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Chapter 1

Introduction

1.1 What is statistical mechanics and thermodynamics?

The main purpose of statistical mechanics is the derivation of laws valid in the macroscopic world using statistical methods, applied to the actual dynamics in the microscopic world.

As such, this seems a trivial statement. Of course, since macroscopic bodies consist of a large number of small constituents, and since the laws governing the behavior of these constituents is well understood, one should expect all insights about properties of macroscopic bodies to be a rather simple corollary of these laws. And in a sense, this is all true, of course, on a fundamental level. Still, without augmented with principles as they are formulated in statistical physics, there is little one can learn from the microscopic laws directly for the macro-world, simply because these rules are way too detailed. The systems we have in mind in statistical physics consist of 10^{23} particles and more, and it seems ridiculous to think that we can and should derive properties of these systems from the dynamics of individual constituents:

- We cannot, simply because there is no way to keep track of so much information. In a classical description, we would have to store the position and the momentum of each of these 10^{23} particles in a computer, say, quite an insurmountable challenge. In a quantum mechanical description, the situation is even much worse, as the rule of composing the Hilbert spaces of quantum systems is the tensor product, the dimension of which scales exponentially in the number of constituents. So the Hilbert space dimension of 10^{23} spin-1/2 particles would be about $2^{10^{23}}$, a ridiculously large number. Frankly, there is no way to capture the exact dynamics of so many particles on any computer, let alone in a sophisticated analytical formulation.

- We should not, in that this knowledge would be much too detailed anyway. If we had a long list of all positions and momenta of each particle, it would not necessarily be trivial to compute the relevant macroscopic property from that knowledge. Fortunately, in order to arrive at statements on such macroscopic properties, it usually does not matter where each particle is in a contained filled with a gas. It is merely statistical properties that matter. And this is what statistical mechanics is concerned with.

So it is the main aim of statistical physics to derive the macroscopic laws from the (assumed to be fundamental) basic physical laws applying to the constituents. The description of stationary states is best developed, and we will see how notions of thermodynamics emerge from statistical physics. To an extent, however, the theory can also describe how irreversibility emerges. Not all aspects of the exact dynamics leading to the actual stationary states are all that well understood, however, and at several instances of this course we will point to actual modern research.

The key insight underlying statistical physics is quickly stated: There are just many different microstates that correspond to the same macro-state. Hence, one often resorts to notions of probability theory, asking how likely it is that a given system is in a particular state. The law of large numbers is then responsible for macroscopic laws looking "deterministic", even if the microdynamics is "chaotic". In classical statistical physics, probability theory is the main instrument, in quantum statistical physics, there is an intertwinement of classical and quantum laws.

Note that this course will be both concerned with thermodynamics – at least briefly – as well as with statistical physics. These two fields are closely intertwined, even if not identical. We will start with a brief review of concepts of thermodynamics, in order to move on to describe the basics of classical statistical mechanics. We will then introduce concepts of quantum statistical mechanics. Later in the course, ideas of lattice models, phase transitions and other more sophisticated topics will be considered.[1]

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[1] Note that this script is for internal use only and accompanies the lecture closely. Some parts of the script are close to scripts by others, and I do not claim to have copyright for all material. In particular, the beginning of the course is similar to a script by Reinhard Werner.

1.2 A brief history

For obvious reasons, the history of thermodynamics and of statistical physics are closely intertwined. We will still consider them separately, in their development.

- Quantitative studies of temperature and pressure became possible only with the advent of instruments that rendered the precise measurement of such quantities possible. In the 16th century, researchers made first efforts with grasping notions of temperature. In particular, Galileo Galilei (1564-1642) was concerned with the construction of temperatures.
- In 1714, Gabriel Daniel Fahrenheit (1686-1736) introduced a temperature scale, as well as
- Rene Antoine Reaumur (1683-1757) in 1730 and
- Anders Celsius (1701-1744) in 1742.
- The first reliable barometer was constructed in 1644 by Evangelista Torricelli (1608-1647).
- A notable line of research finally led to the development of the law of Boyle-Mariotte, stating that for an ideal gas, pV is constant at constant temperature. To this development, Robert Boyle (1627-1691) and Edme Mariotte (1620-1684) had significantly contributed.
- Similarly importantly, the law of Gay-Lussac, stating that V/T is constant at constant pressure, was introduced by John Dalton (1766-1844) and Joseph Gay-Lussac (1788-1850).
- Part of the trigger for the following rapid development following a relatively slow pace was the development of the steam engine in the 18th century. Some basic aspects of the idea of a steam engine go back to the 1st century, when Heron of Alexandria introduced a machine that resembled a steam engine in some ways. Also, in the renaissance era, in the 15th century, people experimented, mostly for demonstration purposes, with prototypes. None of these machines were really practical, though. The first properly working steam engine was devised in 1712 by Thomas Newcomen (1663-1729): He used it in order to pump water out of a mine.

- Key to the further development was the work of Sadi Carnot (1796-1832) on the theory of thermal machines, clearly inspired by the technological development of the time. He correctly derived the maximum efficiency of a heat engine. Since he was assuming a sort of indestructible elementary carrier of heat, he was conceptually quite off, so his work is partly contradictory. Still, after he had died, people found conceptually correct derivations in his personal notes.

- Emile Clapeyron (1799-1864) developed the ideas of Carnot further.

- Another key step was the formulation of the first law of thermodynamics by Julius Robert Mayer (1814-1878), James Prescott Joule (1818-1889), and Hermann von Helmholtz (1824-1907). Based on this work, Lord Kelvin (1824-1907, the same years) was able to give an absolute definition of temperature.

- Finally, the second law of thermodynamics goes back to Rudolf Clausius (1822-1888), starting from the impossibility of constructing a perpetuum mobile of second kind. Lord Kelvin arrived independently at the same result. It was also Clausius who first defined the concept of entropy.

- Finally, the third law of thermodynamics was formulated by Walter Nernst (1864-1941), in the first years of the 20th century.

Now turning to the history of statistical physics:

- Again, the roots of statistical physics are in the studies of the ancient Greeks.

- The presumably first attempts to derive properties of macroscopic bodies from laws of constituents were done by Daniel Bernoulli (1700-1782). He indeed was able to derive the gas law by assuming the existence of small particles that are in constant movement. He is hence in a sense the inventor of the kinetic gas theory.

- Benjamin Thomson (1753-1814) realized in his attempt to create muzzles (“Kanonenrohre”) that heat can be created by friction. He therefore correctly assumed that heat was no material substance, but is rather related to the motion of particles.

- One of the brightest figures of statistical mechanics was James Clerk Maxwell (1831-1879): He was the first to apply ideas of probability theory, by then already introduced by Laplace and others, to the kinetic gas theory. In this way, he was, e.g., able to derive the famous formula for the distribution of velocities of particles at a given temperature.

- Similarly importantly, Ludwig Boltzmann (1844-1906) made very important contributions to the field. He was the first to study transport properties, and was famously with notions of irreversibility in statistical physics. His genius was not that much appreciated at the time, though, and his personal life was very tragic, and he ended his life in suicide.

- Another protagonist to statistical physics was no other than Albert Einstein (1879-1955), who first explained Brownian motion.

- Finally, Josiah Willard Gibbs (1939-1903) can be seen as one of the inventors of modern statistical mechanics, in particular when it comes to linking thermodynamical with statistical ideas.

This brief history should not give the impression, however, that statistical physics is merely of historical interest. It is not only still used in countlessly many contexts and an enormously successful theory. It is in fact also still the subject of active research. In particular, it is in many circumstances far from clear how systems dynamically reach the equilibrium states discussed in statistical physics.

1.3 Systems and macro-variables

1.3.1 Open, closed, and isolated systems

We have already mentioned that it is pointless to think of keeping track of the movement of each individual particle in a macroscopic body. Instead, it is the macro-state that takes centre stage here, defined by a sufficiently large set of macro-variables, such as volume, pressure, total energy, and so on. In the context of thermodynamics, "state" always refers to the macro-state. In contrast to the situation of non-equilibrium, typical equilibrium situations are captured by only very few such macro-variables.

The optimal choice of these variables depends on the context. For simple gases, e.g., merely two parameters are sufficient, such as (p, V), (T, p), or (T, S). Relationships between these quantities are called equations of state.

Thermodynamics and statistical physics – and in fact most of physics – are about properties of systems. A system is a conceptually and practically distinguished part of the physical world, defined also by specifying some boundary conditions. We have to be able to prepare such systems in the same way (at least as far as the macro-variables are concerned), and make experiments with them. All that is outside this system is treated as a kind of environment of this system. In this mindset, it makes a lot of sense to distinguish open, closed, and isolated systems.

Open, closed, and isolated systems:

- An isolated system is one that is entirely decoupled from its environment, not exchanging any energy or matter.
- A closed system is one that exchanges no matter with its environment.
- An open system is one that is neither isolated or closed.

1.3.2 Extensive and intensive quantities and quasi-static processes

We distinguish extensive quantities and intensive ones. Extensive quantities such as volume, particle number, inner energy, entropy grow proportionally in the system size. Intensive quantities such as the temperature, the pressure or the density would remain constant if the system size is doubled. These variables belonging to the system itself are also called inner variables.

Particularly important are control parameters. These are parameters that can be freely chosen from the outside, by “turning a knob”. Then the other parameters take their values accordingly. Such variables are also referred to as being outer variables. A system is called simple if its state is characterised by merely one more parameter than the number of control parameters.

If one alters these control parameters in a sufficiently slow way, so in case one allows the system to take the appropriate other quantities take their equilibrium value at each instance in time, one refers to a quasi-stationary process. It depends on the context how slow “sufficiently slow” is. This idea of quasi-stationary processes was surely good enough to construct steam engines. :)

1.4 A glimpse at statistical mechanics and thermodynamics

1.4.1 Phases

We will later turn to a refined picture of a phase. For the moment being, we will consider a phase a with respect to physical and chemical properties homogeneous part of a physical system. As an example of a system composed of two phases, consider a mixture of water and steam. Between these phases, there are thin boundary layers, also called phase boundaries. According to the definition of a phase, within a phase the state variables are independent of position and are homogeneous throughout the phase.

