta W &= \oint \delta W = \oint P\mathrm{d}V \\ &= \oint (P\mathrm{d}V + \mathrm{d}E) \\ &= \oint T\mathrm{d}S. \end{aligned}$$

If A is the domain enclosed by the rectangular curve describing the process in the T-S diagram, Gauss' theorem gives

$$\begin{aligned} \Delta W &= \oint T\mathrm{d}S = \int_A \mathrm{d}(T\mathrm{d}S) = \int_A \mathrm{d}T\mathrm{d}S \\ &= (T_H - T_C)(S_{II} - S_I), \end{aligned}$$

from which it immediately follows that the efficiency η_{Carnot} is given by

$$\eta_{\text{Carnot}} = \frac{\Delta W}{\Delta Q_{\text{in}}} = \frac{(T_H - T_C)\Delta S}{T_H \Delta S} = 1 - \frac{T_C}{T_H} < 1, \tag{6.53}$$

as before. *Since $T_H > T_C$, the efficiency can never be 100%.*

6.4.2. General Cyclic Processes

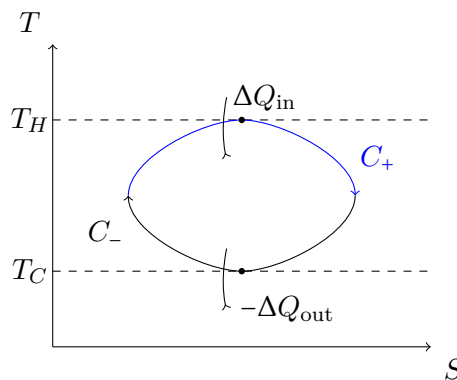Consider now the more general cycle given by the curve C in the (T, S)-diagram depicted in the figure below:

Figure 6.9.: A generic cyclic process in the (T, S)-diagram.

We define $C_\pm$ to be the part of of the boundary curve C where heat is injected resp. given off. Then we have $dS > 0$ on C_+ and $dS < 0$ on C_-. For such a process, we define the efficiency $\eta = \eta(C)$ as before by the ratio of net work ΔW and injected heat ΔQ_{in}:

$$\eta = \frac{\Delta W}{\Delta Q_{\text{in}}}. \tag{6.54}$$

The quantities ΔW and ΔQ_{in} are then calculated as

$$\Delta W = -\oint_C \delta W = \oint_C (T dS - dE) = \oint_C T dS,$$

$$\Delta Q_{\text{in}} = \int_{C_+} T dS,$$

from which it follows that the efficiency $\eta = \eta(C)$ is given by

$$\eta = \frac{\oint_C T dS}{\int_{C_+} T dS} = 1 + \frac{\int_{C_-} T dS}{\int_{C_+} T dS} = 1 - \frac{\Delta Q_{\text{in}}}{\Delta Q_{\text{out}}}. \tag{6.55}$$

Now, if the curve C is completely contained between two isotherms at temperatures $T_H > T_C$, as in the above figure, then

$$0 \le \int_{C_+} T dS \le T_H \int_{C_+} dS \qquad (\text{as } dS < 0 \text{ on } C_+),$$

$$\int_{C_-} T dS \le T_C \int_{C_-} dS \le 0 \quad (\text{as } dS \le 0 \text{ on } C_-).$$

The efficiency η_C of our general cycle C can now be estimated as

$$\eta_C = 1 + \frac{\int_{C_-} T dS}{\int_{C_+} T dS} \le 1 + \frac{T_C \int_{C_-} dS}{T_H \int_{C_+} dS} = 1 - \frac{T_C}{T_H} = \eta_{\text{Carnot}}, \tag{6.56}$$

where we used the above inequalities as well as $0 = \oint dS = \int_{C_+} dS + \int_{C_-} dS$. Thus, we conclude that an arbitrary process is always less efficient than the Carnot process. This is why the Carnot process plays a distinguished role.

We can get a more intuitive understanding of this important finding by considering the following process:
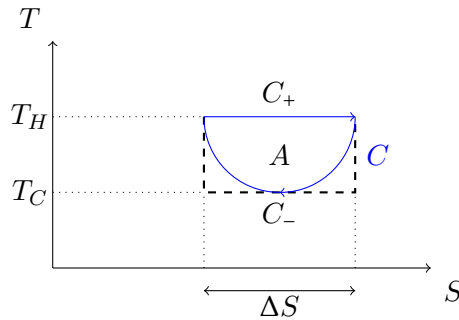
The heat ΔQ_{in} is given by $\Delta Q_{\text{in}} = T_H \Delta S$, and as before $\Delta W = \int_C T \mathrm{d}S = \int_A \mathrm{d}T \mathrm{d}S$. Thus, ΔW is the area A enclosed by the closed curve C. This is clearly smaller than the area enclosed by the corresponding Carnot cycle (dashed rectangle). Now divide a general cyclic process into $C = C_1 \cup C_2$, as sketched in the following figure:
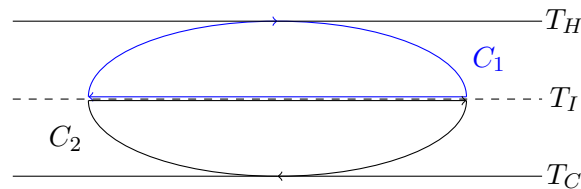
Figure 6.10.: A generic cyclic process divided into two parts by an isotherm at temperature T_I.

This process describes two cylic processes acting one after the other, where the heat dropped during cycle C_1 is injected during cycle C_2 at temperature T_I. It follows from the discussion above that

$$\eta(C_2) = \frac{\Delta W_2}{\Delta Q_{2,\text{in}}} \leq \frac{T_I - T_C}{T_I} = 1 - \frac{T_C}{T_I}, \tag{6.57}$$

which means that the cycle C_2 is less efficient than the Carnot process acting between temperatures T_I and T_C. It remains to show that the cycle C_1 is also less efficient than the Carnot cycle acting betweeen temperatures T_H and T_I. The work ΔW_1 done along C_1 is again smaller than the area enclosed by the latter Carnot cycle, i.e. we have $\Delta W_1 \leq (T_H - T_I)\Delta S$. Furthermore, we must have $\Delta Q_{1,\text{in}} \geq \Delta Q_{1,\text{out}} = T_I \Delta S$, which yields

$$\eta(C_1) = \frac{\Delta W_1}{\Delta Q_{1,\text{in}}} \leq \frac{T_H - T_I}{T_I} \leq 1 - \frac{T_I}{T_H}.$$

Thus, the cycle C_1 is less efficient than the Carnot cycle acting between temperatures T_H and T_I. It follows that the cycle $C = C_1 \cup C_2$ must be less efficient than the Carnot cycle acting between temperatures T_H and T_C.

6.4.3. The Diesel Engine

Another example of a cyclic process is the **Diesel engine**. The idealized version of this process consists of the following 4 steps:

      I → II: isentropic (adiabatic) compression

      II → III: reversible heating at constant pressure

      III → IV: adiabatic expansion with work done by the expanding fluid

      IV → I: reversible cooling at constant volume
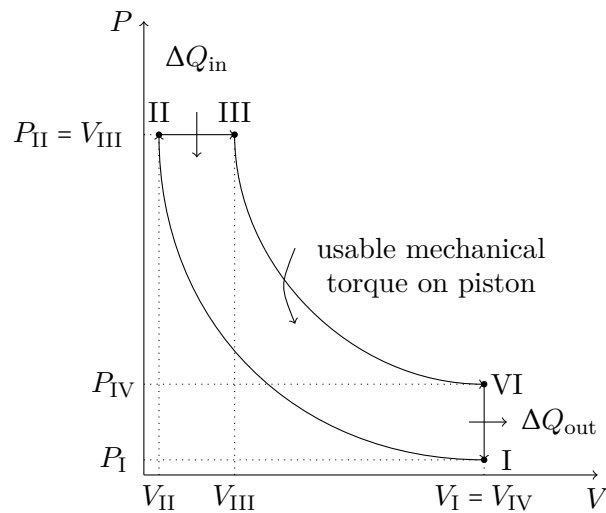
Figure 6.11.: The process describing the Diesel engine in the (P, V)-diagram.