1.4.2 Law of Boyle Mariotte

Let us have a brief look at a situation in statistical physics that already has a flavor of the type of situations that we will encounter later. We consider a container filled with n particles, having the volume V. This container is closed by a movable lid of area A, sitting on top of the container. Given its mass M the force due to the lid is given by $F = Mg$. The pressure in turn is given by $p = F/A$.

Now we consider the movement of the particles in the container. They will have a time-varying velocity $(v_1, \dots, v_n)$, where each of these entries is a vector in $\mathbb{R}^3$. Let us assume that the mass of each particle is m.

Now let us single out a single particle for a moment, with velocity v and z-component v_z. The conservation of momentum and energy in case of an elastic collision of a particle with the lid at velocity $v_{z,\mathrm{lid}}$ lead to

$$\begin{aligned} mv_z &= mv_z' + Mv_{z,\mathrm{lid}}, && (1.1)\\ \frac{1}{2}mv_z^2 &= \frac{1}{2}m{v_z'}^2 + \frac{1}{2}Mv_{z,\mathrm{lid}}^2, && (1.2)\end{aligned}$$

where $v_{z,\mathrm{lid}}$ is the velocity of the lid, initially assumed to be zero without loss of generality, which implies that

$$Mv_{z,\mathrm{lid}} = \frac{2mv_z}{1 + \frac{m}{M}}. \quad (1.3)$$

In the approximation where $m/M \ll 1$, which we can safely assume, the transfer of momentum is hence

$$Mv_{z,\mathrm{lid}} = 2mv_z. \quad (1.4)$$

We also know the rate at which particles with $|v_z|$ hit the lid, this is $A|v_z|/2$. Hence, the average rate of momentum transfer is given by

$$F = \frac{N}{V} A m \langle v_z^2 \rangle. \tag{1.5}$$

The pressure is hence

$$p = \frac{F}{A} = \frac{N}{V} m \langle v_z^2 \rangle. \tag{1.6}$$

Assuming that $\langle v_z^2 \rangle$ is independent of the volume, which we will confirm later, we find that

$$p = \frac{c}{V}, \tag{1.7}$$

with c being a constant. This is the law of Boyle-Mariotte. So we have a first glimpse how the macroscopic property is related to the statistical behavior of the particles.

1.4.3 The paradox of Maxwell's damon

In such a still rather naive reading of statistical arguments we can, however, easily arrive at paradoxes. A famous one is the one first discussed by James Maxwell in 1871. We already know from earlier lectures that systems tend to equilibrium. If two containers with different temperatures will be connected, one will later find a temperature that interpolates the two previous temperatures. One does not observe parts of a system to spontaneously develop a difference in temperature. This, in fact, would contradict the second law of thermodynamics.

However, Maxwell considered a situation that seems to contradict this insight. Think of system composed of two containers which are connected by a small hole. This hole can be opened and closed by moving a small gate. We can open and close this gate at any time. In fact, not only we can do it, but also a fictitious being, Maxwell's demon.

This damon has the ability to open the gate exactly in moments when a fast particle is moving to the right. It lets these fast particles pass. In contrast, when a slow particle comes along, the damon closes the gate. Surely this is not so easy, and requires a lot of knowledge of the precise situation at hand. The damon being a damon, this is a piece of cake for him. We assume that the damon knows exactly what he (are damons male?) is doing.

The consequences of this are obvious: The right container will become hotter, while the left one will cool down. We have violated the second law of thermodynamics. How is this possible? Well, it is not, and we will see later why, and the answer is related to the energy consumption of desktop computers.

1.5 Suggested reading

There are a number of good books available on thermodynamics and statistical physics.

- G. Kluge and G. Neugebauer, “Grundlagen der Thermodynamik” (Spectrum).

  A great book on phenomenological thermodynamics. This book really manages to present thermodynamics as a genuinly exciting physical theory. Remarkable is in particular the chapter on irreversible dynamics. To me, the best book on thermodynamics.

- K. Huang, “Statistical mechanics” (Wiley).

  This is to my taste a really strong book on statistical mechanics. It covers more than we will be able to cover in this course (and in some aspects less), but knowing what Kerson Huang speaks about surely amounts to having a pretty good understanding of statistical mechanics. A recommended read.

- H. Roemer and T. Filk, “Statistische Mechanik” (VCH).

  I can recommend only parts of this book. What is nice is how the equivalence of ensembles is being discussed and motivated. In the copy I have, I found more than 200 mistakes. In many ways, it is sloppy and careless. Yet, for selected chapters, it can well be worth to have a look.

- F. Schwabl, “Statistical Mechanics” (Springer).

  The same applies as what can be said about the books on quantum mechanics by the same author. Refreshingly pragmatic, an easy read, and a good book. In instances, quite imprecise, so has to be read with some care. If this is not the only book, I highly recommend this one.

- W. Nolting, “Grundkurs theoretische Physik 6: Statistische Physik” (Springer).

  To be honest, I do not know this book so well. But people say it is a very reasonable one.

There will also be some selected chapters on topics not covered by any of the above books, but I will then give hints on literature.

Chapter 2

Thermodynamics

In this course, we will start by thermodynamic considerations, or rather with the field called phenomelogical thermodynamics. As mentioned before, this field is closely related with statistical physics. Yet, it is not true that it has become totally obsolete by the advent of statistical physics. Partly for the mentioned reason that one does not want to keep track of the micro-state of every system. Partly also because some links between statistical physics and thermodynamics being still not quite fully understood (although I do not want to advocate a paranoid position here). There are some people who say that in the future, when our physical theories will look very different, thermodynamics will still be valid.

2.1 Some preliminary comments on forms

In this course, we will take a pragmatic attitude as far as mathematics is concerned. For example, we will consider small, "infinitesimal" changes of state variables. Formally, expressions of the type

$$\delta F = \sum_{j=1}^{k} F_j dG_j \tag{2.1}$$

are differential forms, in fact 1-forms, where the $F_j, G_j : \mathcal{A} \to \mathbb{R}$ are differentiable functions in state space $\mathcal{S}$. We will not try to get too much side-tracked by considering geometric features here. It will be useful to view them as integrands of a line integral: We define

$$\int_{\mathcal{C}} \delta F = \int_{\mathcal{C}} \sum_{j=1}^{k} F_j dG_j = \int_I dt F_j(z(t)) \frac{d}{dt} G_j(z(t)). \tag{2.2}$$

The parametrization of the curve does not matter here.

For a scalar function G we call dG the differential of G. This is a special kind of differential form. In general, a differential form that is the differential of a scalar is called an exact differential form. In particular, the integral then does not depend on the curve at all, and

$$\int_{\mathcal{C}} dG = G(\text{End}) - G(\text{Beginning}). \tag{2.3}$$

(This differential form, applied to a vector field, gives the directional derivative in a point.)

If $\mathcal{S}$ is n-dimensional and $(x_1, \ldots, x_n)$ form a coordinate system, then the functions F_j in the decomposition $\delta F = \sum_{j=1}^{n} F_j dx_j$ are unique.

For an exact differential form, so for the differential of G, we have

$$dG = \sum_{j=1}^{n} \frac{\partial G}{\partial x_j} dx_j. \tag{2.4}$$

It should be clear that a partial derivative of the form $\partial G/\partial x_j$ merely depends on G and the coordinate x_1, but in fact also of the other coordinates $x_2, \ldots, x_n$. This is usually expressed as follows, writing

$$\left(\frac{\partial G}{\partial x_1}\right)_{x_2, \ldots, x_n}. \tag{2.5}$$

One reads this as the "change of G with x_1, while holding $x_2, \ldots, x_n$ constant".

If $\delta F = \sum_{j=1}^{n} F_j dx_j$ is exact (so the differential of a scalar function), then one also has that

$$\left(\frac{\partial F_k}{\partial x_j}\right) = \left(\frac{\partial F_j}{\partial x_k}\right) \tag{2.6}$$

for all j, k, as follows from the interchangeability of the second derivatives. This condition is called integrability condition and forms satisfying this is called closed. Hence, every exact form is closed. For simply connected state spaces, closed forms are also exact.

2.2 First law of thermodynamics

We consider a system with control parameters $\alpha_1, \ldots, \alpha_k$. The energy given away by the system can be captured by (taken, in case of negative sign)

$$\delta A = \sum_j K_j d\alpha_j, \tag{2.7}$$

the work differential. For a simple gas, we have

$$\delta A = p dV, \tag{2.8}$$

with the volume V being the only control parameter. Other summands are MdB with magnetization M and induction B. Or μdN for chemical potential μ and particle number N.

Note that work and heat are no state variables. Hence, they cannot be associated equilibrium states.

We now assume that the system is isolated from its environment, meaning that the change of energy is possible only by an alteration of the control parameters. One also says that the process is done in an adiabatic fashion. The first law of thermodynamics is the law of conservation of energy in such a situation.

First law of thermodynamics: Every thermodynamic system is associated a quantity inner energy $U : \mathcal{S} \to \mathbb{R}$. Along adiabatic curves in state space one has that

$$dU + \delta A = 0. \tag{2.9}$$

Except from applying work the inner energy can also be altered by exchange of heat. The heat flow δQ is

$$\delta Q = dU + \delta A. \tag{2.10}$$

The energy of an isolated system, $\delta Q = 0$, $\delta A = 0$, is constant, $dU = 0$.

As an example, let us have a closer look at an ideal gas: The equation of state for the inner energy is

$$U = cpV, \tag{2.11}$$

with some constant $c > 0$. The work differential is $\delta A = pdV$. We now look at the adiabatic plane: This is the plane that be reached by a reversible and adiabatic, i.e., $\delta Q = 0$ process. We have that

$$0 = dU + \delta A = c(pdV + Vdp) + pdV = (c+1)pdV + cVdp. \tag{2.12}$$

Introducing the adiabatic coefficient

$$\kappa = \frac{c+1}{c} \tag{2.13}$$

we get

$$0 = \kappa \frac{1}{V} dV + \frac{1}{p} dp = d(\kappa \ln V + \ln p) = d(\ln V^{\kappa} + \ln p), \tag{2.14}$$

that is to say, the adiabatic planes have to satisfy pV^{κ} is constant.

Since δA is no exact differential, the integral

$$\int_{\mathcal{C}} \delta A \tag{2.15}$$

depends on the parametrized curve, and is hence different from zero even for closed curves $\mathcal{C}$.

There is a simple consequence of the first law of thermodynamics. In fact, it is equivalent to the first statement of the above formulation of the first law of thermodynamics.

> Impossibility of perpetual mobile of first kind: It is impossible to devise a periodically working machine delivering energy.

2.3 Zeroth law of thermodynamics

Experience teaches us that in thermodynamical systems, state variables such as temperature, inner energy and entropy play an important role. In the laws of thermodynamics these quantities are introduced in an axiomatic form. It is hence convenient to put at the beginning of this axiomatic framework the concept of temperature, in the zeroth law of thermodynamics.

We surely have the means, as humans, to judge to some extent whether two bodies have the same temperature. Such a notion can be made more precise as follows: If two systems are put into contact with each other, a equilibration of the energy will take place, in a way such that the total energy $U = U^{(1)} + U^{(2)}$ is conserved. We say that two systems are in thermal equilibrium, if no such distribution of energy takes place.

> Zeroth law of thermodynamics: Thermal equilibrium is an equivalence relation.

These equivalence classes can be parametrized by means of the state of a suitable test system. A function $\hat{T} : \mathcal{S} \to \mathbb{R}$ is called empirical temperature if

$$\hat{T}(z_1) = \hat{T}(z_2) \tag{2.16}$$

exactly if z_1 and z_2 are in thermal equilibrium. Using the zeroth law of thermodynamics, these scales are usable for different kinds of thermodynamical systems. So in a sense, this law merely says that "temperature exists", but is unspecific about the precise scale that is being used.

Two systems that are in contact give rise to a new thermodynamic system. If the parts have $k^{(1)}$ and $k^{(1)}$ control parameters, so if the state spaces are $k^{(1)} + 1$ and $k^{(2)} + 1$ dimensional, then the joint system has

$$k^{(1)} + k^{(2)} \tag{2.17}$$

control parameters. The inner energies of each part are no longer independent variables, but only the total energy $U = U^{(1)} + U^{(2)}$. So again, in addition to the control parameters, a single parameter is required to define the system's state, and again the system is simple.

2.4 Second law of thermodynamics

2.4.1 Perpetua mobilia of second kind

We now turn to the second law of thermodynamics. We consider systems that are composed of several simple thermodynamic systems. Some of those systems may be so large that they hardly change their state when they are brought into contact with small systems. Such systems are called heat baths. What is more, the joint system should embody a reservoir for mechanical work.

We assume that it is possible to bring parts into contact with each other and to also interrupt this contact, at free will. On top of the processes that are resulting from parts coming to equilibrium, we allow for those processes that are a result of us changing the control parameters in the subsystems.

It is clear, from the first law of thermodynamics, that the total energy of the system has to be preserved: The reservoir for mechanical work can not be loaded up without changing the rest of the system. In this sense, mechanical work cannot be created from nothing. This would indeed be a perpetual mobile of first kind.

A perpetual mobile of second kind is a device or a process that is able to load the reservoir of mechanical work, but at the expense of only the inner energy of one of the subsystems, but without any change to any of the other subsystems. The second law of thermodynamics states that this does not exist:

Second law of thermodynamics (Planck's formulation): A perpetual mobile of second kind does not exist.

There is a simple yet very important consequence of this law, when applied to a single simple system. We consider an adiabatic process in which control parameters are changed in a circular process. In the course of this process, the alteration of the inner energy dU can be read off the condition $0 = \delta Q = dU + \delta A$ and integrated up. So let us compare the inner energies $U(0)$ and $U(1)$ at the beginning and at the end of the process. If we had

$$U(1) < U(0), \tag{2.18}$$

we would have done work on the basis of only using up inner energy, which is forbidden by the second law of thermodynamics. If in contrast,

$$U(0) < U(1), \tag{2.19}$$

the same would be true for the process run in the converse direction. That is to say, $U(0) = U(1)$. The curves with fixed beginning and end point and δQ span indeed a plane in $\mathcal{S}$, adiabatic planes. Now there exists a function $\hat{S} : \mathcal{S} \to \mathbb{R}$, the planes of constant values are exactly the adiabatic planes. This function is called empirical entropy.

The observation that is behind this concept of entropy is that real processes in nature are usually irreversible. When a hot body and a cold one is put into contact with each other, they will equilibrate. Never it is observed that one part becomes even colder whereas the hotter body becomes hotter still. Or, if a stone is thrown into a pool, the pool will become a little bit warmer and the stone will sink to the ground. It is never observed that a stone is jolting out of the surface of a pool, while the water cools down. These processes would not be in contradiction with the first law of thermodynamics, though. It is the second law of thermodynamics that forbids them. Real processes are irreversible. And it is the entropy that captures that irreversibility. We will say more about the interpretation of the entropy in a minute.

2.4.2 Carnot engines

A Carnot process is a circular process involving a simple system that consists of four steps in contact with two heat baths at empirical temperatures $\hat{T}_+$ and $\hat{T}_-$. At the beginning, the system has an empirical entropy $\hat{S}_-$ and an empirical temperature $\hat{T}_+$.

Steps of the Carnot process:

Step	Contact with	Entropy	Heat exchange	Work done
1	$\hat{T}_+$		$Q_1 > 0$	A_1
2		$\hat{S}_+$		A_2
3	$\hat{T}_-$		$Q_3 < 0$	A_3
4		$\hat{S}_-$		A_4

We are not so much concerned with the details of the process, but rather that isothermal and adiabatic steps follow each other, at the respective empirical temperatures and entropies. Also, the end state at $\hat{T}_+$ and $\hat{S}_-$ should be identical with the state at the beginning.

Now note that an isothermal process is in fact nothing but an adiabatic process of the system and the heat bath it is in contact with. Therefore, we can – just as for an adiabatic process – run the process in the converse direction, where the signs of Q_i and A_i then change. Because

$$0 = \int_{\mathcal{C}} dU = \sum_j Q_j - \sum_j A_j \tag{2.20}$$

is

$$Q_1 + Q_3 = A := \sum_j A_j, \tag{2.21}$$

where A is the work done in total. Because of the second law of thermodynamics the signs of Q_1 and Q_3 have to be different. Since in step 1 the empirical temperature is higher,

$$Q_1 > 0 > Q_3 \tag{2.22}$$

and we expect $Q_1 + Q_3 > 0$. In the given direction, the machine is hence a heat engine (getting work done from heat), whereas run in the converse direction is a heat pump (getting a temperature difference using work). An important property of Carnot processes is the following one:

Efficiency of the Carnot engine: For all Carnot processes run at empirical temperatures $\hat{T}_+ > \hat{T}_-$ the ratio

$$\frac{|Q_3|}{Q_1} \tag{2.23}$$

is the same. The efficiency of a heat engine is the quotient

$$\eta = \frac{\text{Work done}}{\text{Heat taken up}} = \frac{-(Q_1 + Q_3)}{Q_1} = 1 - \frac{|Q_3|}{Q_1}. \tag{2.24}$$

That is to say, all Carnot engines have the same efficiency. The idea of the proof is as follows: Surely the only thing that can matter is the ratios of the Q_i as we can run each process several times. We can hence assume that we have two processes, and that $Q'_1 = Q_1$. If now $A' < A$ was true, so if the new machine could do less work, and hence $Q'_3 > Q_3$, then we could run the new process as a heat pump and would have a new total process, delivering the work $A - A' > 0$, only at the expense of taking the heat $Q_3 - Q'_3$ from the colder reservoir. This is in contradiction with the second law.

2.4.3 Absolute temperature

According to the above observation,

$$f(\hat{T}_+, \hat{T}_-) = \frac{|Q_3|}{Q_1} \tag{2.25}$$

is a well-defined function of the empirical temperatures. If we now have three heat baths, at empirical temperatures

$$\hat{T}_+ > \hat{T}_0 > \hat{T}_- \tag{2.26}$$

we can compose suitable Carnot processes between $\hat{T}_+$ and $\hat{T}_0$ (with heat exchange Q'_1 and Q'_3) as well as between $\hat{T}_0$ and $\hat{T}_-$ (with heat exchange Q_1 and Q_3) to a new process. We run it in a way that step 1 of the process at lower temperature is the reverse of step 3 of the process at higher temperature. That is,

$$Q'_3 = -Q_1. \tag{2.27}$$

We can hence simply not do that step. The composed process has

$$Q_1'' = Q_1', \tag{2.28}$$

$$Q_3'' = Q_3. \tag{2.29}$$

Therefore,

$$f(\hat{T}_+, \hat{T}_-) = \frac{|Q_3''|}{Q_1''} = \frac{|Q_3|}{Q_1}\frac{|Q_3'|}{Q_1'} = f(\hat{T}_0, \hat{T}_-)f(\hat{T}_+, \hat{T}_0). \tag{2.30}$$

From this, we get an absolute temperature scale! For a randomly picked empirical temperature $\hat{T}_0$ we fix some value T_0. This could be the value 273.15, but this is obviously just a convention. Then we define

$$T(\hat{T}) = f(\hat{T}_0, \hat{T})\hat{T}_0. \tag{2.31}$$

This is called the absolute temperature. The possibility of choosing $\hat{T}_0$ amounts to the fact that the absolute temperature has some dimension. Here, we get the Kelvin scale, needless to say.