As before, we define the thermal efficiency to be

$$\eta_{\text{Diesel}} = \frac{\Delta W}{\Delta Q_{\text{in}}} = \frac{\left(\int_I^{II} + \int_{II}^{III} + \int_{III}^{IV} + \int_{IV}^{I} \right) T \mathrm{d}S}{\int_{II}^{III} T \mathrm{d}S}$$

As in the discussion of the Carnot process we use an ideal gas, with $V = N k_{\text{B}} T$, $E = \frac{3}{2} PV$, and $\mathrm{d}E = T \mathrm{d}S - P \mathrm{d}V$. Since $\mathrm{d}S = 0$ on the paths I → II and III → IV, it follows that

$$\eta_{\text{Diesel}} = 1 + \frac{\int_{IV}^{I} T \mathrm{d}S}{\int_{II}^{III} T \mathrm{d}S}. \tag{6.58}$$

Using (6.42), the integrals in this expression are easily calculated as

$$\int\limits_{IV}^{I} T\mathrm{d}S = \int\limits_{IV}^{I} (\mathrm{d}E + P\mathrm{d}V) = \int\limits_{IV}^{I} \left(\frac{3}{2}V\mathrm{d}P + \frac{5}{2}P \underbrace{\mathrm{d}V}_{=0} \right)$$

$$= \frac{3}{2}N\mathrm{k_B}(T_I - T_{IV}),$$

$$\int\limits_{II}^{III} T\mathrm{d}S = \int\limits_{II}^{III} (\mathrm{d}E + P\mathrm{d}V) = \int\limits_{II}^{III} \left(\frac{3}{2}V \underbrace{\mathrm{d}P}_{=0} + \frac{5}{2}P\mathrm{d}V \right)$$

$$= \frac{5}{2}N\mathrm{k_B}(T_{III} - T_{II}),$$

which means that the efficiency η_{Diesel} is given by

$$\eta_{\text{Diesel}} = 1 - \frac{3}{5}\frac{T_{IV} - T_I}{T_{III} - T_{II}} \tag{6.59}$$

6.5. Thermodynamic potentials

The first law can be rewritten in terms of other "thermodynamic potentials", which are sometimes useful, and which are naturally related to different equilibrium ensembles. We start from the 1$^{\text{st}}$ law of thermodynamics in the form

$$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N + \dots \left(= T\mathrm{d}S + \sum_{i=1}^{n} J_i \, \mathrm{d}X_i \right). \tag{6.60}$$

By (6.60) E is naturally viewed as a function of (S, V, N) (or more generally of S and $\{X_i\}$). To get a thermodynamic potential that naturally depends on (T, V, N) (or more generally, T and $\{X_i\}$), we form the **free energy**

$$\boxed{F = E - TS}. \tag{6.61}$$

Taking the differential of this, we get

$$\mathrm{d}F = \mathrm{d}E - S\mathrm{d}T - T\mathrm{d}S$$

$$= T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N + \dots - S\mathrm{d}T - T\mathrm{d}S$$

$$= -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N + \dots$$

$$\left(= -S\mathrm{d}T + \sum_{i=1}^{n} J_i \, \mathrm{d}X_i \right).$$

Writing out the differential dF as

$$dF = \left.\frac{\partial F}{\partial T}\right|_{V,N} dT + \left.\frac{\partial F}{\partial V}\right|_{T,N} dV + \dots \tag{6.62}$$

and comparing the coefficients, we get

$$0 = \left(\left.\frac{\partial F}{\partial T}\right|_{V,N} + S\right)dT + \left(\left.\frac{\partial F}{\partial V}\right|_{T,N} + P\right)dV + \left(\left.\frac{\partial F}{\partial N}\right|_{T,V} - \mu\right)dN + \dots . \tag{6.63}$$

This yields the following relations:

$$\boxed{S = -\left.\frac{\partial F}{\partial T}\right|_{V,N}, \quad P = -\left.\frac{\partial F}{\partial V}\right|_{T,N}, \quad \mu = \left.\frac{\partial F}{\partial N}\right|_{T,V}, \quad \dots} . \tag{6.64}$$

By the first of these equations, the entropy $S = S(T,V,N)$ is naturally a function of (T,V,N), which suggests a relation between F and the **canonical ensemble**. As discussed in section 4.3, in this ensemble we have

$$\rho = \rho(T,V,N) = \frac{1}{Z}e^{-\frac{H(N,V)}{k_B T}} \quad \text{and} \quad S = -k_B \text{tr}\rho \log \rho. \tag{6.65}$$

We now seek an F satisfying $S = -\left.\frac{\partial F}{\partial T}\right|_{V,N}$. A simple calculation shows

$$\boxed{F(T,V,N) = -k_B T \log Z(T,V,N)} \tag{6.66}$$

Indeed:

$$\frac{\partial F}{\partial T} = -k_B \left\{ \log \text{tr}e^{-\frac{H}{k_B T}} + \frac{1}{k_B T}\frac{\text{tr}He^{-\frac{H}{k_B T}}}{\text{tr}e^{-\frac{H}{k_B T}}} \right\}$$

$$= k_B \text{tr}\rho \log \rho = -S$$

In the same way, we may look for a function G of the variables (T,μ,V). To this end, we form the **grand potential**

$$\boxed{G = E - TS - \mu N = F - \mu N} \tag{6.67}$$

The differential of G is

$$\mathrm{d}G = \mathrm{d}F - \mu\mathrm{d}N - N\mathrm{d}\mu$$

$$= -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N - \mu\mathrm{d}N - N\mathrm{d}\mu$$

$$= -S\mathrm{d}T - P\mathrm{d}V - N\mathrm{d}\mu$$

Writing out $\mathrm{d}G$ as

$$\mathrm{d}G = \left.\frac{\partial G}{\partial T}\right|_{V,\mu} \mathrm{d}T + \left.\frac{\partial G}{\partial V}\right|_{T,\mu} \mathrm{d}V + \dots$$

and comparing the coefficients, we get

$$0 = \left(\left.\frac{\partial G}{\partial T}\right|_{V,\mu} + S\right)\mathrm{d}T + \left(\left.\frac{\partial G}{\partial V}\right|_{T,\mu} + P\right)\mathrm{d}V + \left(\left.\frac{\partial G}{\partial \mu}\right|_{T,V} + N\right)\mathrm{d}\mu,$$

which yields the relations

$$S = -\left.\frac{\partial G}{\partial T}\right|_{V,\mu}, \qquad N = -\left.\frac{\partial G}{\partial \mu}\right|_{T,V}, \qquad P = -\left.\frac{\partial G}{\partial V}\right|_{T,\mu}. \tag{6.68}$$

In the first of these equations, S is naturally viewed as a function of the variables (T,μ,V), suggesting a relationship between G and the **grand canonical ensemble**. As discussed in section 4.4, in this ensemble we have

$$\rho(T,\mu,V) = \frac{1}{Y}e^{-\frac{(H(V)-\mu\hat{N})}{k_{\mathrm{B}}T}} \quad \text{and} \quad S = -k_{\mathrm{B}}\mathrm{tr}\rho\log\rho. \tag{6.69}$$