Using the definition of the absolute temperature, we get

$$f(\hat{T}_+, \hat{T}_-) = \frac{T(\hat{T}_-)}{T(\hat{T}_+)} = \frac{T_-}{T_+}, \tag{2.32}$$

and hence for the efficiency of the Carnot engine

$$\eta = 1 - \frac{T_-}{T_+}. \tag{2.33}$$

Since the empirical temperature was a random choice anyway related to picking representatives of equivalence classes, we will from now on use the absolute temperature only.

2.4.4 Absolute entropy

We can continue with our effort of making quantities "absolute" and can think of a notion of the absolute entropy. We fix an adiabatic plane and call its entropy S_0. For another adiabatic plane we pick the value

$$S = S_0 + \frac{1}{T}\int_{\mathcal{C}} \delta Q, \tag{2.34}$$

where $\mathcal{C}$ is some isothermal path that connects the reference plane to the new adiabatic plane. This definition does not depend on the chosen path, as follows from our above observation of Carnot processes: Two different paths we could, with many appropriate adiabatic pieces, connect to a Carnot engine, so that the integrals in both entropy definitions would become the heat values Q_1 and Q_3. We call the above quantity the absolute entropy.

We can even simplify our expression of the absolute entropy. Surely δQ and dS will vanish on the adiabatic steps. Hence, there must be some integrating factor λ with $dS = \lambda \delta Q$. This factor we can determine along any isothermal path, and find from Eq. (2.34) $\lambda = 1/T$. Hence,

$$dS = \frac{\delta Q}{T}. \tag{2.35}$$

We can hence compute S as a line integral of $\delta Q/T$ over an arbitrary path.

We can now define the total entropy of a composite quantum system as the sum of the entropies of the parts. This definition is perfectly compatible with the composition of parts under heat contact. Since $U = U^{(1)} + U^{(2)}$ and since the control parameters are the sum of the control parameters of the parts,

$$\delta A = \delta A^{(1)} + \delta A^{(2)}. \tag{2.36}$$

Therefore

$$\delta Q = \delta Q^{(1)} + \delta Q^{(2)}. \tag{2.37}$$

and since in contact with a heat bath the temperature is held constant,

$$dS = \frac{1}{T}\delta Q = dS^{(1)} + dS^{(2)}. \tag{2.38}$$

It is clear that this total entropy is conserved as long as merely adiabatic processes take place in its parts. Also, for the Carnot process, the total entropy of system and its bath is conserved.

Another consequence of the second law of thermodynamics is that if two systems at different temperatures are put into contact with each other, the energy can only spontaneously flow from the hotter to the colder body. Otherwise, one could gain work from a subsequent Carnot engine. If two systems at temperatures $T_+ > T_-$ are put into contact, hence $\delta Q_- = -\delta Q_+ > 0$, and therefore

$$dS = dS^{(1)} + dS^{(2)} = \frac{\delta Q_-}{T_-} + \frac{\delta Q_+}{T_+} = \delta Q_- \left(\frac{1}{T_-} - \frac{1}{T_+} \right) > 0. \tag{2.39}$$

Since every process we considered is either isothermal or adiabatic, this means that the entropy can only grow.

Processes that do not involve steps of spontaneous heat exchange between parts of different temperature, but merely adiabatic processes of composite systems, can be reversed by reversing the switching of the control parameters. They are hence reversible and satisfy $dS = 0$. Also, one can show that every change of state with $dS = 0$ can be reached in this fashion. Processes with $dS > 0$ are hence exactly the irreversible processes. In fact, this observation, which is here a consequence of the laws as we introduced them, is usually referred to as the Sommerfeld formulation of the second law of thermodynamics.

> Second law of thermodynamics (Sommerfeld's formulation): Every system has an extensive quantity S, the entropy. Its change in reversible processes is obtained by taking the added heat and deviding it by the temperature at which this process is performed. In all irreversible processes, inner entropy is being generated.

Often, one writes the balance in the change of entropy as

$$dS = d_i S + d_e S, \tag{2.40}$$

meaning that the entropy can change either by it being altered in the system itself ($d_i S$), or by a flow of entropy to or out of the system $d_e S$. A way of putting this irreversibility is that

$$d_i S \geq 0. \tag{2.41}$$

The entropy exchanged $d_e S$ with a heat bath and the heat δQ that is exchanged at temperature T in a reversible fashion is

$$d_e S = \frac{1}{T} \delta Q. \tag{2.42}$$

The above statements

$$dS = d_e S + d_i S \tag{2.43}$$

and

$$d_e S = \frac{\delta Q}{T}, \ d_i S \geq 0 \tag{2.44}$$

are combined to

$$dS \geq \frac{\delta Q}{T}. \tag{2.45}$$

2.4.5 Gibbs' fundamental equation

We now want to combine the first and the second laws in a single expression. We find for reversible processes

$$dS = \frac{1}{T}dU - \frac{1}{T}\delta A. \tag{2.46}$$

Writing δA as

$$\delta A = \sum_j K_j d\alpha_j, \tag{2.47}$$

we have the following:

Gibbs' fundamental equation:

$$dS = \frac{1}{T}dU - \frac{1}{T}\sum_j K_j d\alpha_j. \tag{2.48}$$

2.4.6 Entropy of an ideal gas

Let us as an example consider a simple ideal gas, defined as a substance for which the isothermals are of the form $pV = \theta$ (const), and the inner energy of which is

$$U = \frac{f}{2}\theta. \tag{2.49}$$

We can express the differential form dS in the coordinate system (θ, V),

$$dS = \frac{f}{2T}d\theta + \frac{\theta}{VT}dV. \tag{2.50}$$

Since this is a closed differential form, and since T merely depends on θ, we have to have

$$0 = \left(\frac{\partial(f/(2T))}{\partial V}\right)_\theta = \left(\frac{\partial(\theta/(TV))}{\partial \theta}\right)_V. \tag{2.51}$$

This means that

$$\lambda := \frac{\theta}{T} \tag{2.52}$$

is independent of θ. Using this fact, we get

$$dS = \lambda\left(\frac{f}{2}\frac{dT}{T} + \frac{dV}{V}\right), \tag{2.53}$$

and therefore,

$$S(T,V) = S_0 + \lambda\left(\frac{f}{2}\ln\frac{T}{T_0} + \ln\frac{V}{V_0}\right). \tag{2.54}$$

Using the relation

$$U = \frac{f}{2}\lambda T, \tag{2.55}$$

we can in the variables (U,V) express this also as

$$S(U,V) = S_0 + \lambda\left(\frac{f}{2}\ln\frac{U}{U_0} + \ln\frac{V}{V_0}\right). \tag{2.56}$$

This is the desired expression of the entropy of the ideal gas.

2.5 Thermodynamic potentials

2.5.1 Conditions for equilibrium

If two simple systems are brought into contact with each other, they will arrive at an equilibrium state at some temperature $T^{(1)} = T^{(2)}$. If the systems are initially not in equilibrium, then the final state reached will depend on the specifics of how this equilibrium is reached. In particular, it will depend on whether mechanical work is being generated or not. If the temperature equilibration happens spontaneously, then the entropy will increase, as explained above, until the state maximum entropy given the fixed total energy has been reached. In case that when reaching equilibrium work is being performed using reversibly operating heat engines, then the entropy will be constant, and the inner energy will change, until equilibrium is reached.

Let us first look at the situation of maximising the entropy under fixed control parameters. Denoting all quantities of one container with (1) and the other with (2), we have

$$dS = dS^{(1)} + dS^{(2)} = \frac{1}{T^{(1)}}dU^{(1)} + \frac{1}{T^{(1)}}dU^{(2)} = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right)dU_1 \geq 0, \tag{2.57}$$

which means that in equilibrium,

$$T^{(1)} = T^{(2)}. \tag{2.58}$$

Also, if we maximise the inner energy when holding the entropy constant at fixed control parameters, again

$$dU = dU^{(1)} + dU^{(2)} = T^{(1)}dS^{(1)} + T^{(2)}dS^{(2)} = (T^{(1)} - T^{(2)})dS^{(1)} \tag{2.59}$$

from which again $T^{(1)} = T^{(2)}$ follows in equilibrium.

In this discussion, we have assumed that the control parameters are static. We can also look at equilibrium values in situations where we can tune the control parameters appropriately, using the method of Lagrange parameters[1]. For example, let us think of two containers that are coupled via a movable object, in a way that

$$\frac{V^{(1)}}{a_1} + \frac{V^{(2)}}{a_2} = \text{const.} \tag{2.63}$$

If we release this system in a non-equilibrium initial condition, then we will encounter some oscillations. Eventually, by means of irreversible dynamics, these oscillations will be dampened, generating entropy, until the maximum is reached. We can also shift the initial potential energy to a reservoir for mechanical work, until no longer a force acts onto the movable object. The equilibrium condition is hence that U is extremal, under the three constraints

$$\frac{V^{(1)}}{a_1} + \frac{V^{(2)}}{a_2} = \text{const}, \tag{2.64}$$

$$S^{(1)} = \text{const}, \tag{2.65}$$

$$S^{(2)} = \text{const}. \tag{2.66}$$

The two entropies will be held constant separately, since we think of both parts of the system being thermally isolated. The inner energies of the two parts are

$$dU^{(i)} = T^{(i)} dS^{(i)} - p^{(i)} dV^{(i)}, \tag{2.67}$$

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[1] In general, consider functions $f, g_1, \ldots, g_J : \mathbb{R}^n \to \mathbb{R}$. If one wants to solve the problem

$$\min \quad f(\mathbf{x}), \tag{2.60}$$

$$\text{subject to} \quad g_j(\mathbf{x}) = c_j, \tag{2.61}$$

$j = 1, \ldots, J$, then one can look at the stationary points with $dL = 0$ of the Langrangian

$$L(\mathbf{x}, \lambda) = f(\mathbf{x}) - \sum_{j=1}^{J} \lambda_j (g_j(\mathbf{x}) - c_j). \tag{2.62}$$

Under technical conditions (the constraint qualification conditions), then necessary for points to solve the above problem for f under the constraints given by $g_1, \ldots, g_J$ is that the point is stationary.

with $dU = dU^{(1)} + dU^{(2)}$. With the Lagrange parameters $\lambda, \lambda_1, \lambda_2$ we get

$$\begin{aligned} 0 &= dU - \lambda_1 dS^{(1)} - \lambda_2 dS^{(2)} - \lambda d(V^{(1)}/a_1 + V^{(2)}/a_2) \\ &= (T^{(1)} - \lambda_1) dS^{(1)} + (T^{(2)} - \lambda_2) dS^{(2)} \\ &- \left(p^{(1)} + \frac{\lambda}{a_1}\right) dV^{(1)} - \left(p^{(2)} + \frac{\lambda}{a_2}\right) dV^{(2)}. \end{aligned} \tag{2.68}$$

Now these two differentials are linearly independent. Hence, solving for λ gives that we have to have

$$p^{(1)} a_1 = p^{(2)} a_2. \tag{2.69}$$

In particular, when $a_1 = a_2 = 1$, then the condition for equilibrium is simply

$$p^{(1)} = p^{(2)}, \tag{2.70}$$

and the pressure has to be the same on both sides.

2.5.2 Free energy

Let us move on by considering a simple system in contact with a heat bath at temperature T_B. The control parameters $\alpha_1, \ldots, \alpha_k$, such as in the last example the volumes, may be subject to any kind of constraints. The index B labels the heat bath in this case. In order to keep things simple, let us take as coordinates in state space the control parameters as well as the entropy (remember that for simple systems, the dimension of state space is one more than the number of control parameters). We aim at finding the minimum of the inner energy $U + U_B$ for fixed entropy $S + S_B$ and other constraints.

We can compute the minimum in two steps. We first hold the control parameters constant and vary the distribution of entropy between system and bath. Since

$$dU_B = T_B dS_B = -T_B dS, \tag{2.71}$$

with T_B not being dependent on the state (it is a heat bath, after all), this first step amounts to finding the minimum of $U - T_B S$. We define the free energy as

$$F(T_B, \alpha_1, \ldots, \alpha_k) = \min \{U - T_B S : (\alpha_1, \ldots, \alpha_k) \text{ fixed } \}. \tag{2.72}$$

If we consider the inner energy U as a function of $(S, \alpha_1, \ldots, \alpha_k)$, we merely have to find the value of S for which the minimum is attained. At this point we also have $T = T_B$, surely, so that we can write

$$F = U - TS. \tag{2.73}$$

By introducing the free energy F, the variables of the bath are eliminated, with the exception of T_B, and we only have to find the minimum of $F(T_B, \alpha_1, \ldots, \alpha_k)$, respecting the possibly available constraints to the control parameters $\alpha_1, \ldots, \alpha_k$.

2.5.3 Convexity of extensive functions of state

If we increase the "magnitude" of a homogeneous material by a factor of λ, then one transforms a system with extensive variables $S, U, V, \mathbf{N}$ into one with variables $\lambda S, \lambda U, \lambda V, \lambda \mathbf{N}$. Here, N can stand for the particle number, and more generally the vector $\mathbf{N}$ of particle numbers of particles of different kinds. The function that determines the inner energy, therefore, satisfies

$$U(\lambda S, \lambda V, \lambda \mathbf{N}) = \lambda U(S, V, \mathbf{N}). \tag{2.74}$$

Such functions are also called homogeneous of grade 1. A function that is homogeneous of grade n would satisfy $U(\lambda S, \lambda V, \lambda \mathbf{N}) = \lambda^n U(S, V, \mathbf{N})$. Differentiating this function and then setting $\lambda = 1$, one obtains

$$\left(\frac{\partial U}{\partial S}\right) S + \left(\frac{\partial U}{\partial V}\right) V + \sum_{i=1}^{s} \left(\frac{\partial U}{\partial N_i}\right) N_i = U. \tag{2.75}$$

These partial derivatives have already been identified earlier when discussing work differentials and the definition of the entropy. We have

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial S}\right) dS + \left(\frac{\partial U}{\partial V}\right) dV + \sum_{i=1}^{s} \left(\frac{\partial U}{\partial N_i}\right) dN_i \\ &= TdS - pdV + \sum_{i=1}^{s} \mu_i dN_i. \end{aligned} \tag{2.76}$$

The variables μ_i, $i = 1, \ldots, s$, are called chemical potentials. Since $S, V, \mathbf{N}$ form a coordinate system, the coefficients of the differentials are uniquely determined, so

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,\mathbf{N}} \tag{2.77}$$

and so on. In this way, we get from Eq. (2.75) the following equation.

Gibbs-Duhem equation:

$$U = TS - pV + \sum_{i=1}^{s} \mu_i N_i. \tag{2.78}$$

Finally, we can also come up with an expression for the entropy of an ideal gas as a function of the number of particles of a single kind N, using the expression

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N). \tag{2.79}$$

We can take $N = \lambda N_0$ where N_0 is the number of particles for which we have computed the entropy above, in Eq. (2.56). This way, we get the following equation.

Sackur-Tetrode-equation:

$$S(U, V, N) = N\left(\frac{f}{2}\ln\frac{U}{U_0} + \ln\frac{V}{V_0} - \frac{f+2}{f}\ln\frac{N}{N_0} + \frac{S_0}{N_0}\right). \tag{2.80}$$

By means of differentiation to U and V, respectively, one gets

$$U = \frac{f}{2}NT,\ pV = NT. \tag{2.81}$$

The numbers N_0, V_0, and U_0 here merely reflect the units.

What happens now if we put two systems into heat contact with another, the extensive quantities of which are not proportional? Let us assume that the parts are described by inner energy functions $U^{(1)}$ and $U^{(2)}$, the joint system by the function $U^{(12)}$. We start with an initial state in which the parts are described by $S^{(i)}$, $V^{(i)}$, and $\mathbf{N}^{(i)}$. By means of adiabatic processes, for which

$$S = S^{(1)} + S^{(2)} \tag{2.82}$$

is held constant, one draws energy from the system, until it is in equilibrium. Here, merely the joint volume

$$V = V^{(1)} + V^{(2)} \tag{2.83}$$

is thought to be constrained, and no particles should be generated or destroyed, $\mathbf{N} = \mathbf{N}^{(1)} + \mathbf{N}^{(2)}$. The equilibrium states of the joint system is hence described by $U, V, \mathbf{N}$, and it is

$$U^{(12)}(S, V, \mathbf{N}) \leq U^{(1)}(S^{(1)}, V^{(1)}, \mathbf{N}^{(1)}) + U^{(2)}(S^{(2)}, V^{(2)}, \mathbf{N}^{(2)}). \tag{2.84}$$

The inequality originates from the fact that also work could have been done. We assume that both systems are homogeneous systems, so contain only one kind of particles, the three functions $U^{(1)}$, $U^{(2)}$, and $U^{(12)}$ are in fact the same, and therefore,

$$U(S^{(1)}+S^{(2)},V^{(1)}+V^{(2)},\mathbf{N}^{(1)}+\mathbf{N}^{(2)}) \leq U(S^{(1)},V^{(1)},\mathbf{N}^{(1)})+U(S^{(2)},V^{(2)},\mathbf{N}^{(2)}). \tag{2.85}$$

One also says that the function U is sub-additive. Similarly, replacing the principle of minimal energy by the maximum entropy principle, one arrives at

$$S(U^{(1)}+U^{(2)},V^{(1)}+V^{(2)},\mathbf{N}^{(1)}+\mathbf{N}^{(2)}) \geq S(U^{(1)},V^{(1)},\mathbf{N}^{(1)})+S(U^{(2)},V^{(2)},\mathbf{N}^{(2)}) \tag{2.86}$$

that is to say, the entropy function is super-additive. Any function that is sub additive and homogeneous of grade one is also convex: This means that for any $\lambda \in [0,1]$,

$$\begin{aligned} & U(\lambda S^{(1)} + (1-\lambda)S^{(2)}), \lambda V^{(1)} + (1-\lambda)V^{(2)}, \lambda \mathbf{N}^{(1)} + (1-\lambda)\mathbf{N}^{(2)}) \\ \leq \; & \lambda U(S^{(1)},V^{(1)},\mathbf{N}^{(1)}) + (1-\lambda)U(S^{(2)},V^{(2)},\mathbf{N}^{(2)}). \end{aligned} \tag{2.87}$$

For S, the converse inequality is true, that is, i.e., it is a convace function. These properties may be seen as stability conditions. One can gain work by turning a non-homogeneous state into a homogeneous one.

2.5.4 A bit of convex geometry

Let us do a bit of a detour and have a look at convex functions and sets. This is educational anyway. But in this way, we will also understand the role of Legendre transforms in thermodynamics. A set $S \subset \mathbb{R}^n$ is called convex if the line segment connecting any two elements is also contained in the set, that is,

$$\lambda \mathbf{x} + (1-\lambda)\mathbf{y} \in S \tag{2.88}$$

for all $x, y \in S$. A function $f : \mathbb{R}^n \to \mathbb{R}$ is called convex, if

$$f\left(\sum_i \lambda_i \mathbf{x}_i\right) \leq \sum_i \lambda_i f(\mathbf{x}_i), \tag{2.89}$$

for

$$\lambda_i \geq 0, \; \sum_i \lambda_i = 1. \tag{2.90}$$

Such functions are actually called convex, because their supergraph is a convex set, that is, the set

$$\{(\mathbf{x}, y) \in \mathbb{R}^n \times \mathbb{R} : y \geq f(\mathbf{x})\} \subset \mathbb{R}^{n+1} \tag{2.91}$$

is convex. It is sufficient to check the above inequality for two summands with $\lambda_1 + \lambda_2 = 1$, the general statement follows from induction. It is also convenient to allow for function values ∞ and write $\bar{\mathbb{R}}$ for $\mathbb{R} \cup \infty$. Again, f is concave if $-f$ is convex. A function is both convex and concave, if it is an affine function, so if f is of the form

$$f(x) = \xi \cdot \mathbf{x} - c, \tag{2.92}$$

where $c \in \mathbb{R}$, $\xi \in \mathbb{R}^n$, and the dot stands for the standard scalar product.The pointwise supremum of an arbitrary collection of convex functions is convex.