We now seek a function G satisfying $S = -\left.\frac{\partial G}{\partial T}\right|_{\mu,V}$ and $N = -\left.\frac{\partial G}{\partial \mu}\right|_{T,V}$. An easy calculation reveals

$$G(T,\mu,V) = -k_{\mathrm{B}}T\log Y(T,\mu,V) \tag{6.70}$$

Indeed:

$$\frac{\partial G}{\partial T} = -k_{\mathrm{B}}\left\{\log\mathrm{tr}e^{-\frac{(H-\mu\hat{N})}{k_{\mathrm{B}}T}} + \frac{1}{k_{\mathrm{B}}T}\frac{\mathrm{tr}(H-\mu\hat{N})e^{-\frac{(H-\mu\hat{N})}{k_{\mathrm{B}}T}}}{\mathrm{tr}e^{-\frac{(H-\mu\hat{N})}{k_{\mathrm{B}}T}}}\right\}$$

$$= k_{\mathrm{B}}\mathrm{tr}\rho\log\rho = -S$$

The second relation can be demonstrated in a similar way (with $N = \langle\hat{N}\rangle$). To get a function H which naturally depends on the variables (P,T,N), we form the **free**

enthalpy (or **Gibbs potential**)

$$\boxed{H = E - TS + PV = F + PV} \ . \tag{6.71}$$

It satisfies the relations

$$\boxed{S = -\left.\frac{\partial H}{\partial T}\right|_{P,N} , \quad \mu = \left.\frac{\partial H}{\partial N}\right|_{P,T} , \quad V = \left.\frac{\partial H}{\partial P}\right|_{N,T}} \ . \tag{6.72}$$

or equivalently

$$\mathrm{d}H = -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}N. \tag{6.73}$$

The free[3] enthalpy is often used in the context of chemical processes, because these naturally occur at constant atmospheric pressure. For processes at constant pressure P (isobaric processes) we then have

$$\mathrm{d}H = -S\mathrm{d}T + \mu\mathrm{d}N. \tag{6.74}$$

Assuming that the entropy $S = S(E, V, N_i, \ldots)$ is an extensive quantity, we can derive relations between the various potentials. The extensivity property of S means that

$$S(\lambda E, \lambda V, \lambda N_i) = \lambda S(E, V, N_i), \quad \text{for } \lambda > 0. \tag{6.75}$$

Taking the partial derivative $\frac{\partial}{\partial \lambda}$ of this expression gives

$$S = \left.\frac{\partial S}{\partial E}\right|_{V,N_i} E + \left.\frac{\partial S}{\partial V}\right|_{E,N_i} V + \sum_i \left.\frac{\partial S}{\partial N_i}\right|_{V,E} N_i. \tag{6.76}$$

Together with the relations

$$\left.\frac{\partial S}{\partial E}\right|_{V,N_i} = \frac{1}{T}, \quad , \quad \left.\frac{\partial S}{\partial V}\right|_{E,N_i} = \frac{P}{T}, \quad \left.\frac{\partial S}{\partial N_i}\right|_{V,E} = -\frac{\mu_i}{T} \tag{6.77}$$

we find the **Gibbs-Duhem relation** (after multiplication with T):

$$\boxed{E + PV - \sum_i \mu_i N_i - TS = 0} \ , \tag{6.78}$$

or equivalently

$$H = \sum_i \mu_i N_i. \tag{6.79}$$

---

[3]One also uses the enthalpy defined as $E + PV$. Its natural variables are T, P, N which is more useful for processes leaving N unchanged.

Let us summarize the properties of the potentials we have discussed so far in a table:

Thermodynamic potential	Definition	Fundamental equation	Natural variables
internal energy E		$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N$	S, V, N
free energy F	$F = E - TS$	$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N$	T, V, N
grand potential G	$G = E - TS - \mu N$	$\mathrm{d}G = -S\mathrm{d}T - P\mathrm{d}V - N\mathrm{d}\mu$	T, V, μ
free enthalpy H	$H = E - TS + PV$	$\mathrm{d}H = -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}N$	T, P, N

Table 6.2.: Relationship between various thermodynamic potentials

The relationship between the various potentials can be further elucidated by means of the Legendre transform (cf. exercises). This characterization is important because it makes transparent the convexity respectively concavity properties of G, F following from the convexity of S.

6.6. Chemical Equilibrium

We consider chemical reactions characterized by a k-tuple $\underline{r} = (r_1, \dots, r_k)$ of integers corresponding to a chemical reaction of the form

$$\sum_{r_i < 0} |r_i| \chi_i \leftrightarrows \sum_{r_i > 0} |r_i| \chi_i, \tag{6.80}$$

where χ_i is the chemical symbol of the i-th compound. For example, the reaction

$$\mathrm{C} + \mathrm{O}_2 \leftrightarrows \mathrm{CO}_2$$
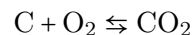
is described by $\chi_1 = \mathrm{C}$, $\chi_2 = \mathrm{O}_2$, $\chi_3 = \mathrm{CO}_2$ and $r_1 = -1, r_2 = -1, r_3 = +1$, or $\underline{r} = (-1, -1, +1)$. The full system is described by some complicated Hamiltonian $H(V)$ and number operators $\hat{N}_i$ for the i-th compound. Since the dynamics can change the particle number, we will have $\left[H(V), \hat{N}_i\right] \neq 0$ in general. We imagine that an entropy $S(E, V, \{N_i\})$ can be assigned to an ensemble of states with energy between $E - \Delta E$ and E, and average particle numbers $\left\{N_i = \langle \hat{N}_i \rangle\right\}$, but we note that the definition of S in microscopic terms is far from obvious because $\hat{N}_i$ is not a constant of motion.

The entropy should be maximized in equilibrium. Since $\underline{N} = (N_1, \dots, N_k)$ changes by

$\underline{r} = (r_1, \ldots, r_k)$ in a reaction, the necessary condition for equilibrium is

$$\frac{d}{dn}S(E, V, \underline{N} + n\underline{r})\Big|_{n=0} = 0. \tag{6.81}$$

Since by definition $\frac{\partial S}{\partial N_i}\Big|_{V,E} = -\frac{\mu_i}{T}$, in equilibrium we must have

$$\boxed{0 = \underline{\mu} \cdot \underline{r} = \sum_{i=1}^{k} \mu_i r_i} \;. \tag{6.82}$$

Let us now assume that in equilibrium we can use the expression for μ_i of an **ideal gas** with k distinguishable components and N_i indistinguishable particles of the i-th component. This is basically the assumption that interactions contribute negligibly to the entropy of the equilibrium state. According to the discussion in section 4.2.3 the total entropy is given by

$$S = \sum_{i=1}^{k} S_i + \Delta S, \tag{6.83}$$

where $S_i = S(E_i, V_i, N_i)$ is the entropy of the i-th species, ΔS is the mixing entropy, and we have

$$\frac{N_i}{V_i} = \frac{N}{V}, \quad \sum N_i = N, \quad \sum V_i = V, \quad \sum E_i = E. \tag{6.84}$$

The entropy of the i-th species is given by

$$S_i = N_i k_B \left[\log \frac{eV_i}{N_i} + \log \left(\frac{4}{3} \frac{E_i}{N_i} \pi e m_i \right)^{\frac{3}{2}} \right]. \tag{6.85}$$

The mixing entropy is given by

$$\Delta S = -N k_B \sum_{i=1}^{k} (c_i \log c_i - c_i), \tag{6.86}$$

where $c_i = \frac{N_i}{N}$ is the concentration of the i-th component. Let $\bar{\mu}_i$ be the chemical potential of the i-th species without taking into account the contribution due to the mixing:

$$\frac{\bar{\mu}_i}{T} = -\frac{\partial S_i}{\partial N_i}\Big|_{V_i, E_i} = k_B \log \left[\frac{V_i}{N_i} \left(\frac{4\pi m_i E_i}{3 N_i} \right)^{\frac{3}{2}} \right]$$

$$= -\frac{S_i}{N_i} + \frac{5}{2} k_B.$$

We have for the total chemical potential for the i-speicies:

$$\mu_i = \bar{\mu}_i + k_B T \log c_i$$

$$= \frac{5}{2} k_B T - \frac{S_i T}{N_i} + k_B T \log c_i$$

$$= \frac{1}{N_i}(E_i + PV_i - TS_i) + k_B T \log c_i$$

$$= \underbrace{h_i}_{\substack{= H_i/N_i = \text{free enthalpy} \\ \text{per particle for species } i}} + k_B T \log c_i,$$

where we have used the equations of state for the ideal gas for each species. From this it follows that the condition for equilibrium becomes

$$0 = \sum_i \mu_i \cdot r_i = \sum_i (h_i r_i + k_B T \log c_i^{r_i}), \tag{6.87}$$

which yields

$$1 = e^{\frac{\Delta h}{k_B T}} \prod_i c_i^{r_i}, \tag{6.88}$$

or equivalently

$$\boxed{e^{-\frac{\Delta h}{k_B T}} = \frac{\prod\limits_{r_i > 0} c_i^{|r_i|}}{\prod\limits_{r_i < 0} c_i^{|r_i|}}}, \tag{6.89}$$

with $\Delta h = \sum_i r_i h_i$ the enthalpy increase for one reaction. The above relation is sometimes called the "mass-action law". It is clearly in general not an exact relation, because we have treated the constituents as ideal gases. Nevertheless, it is often a surprisingly good approximation.

6.7. Phase Co-Existence and Clausius-Clapeyron Relation

We consider a system comprised of k compounds with particle numbers $N_1, \ldots, N_k$. It is assumed that chemical reactions are *not* possible, so each N_i is conserved. The entropy is assumed to be given as a function of $S = S(\underline{X})$, where $\underline{X} = (E, V, N_1, \ldots, N_k)$ (here we also include E into the thermodynamic coordinates.) We assume that the system is in an equilibrium state with coexisting pure phases which are labeled by $\alpha = 1, \ldots, \varphi$. The equilibrium state for each phase α is thus characterized by some vector $\underline{X}^{(\alpha)}$, or rather the corresponding ray $\{\lambda \underline{X}^{(\alpha)} \mid \lambda > 0\}$ since we can scale up the volume, energy, and numbers of particles by a positive constant. The temperature T, pressure P, and

chemical potentials μ_i must have the same value in each phase, i.e. we have for all α:

$$\frac{\partial S}{\partial E}(\underline{X}^{(\alpha)}) = \frac{1}{T}, \quad \frac{\partial S}{\partial V}(\underline{X}^{(\alpha)}) = \frac{P}{T}, \quad \frac{\partial S}{\partial N_i}(\underline{X}^{(\alpha)}) = -\frac{\mu_i}{T}. \tag{6.90}$$

We define a $(k+2)$-component vector $\underline{\xi}$, which is is independent of α, as follows:

$$\underline{\xi} = \left(\frac{1}{T}, \frac{P}{T}, -\frac{\mu_1}{T}, \dots, -\frac{\mu_k}{T} \right) \tag{6.91}$$

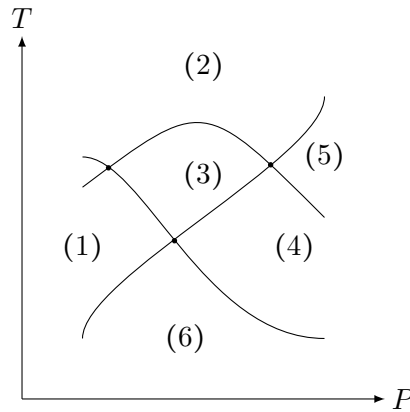As an example consider the following phase diagram for 6 phases:

Figure 6.12.: Imaginary phase diagram for the case of 6 different phases. At each point on a phase boundary which is not an intersection point, $\varphi = 2$ phases are supposed to coexist. At each intersection point $\varphi = 4$ phases are supposed to coexist.

From the discussion in the previous sections we know that

(1) S is **extensive** in equilibrium:

$$S(\lambda \underline{X}) = \lambda S(\underline{X}), \quad \lambda > 0. \tag{6.92}$$

(2) S is a **concave** function in $\underline{X} \in \mathbb{R}^{k+2}$ (subadditivity), and

$$\sum_\alpha \lambda^{(\alpha)} S(\underline{X}^{(\alpha)}) \leq S(\sum_\alpha \lambda^{(\alpha)} \underline{X}^{(\alpha)}), \tag{6.93}$$

as long as $\sum_\alpha \lambda^{(\alpha)} = 1, \lambda^{(\alpha)} \geq 0$. Since the coexisting phases are in equilibrium with each other, we must have "=" rather than "<" in the above inequality. Otherwise, the entropy would be maximized for some non-trivial linear combination $\underline{X}_{\min} = \sum_\alpha \lambda^{(\alpha)} \underline{X}^{(\alpha)}$, and only one homogeneous phase given by this minimizer $\underline{X}_{\min}$ could be realized.

By (1) and (2) it follows that in the region $C \subset \mathbb{R}^{2+k}$, where several phases can coexist,

S is **linear**, $S(\underline{X}) = \underline{\xi} \cdot \underline{X}$ for all $\underline{X} \in C$, $\underline{\xi}$ = const. in C, and C consists of **positive** linear combinations

$$C = \left\{ \underline{X} = \sum_{\alpha=1}^{\varphi} \lambda^{(\alpha)} \underline{X}^{(\alpha)} \quad : \quad \lambda^{(\alpha)} \geq 0 \right\}, \tag{6.94}$$

in other words, the coexistence region C is a convex cone generated by the vectors $\underline{X}^{(\alpha)}, \alpha = 1, \ldots, \varphi$. The set of points in the space $(P, T, \{c_i\})$ where equilibrium between φ phases holds (i.e. the phase boundaries in a $P - T - \{c_i\}$ –diagram) can be characterized as follows. Since $\underline{\xi}$ is constant within the convex cone C, we have for any $\underline{X} \in C$ and any $\alpha = 1, \ldots, \varphi$ and any I:

$$0 = \frac{d}{d\lambda} \xi_I(\underline{X} + \lambda \underline{X}^{(\alpha)}) \bigg|_{\lambda=0} = \sum_J X_J^{(\alpha)} \frac{\partial}{\partial X_J} \xi_I(\underline{X}) = \sum_J X_J^{(\alpha)} \frac{\partial^2}{\partial X_J \partial X_I} S(\underline{X})$$

$$= \sum_J X_J^{(\alpha)} \frac{\partial^2}{\partial X_I \partial X_J} S(\underline{X})$$

$$= \sum_J X_J^{(\alpha)} \frac{\partial}{\partial X_I} \xi_J(\underline{X}) ,$$

where we denote the $k + 2$ components of $\underline{X}$ by $\{X_I\}$. Multiplying this equation by dX_I and summing over I, this relation can be written as

$$\boxed{\underline{X}^{(\alpha)} \cdot d\underline{\xi} = 0,} \tag{6.95}$$

which must hold in the coexistence region C. Since the equation must hold for all $\alpha = 1, \ldots, \varphi$, the coexistence region is is subject to φ constraints, and we therefore need $f = (2 + k - \varphi)$ parameters to describe the coexistence region in the phase diagram. This statement is sometimes called the **Gibbs phase rule**.

Example:

Consider the following example of a phase boundary between coffee and sugar:

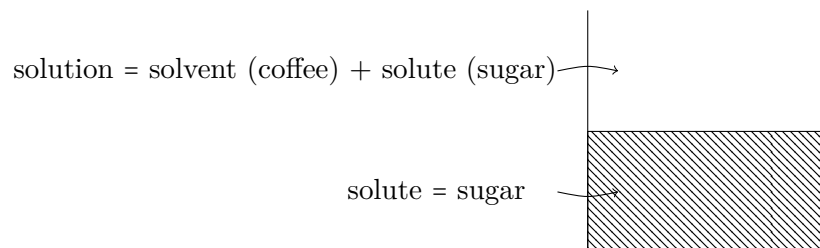solution = solvent (coffee) + solute (sugar)

solute = sugar

Figure 6.13.: The phase boundary between solution and a solute.

In this example we have $k = 2$ compounds (coffee, sugar) with $\varphi = 2$ coexisting phases (solution, sugar at bottom). Thus we need $f = 2 + 2 - 2 = 2$ independent parameters to describe phase equilibrium, such as the temperature T of the coffee and the concentration

c of sugar, i.e. sweetness of the coffee.