A twice differentiable function $f : \mathbb{R} \to \mathbb{R}$ is convex exactly if $f''(x) \geq 0$ for all $\mathbf{x}$. For functions of many variables, it is sufficient to look at the directional derivative along arbitrary lines. This is equivalent with the positive-definiteness of the matrix M with entries

$$M_{j,k} = \frac{\partial^2 f}{\partial x_j \partial x_k}(\mathbf{x}). \tag{2.93}$$

This means that this matrix has non-negative eigenvalues only, also written as

$$M \geq 0. \tag{2.94}$$

For this, needless to say, one needs that the function is twice differentiable.

2.5.5 Legendre transforms

For every set $K \subset \mathbb{R}^n$ there is a smallest convex set $S \supset K$ that contains K. This is called the convex hull of K, denoted as $\mathrm{co}(K)$. Via the supergraph construction, $\mathrm{co}f$ is the largest convex function that is smaller than f.

In order to make sure that $\mathrm{co}f$ exists, we have to know that there is an affine function that bounds f from below. We now look for a fixed ξ the largest affine function that is below f. The condition

$$f(\mathbf{x}) \geq l(\mathbf{x}) = \xi \cdot \mathbf{x} - c \tag{2.95}$$

for all $\mathbf{x}$ is equivalent with

$$c \geq \xi \cdot \mathbf{x} - f(\mathbf{x}). \tag{2.96}$$

Legendre transform:

$$c \geq \tilde{f}(\xi) := \sup_{\mathbf{x}} \left\{ \xi \cdot \mathbf{x} - f(\mathbf{x}) \right\}. \tag{2.97}$$

The function $\tilde{f} : \mathbb{R}^n \to \bar{\mathbb{R}}$ is called Legendre transform of f.

The function $\tilde{f}$ is convex, as a supremum of affine functions. In fact,

$$\mathrm{co}f(\mathbf{x}) = \sup_{\xi} \left\{ \xi \cdot \mathbf{x} - \tilde{f}(\xi) \right\} = \tilde{\tilde{f}}(\mathbf{x}). \tag{2.98}$$

If f was convex in the first place, of course $\tilde{\tilde{f}} = f$. These Legendre transforms will play a role in a minute, when we discuss thermodynamic potentials.

2.5.6 Thermodynamic potentials

Thermodynamic potentials are functions which contain the complete information about the thermostatic properties of a system. The for our purposes most important such functions are $U(S, V, \mathbf{N})$, the free energy $F(T, V, \mathbf{N})$, the enthalpy $G(T, p, \mathbf{N})$, which we will encounter in a minute, the grand canonical potential $J(T, V, \mu)$, which we will also learn about soon. We do not mean the state variables of the same name, but really the full functions of the respective variables. Each of the potentials describes under appropriate conditions the work done by the system, hence we will find an extremal principle, which will correspond to certain convexity properties.

The best studied function of this type so far is the inner energy. The differential of the inner energy is

$$dU = TdS - pdV + \sum_{i=1}^{s} \mu_i N_i = TdS - \delta A. \tag{2.99}$$

Since $(S, V, \mathbf{N})$ is a coordinate system, we find, or rather have found already,

$$\begin{aligned} T(S, V, \mathbf{N}) &= \left(\frac{\partial U}{\partial S} \right)_{V, \mathbf{N}}, && (2.100) \\ p(S, V, \mathbf{N}) &= -\left(\frac{\partial U}{\partial V} \right)_{S, \mathbf{N}}, && (2.101) \\ \mu_i(S, V, \mathbf{N}) &= \left(\frac{\partial U}{\partial N_i} \right)_{S, V}. && (2.102) \end{aligned}$$

From the first relations we can by elimination of S get the pressure p as a function of $(T, V, \mathbf{N})$. As we know from the ideal gas, the knowledge of $p(T, V, \mathbf{N})$ is not enough to reconstruct U, as the parameter f remains uncertain. This function is hence not a thermodynamical potential in our sense.

In adiabatic processes with $dS = 0$ we have $dU = -\delta A$. This we have put into relationship with a minimality principle for energy. The point was as follows: Given two systems that are each in equilibrium, but not with each other. Then we can draw work from the joint system in an adiabatic fashion (under the given constraints) until equilibrium has been reached. In equilibrium hence U becomes minimal for an adiabatically isolated joint system. From this, we have concluded the convexity of the function

$$(S, V, \mathbf{N}) \mapsto U(S, V, \mathbf{N}). \tag{2.103}$$

This, in turn, leads to inequalities for the second derivatives of U, so the first derivatives of $T, p, \mu_1, \ldots, \mu_s$. For example,

$$\left(\frac{\partial p}{\partial V}\right)_{S,\mathbf{N}} = -\left(\frac{\partial^2 U}{\partial V^2}\right)_{S,\mathbf{N}} \leq 0. \tag{2.104}$$

In the p-V-diagram adiabatic curves with S being constant hence have a negative slope. So again, we get statements on the shape of adiabatic curves from the convexity of the inner energy function.

We now turn to the free energy. We have defined it as

$$\begin{aligned} F(T_B, V, \mathbf{N}) &= \inf_S \{U(S, V, \mathbf{N}) - T_B S\} = -\sup_S \{T_B S - U(S, V, \mathbf{N})\} \\ &= -\left(\tilde{U}(., V, \mathbf{N})\right)(T_B). \end{aligned} \tag{2.105}$$

Up to the sign, this is hence the Legendre transform of U as a function of S, at constant V and $\mathbf{N}$. Since we can from F determine U again by a Legendre transform, since it is convex (for convex functions, the "double Legendre transform is the function itself"), it is clear that F – just as well as U – must contain the complete information about the thermodynamic system. Since the infimum of F is obtained by definition at the temperature

$$T_B = \left(\frac{\partial U}{\partial S}\right)_{V,\mathbf{N}} = T, \tag{2.106}$$

one has

$$F = U - TS, \tag{2.107}$$

hence

$$\begin{aligned} dF &= dU - TdS - SdT = -\delta A - SdT \\ &= -SdT - pdV + \sum_{i=1}^{s} \mu_i dN_i, \end{aligned} \tag{2.108}$$

using the familiar expression of the work differential. We have taken $(T, V, \mathbf{N})$ as the coordinate system, so can again consider the partial derivatives to "their" variables.

In order to compute the free energy for an ideal gas, say, one can eliminate the inner energy in the expression $F = U - TS$ by using S as in Eq. (2.80) and

$$U = \frac{f}{2} NT. \tag{2.109}$$

In this way, one obtains

$$F(T, V, N) = NT \left(\frac{f}{2} \left(1 - \ln \frac{T}{T_0} \right) - \ln \frac{V}{V_0} + \ln \frac{N}{N_0} - \frac{S_0}{N_0} \right). \tag{2.110}$$

In case a process is performed in an isothermal fashion, in contact with a bath of temperature T, then $dT = 0$, so

$$dF = -\delta A. \tag{2.111}$$

Along isothermal paths in state space, one can hence integrate the work done to

$$\Delta F = F(T, \mathrm{End}) - F(T, \mathrm{Beginning}). \tag{2.112}$$

We again arrive at an extremity principle: We can bring two parts together, both of which are in contact with the same heat bath. If we allow – under appropriate constraints – the variation of the parameters $V^{(i)}$ and $\mathbf{N}^{(i)}$, then a new equilibrium will be reached. We can arrive at this equilibrium by taking out as much energy as possible (see the above work differential). Since this happens in an isothermal fashion, we have to find the state of minimal free energy, given the constraints. In a way, the free energy is constructed to just capture such isothermal situations.

We also find that F has to be subadditive as a function of V and $\mathbf{N}$. Using the homogeneity (of the function), again again the argument that we can draw work from the system until the free energy is minimal, we find that $(V, \mathbf{N}) \mapsto F(T_B, V, \mathbf{N})$ has to be a convex function, at fixed T. A simple consequence of the convexity of F is

$$\left(\frac{\partial p}{\partial V} \right)_{T,\mathbf{N}} = - \left(\frac{\partial^2 F}{\partial V^2} \right)_{T,\mathbf{N}} \leq 0. \tag{2.113}$$

The isothermal lines in the p-V-diagram hence have, just as the adiabatic lines, a negative slope. Again, this is a quite sophisticated argument on the shape of isothermal lines.

The next potential is the free enthalpy $G(T,p,\mathbf{N})$, also called Gibbs potential. Just as the free energy it is particularly suitable to grasp systems in contact with a heat bath. But the free enthalpy is particularly useful in situations that in addition allow for an exchange of volume with their environment. We define G as the Legendre transform of U with respect to the variable pair (S,V), so

$$G(T_B,p_b,\mathbf{N}) = \inf_{S,V}\left\{U(S,V,\mathbf{N}) - T_BS + p_BV\right\}. \tag{2.114}$$

The infimum is taken at

$$T_B = \left(\frac{\partial U}{\partial S}\right)_{V,\mathbf{N}} = T \tag{2.115}$$

and

$$p_B = -\left(\frac{\partial U}{\partial V}\right)_{S,\mathbf{N}} = p. \tag{2.116}$$

On using the Gibbs-Duhem equation, one gets

$$G = U - TS + pV = \sum_{i=1}^{s}\mu_iN_i. \tag{2.117}$$

and

$$dG = -TdS + Vdp + \sum_{i=1}^{s}\mu_i dN_i. \tag{2.118}$$

Just as the free energy takes the free enthalpy the in the situation it is designed for (both T and p being constant) the role of the usable work. Again, we can take similar steps as above to get an explicit formula for the free enthalpy of the ideal gas. We get, for one species of particles,

$$G(T,p,N) = NT\left(-\frac{f}{2}\ln\frac{T}{T_0} + \ln\frac{p}{p_0} + \left(\frac{f+2}{2} - \frac{S_0}{N_0}\right)\right). \tag{2.119}$$

The last potential, which we only briefly mention, is the great canonical potential $J(T,V,\mu)$. It is the Legendre transform of $(S,N)\mapsto U(S,V,N)$ at fixed V. As such, it is useful for systems in contact with a heat bath, which in addition can exchange particles with their environment.