Another example is the ice-vapor-water diagram where we only have $k = 1$ substance (water). At the triple point, we have $\varphi = 3$ coexisting phases and $f = 1 + 2 - 3 = 0$, which is consistent because a point is a 0-dimensional manifold. At the water-ice coexistence line, we have $\varphi = 2$ and $f = 1 + 2 - 2 = 1$, which is the correct dimension of a line.

Now consider a 1-component system ($k = 1$), such that $\underline{X} = (E, N, V)$ and $\underline{\xi} = (\frac{1}{T}, \frac{P}{T}, -\frac{\mu}{T})$ The φ different phases are described by

$$\underline{X}^{(1)} = (E^{(1)}, N^{(1)}, V^{(1)}), \ldots, \underline{X}^{(\varphi)} = (E^{(\varphi)}, N^{(\varphi)}, V^{(\varphi)}).$$

In the case of $\varphi = 2$ different phases we thus have

$$E^{(1)}\mathrm{d}\left(\frac{1}{T}\right) + V^{(1)}\mathrm{d}\left(\frac{P}{T}\right) - N^{(1)}\mathrm{d}\left(\frac{\mu}{T}\right) = 0$$

$$E^{(2)}\mathrm{d}\left(\frac{1}{T}\right) + V^{(2)}\mathrm{d}\left(\frac{P}{T}\right) - N^{(2)}\mathrm{d}\left(\frac{\mu}{T}\right) = 0.$$

We assume that the particle numbers are equal in both phases, $N^{(1)} = N^{(2)} \equiv N$, which means that $f = 2 + k - \varphi = 1.$Thus,

$$\left[E^{(1)} - E^{(2)} + P(V^{(1)} - V^{(2)})\right]\frac{\mathrm{d}T}{T^2} = (V^{(1)} - V^{(2)})\frac{\mathrm{d}P}{T}, \tag{6.96}$$

or, equivalently,

$$\frac{\mathrm{d}P(T)}{\mathrm{d}T} = \frac{\Delta E + P\Delta V}{T\Delta V}. \tag{6.97}$$

Together with the relation $\Delta E = T\Delta S - P\Delta V$ we find the **Clausius-Clapeyron-equation**

$$\boxed{\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta S}{\Delta V}}. \tag{6.98}$$

As an application, consider a solid (phase 1) in equilibrium with its vapor (phase 2). For the volume we should have $V^{(1)} \ll V^{(2)}$, from which it follows that $\Delta V = V^{(1)} - V^{(2)} \approx -V^{(2)}$. For the vapor phase, we assume the relations for an ideal gas, $PV^{(2)} = \mathrm{k_B}TN^{(2)} = \mathrm{k_B}TN$. Substitution for P gives

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta Q}{N}\frac{P}{\mathrm{k_B}T^2}, \quad \text{with } \Delta Q = -\Delta S \cdot T. \tag{6.99}$$

Assuming $\Delta q = \frac{\Delta Q}{N}$ to be roughly independent of T, we obtain

$$\boxed{P(T) = P_0 e^{-\frac{\Delta q}{\mathrm{k_B}T}}} \tag{6.100}$$

on the phase boundary, see the following figure:

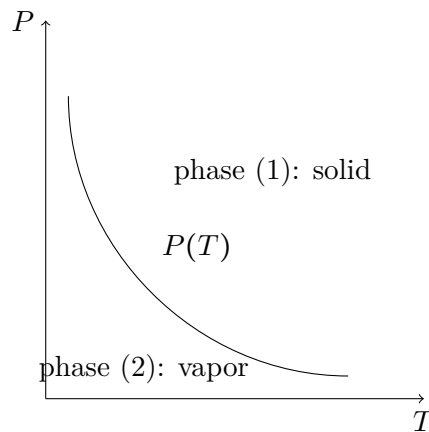
Figure 6.14.: Phase boundary of a vapor-solid system in the (P, T)-diagram

6.8. Osmotic Pressure

We consider a system made up of two compounds and define

$$N_1 = \text{ particle number of "ions" (solute)}$$

$$N_2 = \text{ particle number of "water molecules" (solvent)}.$$

The corresponding chemical potentials are denoted μ_1 and μ_2. The grand canonical partition function,

$$Y(\mu_1, \mu_2, V, \beta) = \text{tr}\left[e^{-\beta\left(H(V) - \mu_1 \hat{N}_1 - \mu_2 \hat{N}_2\right)} \right],$$

can be written as

$$Y(\mu_1, \mu_2, V, \beta) = \sum_{N_1=0}^{\infty} Y_{N_1}(\mu_2, \beta, V) e^{\beta \mu_1 N_1}, \tag{6.101}$$

where Y_{N_1} is the grand canonical partition function for substance 2 with a fixed number N_1 of particles of substance 1[4]. Let now $y_N := \frac{1}{V} \frac{Y_N}{Y_0}$. It then follows that

$$\log Y \equiv \log Y_0 + \log \frac{Y}{Y_0} = \log Y_0 + \log\left[1 + \sum_{N_1>0} V y_{N_1} e^{\beta \mu_1 N_1} \right], \tag{6.102}$$

hence

$$\log Y = \log Y_0 + V \underbrace{y_1(\mu_2, \beta)} e^{\beta \mu_1} + \mathcal{O}(e^{2\beta \mu_2}). \tag{6.103}$$

$$\text{no } V \text{ dependence for large}$$
$$\text{systems as free energy}$$
$$G = -k_B T \log Y \sim V$$

---

[4]Here we assume implicitly that $\left[H, \hat{N}_1 \right] = 0$ so that H maps subspaces of N_1-particles to itself.

For the (expected) particle number of substance 1 we therefore have

$$N_1 = -\frac{1}{\beta} \frac{\partial}{\partial \mu_1} \log Y(\mu_1, \mu_2, V, \beta), \tag{6.104}$$

which follows from

$$\mathrm{d}G = -S\mathrm{d}T - P\mathrm{d}V - N_1 \mathrm{d}\mu_1 - N_2 \mathrm{d}\mu_2, \tag{6.105}$$

using the manipulations with thermodynamic potentials reviewed in section 6.5. Because $\log Y_0$ does not depend on μ_1, we find

$$N_1/V = n_1 = y_1(\mu_2, \beta)e^{\beta \mu_1} + \mathcal{O}(e^{2\beta \mu_1}). \tag{6.106}$$

On the other hand, we have for the pressure (see section 6.5)

$$P = -\frac{1}{\beta} \frac{\partial}{\partial V} \log Y(\mu_1, \mu_2, V, \beta), \tag{6.107}$$

which follows again from (6.105). Using that y_1 is approximately independent of V for large volume, we obtain the following relation:

$$P(\mu_2, N_1, \beta) = P(\mu_2, N_1 = 0, \beta) + y_1(\mu_2, T)e^{\beta \mu_1}/\beta + \mathcal{O}(e^{2\beta \mu_1}).$$

Using $e^{\beta \mu_1} = \frac{n_1}{y_1} + \mathcal{O}\left(n_1^2\right)$, which follows from (6.106), we get

$$P(\mu_2, N_1, T) = P(\mu_2, N_1 = 0, T) + k_B T n_1 + \mathcal{O}(n_1^2). \tag{6.108}$$

Here we note that y_1, which in general is hard to calculate, fortunately does not appear on the right hand side at this order of approximation.

Consider now two copies of the system called A and B, separated by a wall which leaves through water, but not the ions of the solute. The concentration $n_1^{(A)}$ of ions on one side of the wall need not be equal to the concentration $n_1^{(B)}$ on the other side. So we have different pressures $P^{(A)}$ and $P^{(B)}$. Their difference is

$$\Delta P = P^{(A)} - P^{(B)} = k_B T(n_1^{(A)} - n_1^{(B)}),$$

hence, writing $\Delta n = n_1^{(A)} - n_1^{(B)}$, we obtain the **osmotic formula**, due to van 't Hoff:

$$\boxed{\Delta P = k_B T \Delta n .} \tag{6.109}$$

In the derivation of this formula we neglected terms of the order n_1^2, which means that the formula is valid only for *dilute solutions*!

A. Dynamical Systems and Approach to Equilibrium

A.1. The Master Equation

In this section, we will study a **toy model for dynamically evolving ensembles** (i.e. non-stationary ensembles). We will not start from a Hamiltonian description of the dynamics, but rather work with a phenomenological description. In this approach, the ensemble is described by a time-dependent probability distribution $\{p_n(t)\}$, where $p_n(t)$ is the probability of the system to be in state n at time t. Since $p_n(t)$ are to be probabilities , we evidently should have $\sum_{i=1}^{N} p_i(t) = 1$, $p_i(t) \geq 0$ for all t.

We assume that the time dependence is determined by the dynamical law

$$\frac{dp_i(t)}{dt} = \sum_{j \neq i} \left[T_{ij} p_j(t) - T_{ji} p_i(t) \right], \tag{A.1}$$

where $T_{ij} > 0$ is the transition amplitude for going from state j to the state i per unit of time. We call this law the "**master equation**." As already discussed in sec. 3.2, the master equation can be thought of as a version of the Boltzmann equation. In the context of quantum mechanics, the transition amplitudes T_{ij} induced by some small perturbation of the dynamics H_1 would e.g. be given by Fermi's golden rule, $T_{ij} = 2\pi n/h \left| \langle i | H_1 | j \rangle \right|^2$ and would therefore be symmetric in i and j, $T_{ij} = T_{ji}$. In this section, we do not assume that the transition amplitude is symmetric as this would exclude interesting examples.

It is instructive to check that the master equation has the desired property of keeping $p_i(t) \geq 0$ and $\sum_i p_i(t) = 1$. The first property is seen as follows. Suppose that t_0 is the first time that some $p_i(t_0) = 0$. From the structure of the master equation, it then follows that $dp_i(t_0)/dt > 0$, unless in fact all $p_j(t_0) = 0$. This is impossible, because the sum of

the probabilities equal to 1 for all times. Indeed,

$$\frac{d}{dt} \sum_i p_i = \sum_i \frac{d}{dt} p_i$$

$$= \sum_i \sum_{j:j \neq i} (T_{ij} p_j - T_{ji} p_i)$$

$$= \sum_{i,j:i \neq j} T_{ij} p_j - \sum_{i,j:j \neq i} T_{ji} p_i = 0.$$

An *equilibrium state* corresponds to a distribution $\{p_i^{\text{eq}}\}$ which is constant in time and is a solution to the master equation, i.e.

$$\sum_{j:j \neq i} T_{ij} p_j^{\text{eq}} = p_i^{\text{eq}} \sum_{j:j \neq i} T_{ji}. \tag{A.2}$$

An important special case is the case of *symmetric transition amplitudes*. We are in this case for example if the underlying microscopic dynamics is *reversible*. In that case, the uniform distribution $p_i^{\text{eq}} = \frac{1}{N}$ is always stationary (micro canonical ensemble).

Example: Time evolution of a population of bacteria

Consider a population of some kind of bacteria, characterized by the following quantities:

$$
\begin{aligned}
n &= \text{number of bacteria in the population} \\
M &= \text{mortality rate} \\
R &= \text{reproduction rate} \\
p_n(t) &= \text{probability that the population consists of } n \text{ bacteria at instant } t
\end{aligned}
$$

In this case the master equation (A.1) reads:

$$\frac{d}{dt} p_n = \underbrace{R(n-1)p_{n-1}}_{\substack{\text{increase in probability} \\ \text{for } n \text{ bacteria due to} \\ \text{reproduction among group} \\ \text{of } (n-1) \text{ bacteria}}} + \underbrace{M(n+1)p_{n+1}}_{\substack{\text{increase in probability} \\ \text{for } n \text{ bacteria due to} \\ \text{death among group of} \\ (n+1) \text{ bacteria}}} - \underbrace{(M+R)np_n}_{\substack{\text{decrease in probability} \\ \text{for } n \text{ bacteria due to} \\ \text{either reproduction (leading} \\ \text{to more bacteria) or death} \\ \text{(leading to fewer bacteria)}}} , \quad \text{for } (n \geq 1)$$

$$\tag{A.3}$$

$$\frac{d}{dt} p_0 = M p_1. \tag{A.4}$$

It means that the transition amplitudes are given by

$$
\begin{cases}
T_{n(n+1)} & = M(n+1) \\
T_{n(n-1)} & = R(n-1) \\
T_{ij} & = 0 \quad \text{otherwise,}
\end{cases}
\tag{A.5}
$$

and the condition for equilibrium becomes

$$
R(n-1)p_{n-1}^{\text{eq}} + M(n+1)p_{n+1}^{\text{eq}} = (R+M)np_n^{\text{eq}}, \quad \text{with } n \geq 1 \text{ and } p_1 = 0.
\tag{A.6}
$$

It follows by induction that in this example the only possible equilibrium state is given by

$$
p_n^{\text{eq}} =
\begin{cases}
1 & \text{if } n = 0 \\
0 & \text{if } n \geq 1,
\end{cases}
\tag{A.7}
$$

i.e. we have equilibrium if and only if all bacteria are dead.

A.2. Properties of the Master Equation

We may rewrite the master equation (A.1) as

$$
\frac{dp_i(t)}{dt} = \sum_j \mathcal{X}_{ij} p_j(t),
\tag{A.8}
$$

where

$$
\mathcal{X}_{ij} =
\begin{cases}
T_{ij} & \text{if } i \neq j \\
- \sum_{k \neq i} T_{ki} & \text{if } i = j.
\end{cases}
\tag{A.9}
$$

We immediately find that $\mathcal{X}_{ij} \geq 0$ for all $i \neq j$ and $\mathcal{X}_{ii} \leq 0$ for all i. We can obtain $\mathcal{X}_{ii} < 0$ if we assume that for each i there is at least one state j with nonzero transition amplitude T_{ij}. We make this assumption from now on. The formal solution of (A.8) is given by the following matrix exponential:

$$
\underline{p}(t) = e^{t\mathcal{X}} \underline{p}(0) \quad \underline{p}(t) = \left(p_1(t), \ldots, p_N(t) \right).
\tag{A.10}
$$

(We also assume that the total number N of states is finite).

We would now like to understand whether there must always exist an equilibrium state, and if so, how it is approached. An equilibrium distribution must satisfy $0 = \sum_j \mathcal{X}_{ij} p_j^{\text{eq}}$, which is possible if and only if the matrix $\mathcal{X}$ has a zero eigenvalue. Thus, we must have some information about the eigenvalues of $\mathcal{X}$. We note that this matrix need not be symmetric, so its eigenvalues, E, need not be real, and we are not necessarily able to

diagonalize it! Nevertheless, it turns out that the master equation gives us a sufficient amount of information to understand the key features of the eigenvalue distribution. If we define the evolution matrix $A(t)$ by

$$A(t) := e^{t\mathcal{X}} \tag{A.11}$$

then, since $A(t)$ maps element-wise positive vectors $\underline{p} = (p_1, \ldots, p_N)$ to vectors with the same property, it easily follows that $A_{ij}(1) \geq 0$ for all i, j. Hence, by the Perron-Frobenius theorem, the eigenvector $\underline{v}$ of $A(1)$ whose eigenvalue $\lambda_{\max}$ has the largest real part must be element wise positive, $v_i \geq 0$ for all i, and $\lambda_{\max}$ must be *real and positive*,

$$A(1)\underline{v} = \lambda_{\max}\underline{v}, \quad \lambda_{\max} > 0. \tag{A.12}$$