2.6 Phase transitions

We now come to the final section of our chapter on thermodynamics: On phase transitions. We will hear more about phase transitions later in this course. So let us be brief at this point and merely consider a single example, the one of a phase transition between a fluid and a gas in a van der Waals gas. This is a gas that is not ideal. The equation of state is as follows:

State equation of the van der Waals gas:

$$\left(p + \frac{a}{v^2}\right)(v - b) = cT. \tag{2.120}$$

with constants $a, b, c > 0$, where $v = V/N$.

At the critical temperature T_c the two extrema merge and the curve will develop a saddle point, determined by

$$\frac{\partial p}{\partial v} = 0, \ \frac{\partial^2}{\partial v^2} = 0. \tag{2.121}$$

This condition, applied to Eq. (2.120), gives

$$\begin{aligned} -\frac{cT}{(v-b)^2} + \frac{2a}{v^3} &= 0, & (2.122)\\ \frac{2cT}{(v-b)^3} - \frac{6a}{v^4} &= 0. & (2.123) \end{aligned}$$

From this, we finds the critical temperature

$$cT = \frac{8}{27}\frac{a}{b}. \tag{2.124}$$

The saddle point is at

$$v_c = 3b, \ p_c = \frac{a}{27b^2}. \tag{2.125}$$

Now, if one now considers the isothermal lines in the p-V-diagram, one finds “below the critical point” that there is a region where these isotherms are monotone increasing. This contradicts the stability of the system in the form of the convexity of F. At least in this region the van der Waals equation has to be unphysical. A correction is as follows called the Maxwell construction: This means that F is replaced by its convex hull.

In effect, this means that a piece of the isothermal is replaced by a horizontal piece for which p is constant. This is done in a way such that the volume in the p-V-diagram above and below the constant piece is identical. The free enthalpy is having a kink at the points where the horizontal lines end. It should be clear that now, in this particular case, the state is not completely defined by (T, p). The coexistence region proceeds to the critical point, determined above.

The left part corresponds to the gaseous region, to the right one has a fluid. Along the straight lines, both phases are in coexistence. Let us consider the change to the free enthalpy G along the straight lines in the p-V-diagram. Since the particle number of a single species is identical, $dN = 0$, we have

$$-S_{\text{fluid}} dT + V_{\text{fluid}} dp = dG = -S_{\text{gas}} dT + V_{\text{gas}} dp. \tag{2.126}$$

Hence, we have for the coexistence line the following equation.

Clausius-Clapeyron equation:

$$\frac{dp}{dT} = \frac{S_{\text{gas}} - S_{\text{fluid}}}{V_{\text{gas}} - V_{\text{fluid}}} = \frac{N}{T} \frac{\delta q}{V_{\text{gas}} - V_{\text{fluid}}}. \tag{2.127}$$

This equation is usually made use of in the case that

$$V_{\text{fluid}} \ll V_{\text{gas}} \approx NT/p. \tag{2.128}$$

Here, δq is the heat quantity that is necessary per particle number that one has to provide to the fluid in order to transform it into a gas.

For real materials, there are usually a number of other phase transitions, often with a number of qualitatively different solid phases. Point where three phases meet are usually called triple points. In particular for systems consisting of a number of different constituents, phase diagrams can look quite complicated.

Chapter 3

Elements of classical statistical physics

3.1 Elements of classical mechanics and probability theory

3.1.1 Phase spaces and classical mechanics

We start by discussing elements of classical mechanics, in order to lay out the formalism for classical statistical physics. This is surely a meaningful starting point, as many phenomena can be explained in a classical description. Others cannot. We consider a system of N particles, confined to a region $\Omega \subset \mathbb{R}^3$. The phase space of each particle consists hence of the pair $(\mathbf{q}, \mathbf{p})$ with $\mathbf{p} \in \mathbb{R}^3$ and $\mathbf{q} \in \Omega$. The total phase space of all particles is the cartesian product.

Phase space of N particles:

$$\Gamma = (\mathbb{R}^3 \times \Omega)^N. \tag{3.1}$$

Points in phase space are often written as γ. The complete description of a classical system is given by $\gamma \in \Gamma$, as then we know all positions and momenta of all particles. The equations of motion of these particles are determined by the Hamiltonian function $H : \Gamma \to \mathbb{R}$. We take them of the form

$$H(\gamma) = \sum_{i=1}^{N} \left(\frac{\mathbf{p}_i^2}{2m} + V_1(\mathbf{q}_i) \right) + \sum_{i \neq j} V_2(\mathbf{q}_i - \mathbf{q}_j), \tag{3.2}$$

where V_1 is a single particle potential and V_2 is an interaction between the particles. To simplify the notation, we have taken all particles to be the same, with the same mass m. It is often convenient to consider the collection of all positions and all momenta as vectors,

$$\mathbf{p} = (p_{1,1}, p_{1,2}, \ldots, p_{N,3}) = (p_1, \ldots, p_{3N}), \tag{3.3}$$

and similarly for $\mathbf{q}$. In this way, the Hamiltonian equations of motion become

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \tag{3.4}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}. \tag{3.5}$$

At this point, maybe a comment is in order how we treat boundaries here. We assume that the boundary of Ω is reflecting, in that when a particle with $(\mathbf{q}_i, \mathbf{p}_i)$ hits the boundary, then $\mathbf{q}_i$ remains the same but with $\mathbf{p}_i$ being mirrored at the tangential plane.

Solutions of the equations of motion exist for all times. For times $t \in \mathbb{R}$ one hence arrives at at a map $\mathcal{F}_t : \Gamma \to \Gamma$ such that $t \mapsto \mathcal{F}_t(\gamma)$ is the solution of the problem with initial state γ. We have $\mathcal{F}_0(\gamma) = \gamma$ and also, since the Hamiltonian is assumed not to be time dependent,

$$\mathcal{F}_t \circ \mathcal{F}_s = \mathcal{F}_{t+s}, \tag{3.6}$$

for all $s, t \in \mathbb{R}$. The family of such functions $\mathcal{F}_t$ is called the flow in phase space.

Two features are important here. The first one is that the energy is conserved. In our new language, this means that

$$H(\mathcal{F}_t(\gamma)) = H(\gamma). \tag{3.7}$$

The second one is that the volume is preserved under dynamics. The volume is measured in the Liouville measure, written as

$$d\gamma = dp_1 dq_1 \ldots dq_{3N} = d^{3N}p d^{3N}q. \tag{3.8}$$

Preservation of volume means that

$$\int d\gamma f(\mathcal{F}_t(\gamma)) = \int d\gamma f(\gamma). \tag{3.9}$$

If $f = \chi_S$ is the indicator function of an arbitrary set $S \subset \Gamma$, then the right hand side is the volume of S, whereas the left is the volume of the transformed set $\mathcal{F}_t^{-1}(S) = \{\gamma : \mathcal{F}_t(\gamma) \in S\}$.

An important role will be played by the energy shell. Consider for some energy value E the energy surface.

Energy surface: For any E in the image of H, define the energy surface

$$\{\gamma : H(\gamma) = E\}. \tag{3.10}$$

It has dimension $6N-1$. Therefore, subsets of this set will have Liouville measure zero. We can still introduce a meaningful surface measure as follows: For energy E and $\epsilon > 0$, consider the set

$$\{\gamma : E - \epsilon \leq H(\gamma) \leq E\}. \tag{3.11}$$

The integral of a function $f : \Gamma \to \mathbb{R}$ over the energy surface is then

$$\begin{aligned} \int d\gamma \delta(H(\gamma) - E) f(\gamma) &= \lim_{\epsilon \to 0} \frac{1}{\epsilon} \int_{E-\epsilon \leq H(\gamma) \leq E} d\gamma f(\gamma) \\ &= \frac{d}{dE} \int_{H(\gamma) \leq E} d\gamma f(\gamma). \end{aligned} \tag{3.12}$$

So far, we have assumed that we knew the positions and momenta of all particles precisely. As pointed out several times before, this is neither possible nor needed. We hence always have to include a certain degree of randomness in our description. This motivates the next subsection on elements of probability theory.

3.1.2 Distributions and moments

In this subsection, we will be brief and focused. Let us consider systems described by the laws of classical mechanics. The state of the system is then $\gamma \in \Gamma$. We assume Γ to be the above phase space, but the same notion also makes sense for finite state spaces. A common experiment amounts to not exactly preparing γ, but rather a distribution of a set of possible states. We introduce a density ρ, such that $\rho(\gamma)$ is the probability density of having prepared the state γ. From the probability interpretation we have that

$$\rho(\gamma) \geq 0, \tag{3.13}$$

$$\int d\gamma \rho(\gamma) = 1. \tag{3.14}$$

One can interpret this quantity as grasping relative frequencies in a statistical preparation of a state.