This (up to a rescaling) unique vector $\underline{v}$ must also be an eigenvector of $\mathcal{X}$, with real eigenvalue $\log \lambda_{\max} = E_{\max}$. We next show that any eigenvalue E of $\mathcal{X}$ (possibly $\in \mathbb{C}$) has $\mathrm{Re}(E) \leq 0$ by arguing as follows: Let $\underline{w}$ be an eigenvector of $\mathcal{X}$ with eigenvalue E, i.e. $\mathcal{X}\underline{w} = E\underline{w}$. Then

$$\sum_{j \neq i} \mathcal{X}_{ij} w_j = (E - \mathcal{X}_{ii}) w_j, \tag{A.13}$$

and therefore

$$\sum_{j \neq i} \mathcal{X}_{ij} |w_j| \geq |E - \mathcal{X}_{ii}| |w_j|, \tag{A.14}$$

which follows from the triangle inequality and $\mathcal{X}_{ij} \geq 0$ for $i \neq j$. Taking the sum $\sum_i$ and using (A.9) then yields $\sum_i (\mathcal{X}_{ii} + |E - \mathcal{X}_{ii}|) |w_i| \leq 0$ and therefore $(\mathcal{X}_{ii} + |E - \mathcal{X}_{ii}|) |w_i| \leq 0$ for at least one i. Since $\mathcal{X}_{ii} < 0$, this is impossible unless $\mathrm{Re}(E) \leq 0$. Then it follows that $E_{\max} \leq 0$ and then also $\lambda_{\max} \leq 1$. We would now like to argue that $E_{\max} = 0$, in fact. Assume on the contrary $E_{\max} < 0$. Then

$$\underline{v}(t) = A(t)\underline{v} = e^{tE_{\max}}\underline{v} \to 0,$$

which is impossible as evolution preserves $\sum_i v_i(t) > 0$. From this we conclude that $E_{\max} = 0$, or $\mathcal{X}\underline{v} = 0$, and thus

$$p_j^{\mathrm{eq}} = \frac{v_j}{\sum_i v_i} \tag{A.15}$$

is an equilibrium distribution. This equilibrium distribution is unique (from the Perron-Frobenius theorem). Since any other eigenvalue E of $\mathcal{X}$ must have $\mathrm{Re}(E) < 0$, any distribution $\{p_i(t)\}$ must approach this equilibrium state. We summarize our findings:

1. There exists a unique equilibrium distribution $\{p_j^{\mathrm{eq}}\}$.

2. Any distribution $\{p_i(t)\}$ obeying the master equation must approach equilibrium as $|p_j(t) - p_j^{\mathrm{eq}}| = \mathcal{O}(e^{-t/\tau_{\mathrm{relax}}})$ for all states j, where the relaxation timescale is given

by $\tau_{\text{relax}} = -1/E_1$, where $E_1 < 0$ is largest non-zero eigenvalue of $\mathcal{X}$.

In statistical mechanics, one often has

$$\boxed{T_{ij}e^{-\beta\epsilon_j} = T_{ji}e^{-\beta\epsilon_i},} \tag{A.16}$$

where ϵ_i is the energy of the state i. Equation (A.16) is called the **detailed balance condition**. It is easy to see that it implies

$$p_i^{\text{eq}} = e^{-\beta\epsilon_i}/Z.$$

Thus, in this case, the unique equilibrium distribution is the canonical ensemble, which was motivated already in chapter 4.

If the detailed balance condition is fulfilled, we may pass from $\mathcal{X}_{ij}$, which need not be symmetric, to a symmetric (hence diagonalizable) matrix by a change of the basis as follows. If we set $q_i(t) = p_i(t)e^{\frac{\beta E_i}{2}}$, we get

$$\frac{dq_i(t)}{dt} = \sum_{j=1}^{N} \tilde{\mathcal{X}}_{ij}q_j(t), \tag{A.17}$$

where

$$\tilde{\mathcal{X}}_{ij} = e^{\frac{\beta\epsilon_i}{2}} \mathcal{X}_{ij}e^{\frac{-\beta\epsilon_j}{2}}$$

is now symmetric. We can diagonalize it with real eigenvalues $\lambda_n \leq 0$ and real eigenvectors $\underline{w}^{(n)}$, so that $\tilde{\mathcal{X}}\underline{w}^{(n)} = \lambda_n\underline{w}^{(n)}$. The eigenvalue $\lambda_0 = 0$ again corresponds to equilibrium and $w_i^{(0)} \propto e^{-\beta\epsilon_i/2}$. Then we can write

$$p_i(t) = p_i^{\text{eq}} + e^{-\frac{\beta\epsilon_i}{2}} \sum_{n\geq 1} c_n \, e^{t\lambda_n}w_i^{(n)}, \tag{A.18}$$

where $c_n = \underline{q}(0) \cdot \underline{w}^{(n)}$ are the Fourier coefficients. We see again that $p_i(t)$ converges to the equilibrium state exponentially with relaxation time $-\frac{1}{\lambda_1} < \infty$, where $\lambda_1 < 0$ is the largest non-zero eigenvalue of $\tilde{\mathcal{X}}$.

A.3. Relaxation time vs. ergodic time

We come back to the question why one never observes in practice that a macroscopically large system returns to its initial state. We discuss this in a toy model consisting of N spins. A state of the system is described by a configuration C of spins:

$$C = (\sigma_1, \dots, \sigma_N) \in \{+1, -1\}^N. \tag{A.19}$$

The system has 2^N possible states C, and we let $p_C(t)$ be the probability that the system is in the state C at time t. Furthermore, let τ_0 be the time scale for one update of the system, i.e. a spin flip occurs with probability $\frac{dt}{\tau_0}$ during the time interval $[t, t+dt]$. We assume that all spin flips are equally likely in our model. This leads to a master equation (A.1) of the form

$$\frac{dp_C(t)}{dt} = \frac{1}{\tau_0}\left\{\frac{1}{N}\sum_{i=1}^N p_{C_i}(t) - p_C(t)\right\} = \sum_{C'}\mathcal{X}_{CC'}p_{C'}(t). \tag{A.20}$$

Here, the first term in the brackets $\{\ldots\}$ describes the increase in probability due to a change $C_i \to C$, where C_i differs from C by flipping the ith spin. This change occurs with probability $\frac{1}{N}$ per time τ_0. The second term in the brackets $\{\ldots\}$ describes the decrease in probability due to the change $C \to C_i$ for any i. It can be checked from definition of $\mathcal{X}$ that

$$\sum_C \mathcal{X}_{CC'} = 0 \implies \sum_C p_C(t) = 1 \ \forall t. \tag{A.21}$$

Furthermore it can be checked that the equilibrium configuration is given by

$$p_C^{\text{eq}} = \frac{1}{2^N} \qquad \forall C \in \{-1, +1\}^N. \tag{A.22}$$

Indeed: $\sum_{C'}\mathcal{X}_{CC'}p_{C'}^{\text{eq}} = 0$, so in the equilibrium distribution, all states C are equally likely for this model.

If we now imagine a discretized version of the process, where at each time step one randomly chosen spin is flipped, then the timescale over which the system returns to the initial condition is estimated by $\tau_{\text{ergodic}} \approx 2^N\tau_0$ since we have to visit $\mathcal{O}(2^N)$ sites before returning and each step takes time τ_0. We claim that this is much larger than the relaxation timescale. To estimate the latter, we choose an arbitrary but fixed spin, say the first spin. Then we define $p_\pm = \langle\delta(\sigma_1 \mp 1)\rangle$, where the time-dependent average is calculated with respect to the distribution $\{p_C(t)\}$, in other words

$$p_\pm(t) = \sum_{C:\sigma_1=\pm1} p_C(t) = \text{ probability for finding the 1}^{\text{st}} \text{ spin up/down at time } t. \tag{A.23}$$

The master equation implies an evolution equation for p_+ (and similarly p_-), which is obtained by simply summing (A.20) subject to the condition $\sum_{C:\sigma_1=\pm1}$. This gives:

$$\frac{dp_+}{dt} = \frac{1}{\tau_0}\left\{\frac{1}{N}(1-p_+) - \frac{1}{N}p_+\right\}, \tag{A.24}$$

which has the solution

$$p_+(t) = \frac{1}{2} + \left(p_+(0) - \frac{1}{2}\right)e^{-\frac{2t}{N\tau_0}}. \tag{A.25}$$

So for $t \to \infty$, we have $p_+(t) \to \frac{1}{2}$ at an exponential rate. This means $\frac{1}{2}$ is the equilibrium value of p_+. Since this holds for any chosen spin, we expect that the relaxation time towards equilibrium is $\tau_{\text{relax}} \approx \frac{N}{2}\tau_0$ and we see

$$\boxed{\tau_{\text{ergodic}} \gg \tau_{\text{relax}}} \; . \tag{A.26}$$

A more precise analysis of relaxation time involves finding the eigenvalues of the 2^N-dimensional matrix $\mathcal{X}_{CC'}$: we think of the eigenvectors $\underline{u}_0, \underline{u}_1, \underline{u}_2, \dots$ with eigenvalues $\lambda_0 = 0, \; \lambda_1, \lambda_2, \dots$ as functions $u_0(C), \; u_1(C), \; \dots$ where $C = (\sigma_1, \dots, \sigma_N)$. Then the eigenvalue equation is

$$\sum_{C'} \mathcal{X}_{CC'} u_n(C') = \lambda_n u_n(C), \tag{A.27}$$

and we have

$$u_0(C) \equiv u_0(\sigma_1, \dots, \sigma_N) = p_C^{\text{eq}} = \frac{1}{2^N} \quad \forall C. \tag{A.28}$$

Now we define the next N eigenvectors $u_1^j, \; j = 1, \dots, N$ by

$$u_1^j(\sigma_1, \dots, \sigma_N) = \begin{cases} \alpha & \text{if } \sigma_j = +1 \\ \beta & \text{if } \sigma_j = -1. \end{cases} \tag{A.29}$$

Imposing the eigenvalue equation gives $\alpha = -\beta$, and then $\lambda_1 = -\frac{2}{N}$. The eigenvectors are orthogonal to each other. The next set of eigenvectors $u_2^{ij}, \; 1 \le i < j \le N$ is

$$u_2^{ij}(\sigma_1, \dots, \sigma_N) = \begin{cases} \alpha & \text{if } \sigma_i = 1, \; \sigma_j = 1 \\ -\alpha & \text{if } \sigma_i = 1, \; \sigma_j = -1 \\ -\alpha & \text{if } \sigma_i = -1, \; \sigma_j = 1 \\ \alpha & \text{if } \sigma_i = -1, \; \sigma_j = -1, \end{cases} \tag{A.30}$$

The vectors u_2^{ij} are again found to be orthogonal, with the eigenvalue $\lambda_2 = -\frac{4}{N}$. The subsequent vectors are constructed in the same fashion, and we find $\lambda_k = -\frac{2k}{N}$ for the k-th set. The general solution of the master equation is given by (A.10)

$$p_C(t) = \sum_{C'} (e^{t\mathcal{X}})_{CC'} p_{C'}(0), \tag{A.31}$$

which we can now evaluate using our eigenvectors. If we write

$$p_C(t) = p_C^{\text{eq}} + \sum_{k=1}^{N} \sum_{1 \le i_1 < \dots < i_k \le N} a_{i_1 \dots i_k}(t) \; u_k^{i_1 \dots i_k}(C)$$

we get

$$a_{i_1 \dots i_k}(t) = a_{i_1 \dots i_k}(0) e^{-2kt/(N\tau_0)}.$$

This gives the relaxation time for a general distribution. We see that the relaxation time is given by the exponential with the smallest decay (the term with $k = 1$ in the sum), leading to the relaxation time $\tau_{\text{relax}} = N\tau_0/2$ already guessed before. *This is exponentially small compared to the ergodic time!* For $N = 1$ mol we have, approximately

$$\frac{\tau_{\text{ergodic}}}{\tau_{\text{relax}}} = \mathcal{O}(e^{(10^{23})}). \tag{A.32}$$

A.4. Monte Carlo methods and Metropolis algorithm

The **Metropolis algorithm** is based in an essential way on the fact that $\tau_{\text{relax}} \ll \tau_{\text{ergodic}}$ for typical systems. The general aim of the algorithm is to efficiently compute expectation values of the form

$$\langle F \rangle = \sum_C F(C) \frac{e^{-\beta E(C)}}{Z(\beta)}, \tag{A.33}$$

where $E(C)$ is the energy of the state C and F is some observables.

As we have seen, the number of configurations typically scales exponentially with the system size, so it is out of question to do this sum exactly. The idea is instead to generate a small sample $C_1, \dots, C_m$ of configurations which are independent of each other and are distributed with distribution $\propto e^{-\beta E(C)}$. (Note that a simple minded method would be to simply generate a uniformly distributed sample $\tilde{C}_1, \dots, \tilde{C}_u$ where $u \gg 1$ and to approximate $\langle F \rangle \approx \sum_{i=1}^{u} F(\tilde{C}_i) \frac{e^{-\beta E(\tilde{C}_i)}}{Z}$. This is a very bad idea in most cases since the fraction of configurations out of which the quantity $e^{-\beta E(\tilde{C}_i)}$ is not practically 0 is exponentially small!)

To get a sample of configurations distributed according to a distribution $e^{-\beta E(C)}/Z$, we choose any (!) $T_{C,C'}$ satisfying the detailed balance condition (A.16):

$$T_{C,C'} e^{-\beta E(C')} = T_{C',C} e^{-\beta E(C)}, \tag{A.34}$$

as well as $\sum_{C'} T_{C',C} = 1$ for all C. The discretized version of the master equation then becomes

$$p_{C'}(t+1) = \sum_C T_{C',C} p_C(t).$$

In the simplest case, the sum is over all configurations C differing from C' by flipping precisely one spin. If C'_i is the configuration obtained from some configuration C' by flipping spin i, we therefore assume that $T_{C',C}$ is non-zero only if $C = C'_i$ for some i.

One expects, based on the above arguments, that this process will converge to the

equilibrium configuration is $p_C^{\text{eq}} \propto e^{-\beta E(C)}$ after about N iterations. Stating the algorithm in a slightly different way, we can say that, for a given configuration, we accept the change $C \to C'$ randomly with probability $T_{C',C}$. A very simple and practical choice for the acceptance probability (in other words $T_{C',C}$) satisfying our conditions is given by

$$p_{\text{accept}} = \begin{cases} 1 & \text{if } E(C') \leq E(C) \\ e^{-\beta[E(C')-E(C)]} & \text{if } E(C') \geq E(C). \end{cases} \tag{A.35}$$

We may then summarize the algorithm as follows:

Metropolis Algorithm

(1) Choose an initial configuration C.

(2) Choose randomly a spin i and determine the change in energy $E(C) - E(C_i) = \delta_i E$ for the new configuration C_i obtained by flipping one spin i.

(3) Choose a uniformly distributed random number $u \in [0,1]$. If $u < e^{-\beta \delta_i E}$, change $\sigma_i \to -\sigma_i$, otherwise leave σ_i unchanged.

(4) Rename $C_i \to C$.

(5) Go back to (2).

Running the algorithm m times, going through approximately N iterations each time, gives the desired sample $C_1, ..., C_m$ distributed approximately according to $e^{-\beta E(C)}/Z$. The expectation value $< F >$ is then computed as the average of $F(C)$ over the sample $C_1, ..., C_m$. For example, in the case of the Ising model (in one dimension) describing a chain of N spins with $\sigma_i \in \{\pm 1\}$, the energy is given by:

$$E(C) = -J \sum_{0 < i < N} \sigma_i \sigma_{i+1},$$

where J is the strength of the interaction between the i-th and the $(i+1)$-th spin in the chain. The change in energy if we flip one spin is very easy to calculate in this example because the interaction is local, as it is in most models.

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