Observables, expectation value and variance: An observable is a function $f : \Gamma \to \mathbb{R}$ that determines the outcome $f(\gamma)$ if a system is in the state γ. The expectation value (or first moment) is given by

$$\langle f\rangle_\rho = \int d\gamma \rho(\gamma) f(\gamma). \tag{3.15}$$

The variance is

$$\left\langle (f - \langle f\rangle_\rho)^2 \right\rangle_\rho = \langle f^2\rangle_\rho - \langle f\rangle^2)_\rho. \tag{3.16}$$

The expected mean of outcomes in measurements is just the expectation value. If we repeat many measurements, the mean of the outcomes will converge to this value. The variance is the expected deviation from the mean. These are first and second moments, but similarly, higher moments can also be defined.

3.1.3 Composite classical systems

We will a lot be concerned with composite systems, the phase space of which is of the form $\Gamma = \Gamma_1 \times \Gamma_2$. Densities of the joint state will then depend on the pair $(\gamma_1, \gamma_2) \in \Gamma_1 \times \Gamma_2$. Often, we are interested in observables that act only in one state. For functions that depend on γ_1 only (but not on γ_2), we can write

$$\int d\gamma_1 d\gamma_2 \rho(\gamma_1, \gamma_2) f(\gamma_1) = \int d\gamma_1 (R_1\rho)(\gamma_1) f(\gamma_1), \tag{3.17}$$

where

$$(R_1\rho)(\gamma_1) = \int d\gamma_2 \rho(\gamma_1, \gamma_2). \tag{3.18}$$

This distribution is called reduced distribution, or marginal distribution.

Say, take a density ρ in the $6N$-dimensional phase space of N particles. We are interested in an observable f that depends only on the coordinates of the first particle. Then

$$\langle f\rangle_\rho = \int d^3p d^3q (R_1\rho)(\mathbf{p}, \mathbf{q}) f(\mathbf{p}, \mathbf{q}), \tag{3.19}$$

with

$$(R_1\rho)(\mathbf{p}_1, \mathbf{q}_1) = \int d^3p_2 \ldots d^3p_N d^3q_2 \ldots d^3q_N \rho(\mathbf{p}_1, \ldots, \mathbf{q}_N). \tag{3.20}$$

We will now assume that the density does not depend on the numbering of the particles, that is, for every permutation π of $\{1, \ldots, N\}$ we have that

$$\rho(\mathbf{p}_{\pi(1)}, \ldots, \mathbf{p}_{\pi(N)} = \rho(\mathbf{p}_1, \ldots, \mathbf{q}_N). \tag{3.21}$$

Then all density functions of ρ are the same. The expectation of the kinetic energy is hence

$$\left\langle \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} \right\rangle = N \int d^3pd^3q(R_1\rho)(\mathbf{p}, \mathbf{q})\frac{\mathbf{p}^2}{2m}. \tag{3.22}$$

In order to compute the variance of the kinetic energy, or the expectation value of the interaction energy, it is no longer sufficient to know the marginal distribution. In order to compute these quantities, we need to know the marginal distribution over two particles.

In case of a composite system $\Gamma = \Gamma_1 \times \Gamma_2$ the density $\rho(\gamma_1, \gamma_2)$ contains in general more information than both marginal distributions $R_i\rho$ together. The exception are product distributions. If

$$\rho(\gamma_1, \gamma_2) = \rho_1(\gamma_1)\rho_2(\gamma_2), \tag{3.23}$$

then the parts are called statistically independent. To prepare statistically independent distributions is particularly easy: One merely needs to keep the parts separate. Two observables f and g are called independent, if for any functions $F, G : \mathbb{R} \to \mathbb{R}$ it is true that

$$\langle F(f)G(g)\rangle_\rho = \langle F(f)\rangle_\rho \langle G(g)\rangle_\rho. \tag{3.24}$$

In statistical mechanics, one usually considers in addition to acts of preparation discussed here the evolution under Hamiltonian dynamics, captured by $\mathcal{F}_t$. From the equations of motion for position and momentum one gets for $\rho_t = \rho \circ \mathcal{F}_{-t}$ that

$$\frac{d}{dt}\rho_t = \sum_{i=1}^{3N} \frac{\partial \rho}{\partial p_i}\frac{\partial H}{\partial q_i} - \frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i}, \tag{3.25}$$

an expression that is also called Poisson-bracket.

Even if parts have been prepared in a statistically independent fashion, they will not remain independent under time evolution in general. That is,

$$\rho(\mathcal{F}_{-t}(\gamma_1, \gamma_2)) \neq \rho_{1,t}(\gamma_1)\rho_{2,t}(\gamma_2). \tag{3.26}$$

An exception is the case where the flow itself remains factoring. This is exactly the case if the Hamiltonian is a sum of Hamiltonians of each parts, so in an entirely non-interacting situation.

3.2 Microcanonical ensemble

3.2.1 Conceptual issues

We have stated several times that the aim of statistical mechanics is to derive or make plausible the phenomenological findings to thermodynamics. This means that we have to establish some sort of translation table, translating concepts of statistical mechanics to those of thermodynamics. Some of them we have just encountered. The container holding some material corresponds to Γ which restricts all position coordinates. The number of particles N has an obvious equivalent in thermodynamics. Also, there is a correspondence between the inner energy and the energy $H(\gamma)$.

This translation is less straightforward in case of entropy, temperature and other thermodynamical functions. These functions were used to grasp thermodynamical equilibria after all. In thermodynamics these equilibrium conditions were defined as those that are established automatically, if one allows a system to relax. In classical dynamics, we also have a notion of time evolution: The flow $\mathcal{F}_t$ describes how a system evolves in time. So one may be temped to look for those states in classical mechanics that are always reached by themselves, via Hamiltonian dynamics.

This approach is, however, doomed to failure. We have seen that under time evolution, the volume in phase space is preserved. There is no set S of a non-zero volume that $\mathcal{F}_t(S)$ becomes a point later. We have to look for the emergence of equilibria elsewhere.

The second attempt is based on the – in principle correct – assumption that we are not interested in all observables, but only in some special observables that are related to small number of "macroscopic" features. For such macroscopic observables f_i we would like to compute their expectation value, or better even

$$\lim_{t\rightarrow\infty} f(\mathcal{F}_t(\gamma)) \tag{3.27}$$

The previous argument of preservation of volume is no longer valid. Still, also this attempt does not work, as arguments show that have already been discussed around the turn of the 19th to the 20th century.

The first is the Umkehreinwand (I think the German word is used here). There is a time reversal symmetry in classical mechanics, under the map

$$\theta : (\mathbf{p}, \mathbf{q}) \mapsto (-\mathbf{p}, \mathbf{q}) \tag{3.28}$$

that reverses all momenta. It is clear that this time reversal symmetry is not respected in the approach to equilibrium.

The second is the Wiederkehreinwand. There is a theorem that shows that for every initial state, the evolution confined to the energy shell will become arbitrarily close to the initial state for a suitable later time. So again, accompanying a tendency to approach equilibrium, there must be a tendency to go out of it again. But this is not what is observed: Already pretty small systems go to equilibrium and stay there.

We can largely resolve these issues, however. The first thing is that the recurrence times in the Wiederkehreinwand are ridiculously large, much larger than any feature that one is commonly interested in. So in any numerical simulation, say, roundoff errors will have become much more important before this recurrence is observed. We can hence safely ignore that.

One can argue similarly with the other argument: Indeed, if one numerically simulates the time evolution of a model, and at some point performs a time reversal, then the system will indeed go back for some time. But this is extremely fragile to numerical errors. If the numerics is done very precisely, then one can indeed observe that the system goes back to the initial state. Otherwise, the simulation detours from the exact reverse trajectory and again goes to equilibrium.

If one considers an initial set $S \subset \Gamma$ of states we start with, then we can have a look how this set evolves in time. We already know that its volume is conserved. But this does not mean that its shape is conserved. It will become wobbly, and then develop "fingers" and will look more and more complicated in time. Soon, the entire phase space is spread out with structures way too fine to resolve. So "typically", a system will converge to a situation that is indistinguishable from the uniform distribution.

3.2.2 Definition of the ensemble

What does typical mean here? It is clear that the entire dynamics can only happen on the energy shell,

$$H(\mathcal{F}_t(\gamma)) = E. \tag{3.29}$$

If there are no obvious symmetries in the problem, usually such systems have no further constants of motion. Such systems, which have no further constants of motion, are called ergodic. If a system is ergodic, hence there exists only one distribution that is stationary in time. We write expectation values as follows:

Expectation values in the micro canonical ensemble:

$$\begin{aligned}\langle f\rangle_E &= \frac{\int d\gamma\delta(H(\gamma)-E)f(\gamma)}{\int d\gamma\delta(H(\gamma)-E)} \\ &= Z(E)^{-1}\int d\gamma\delta(H(\gamma)-E)f(\gamma).\end{aligned} \tag{3.30}$$

The denominator is determined by $\langle 1\rangle_E = 1$. The value $\langle f\rangle_E$ is called the micro-canonical expectation value of the observable f, and

$$\rho(E) = Z(E)^{-1}\delta(H(\gamma)-E) \tag{3.31}$$

the micro-canonical ensemble. The normalisation is the micro-canonical partition function.

For ergodic systems, for almost all initial states the time average of all observables exists. Since this mean is by definition time-independent, it has to be identical with the micro canonical expectation value,

$$\lim_{t\to\infty}\frac{1}{T}\int_0^T dt f(\mathcal{F}_t(\gamma)) = \langle f\rangle_E, \tag{3.32}$$

for almost all γ with $H(\gamma) = E$. The micro-canonical ensemble is hence the accurate description of this final situation of a homogeneous looking phase space picture. Of course, also in a thermodynamic description one can think of time averages. But since all measurement outcomes converge to the equilibrium values, all time averages are just the same as the equilibrium values. Hence, at least for ergodic systems, we have made great progress in identifying thermodynamical equilibrium properties for particle number N, inner energy E, and volume Ω and microscopic descriptions in the framework of classical mechanics.

The fine print, of course, is to find out whether a system is ergodic in the first place. This is mathematically often exceedingly hard to prove. There are classic results on billiards in two dimensions are ergodic – in a proof that fills a couple of hundred pages. Still, people believe that this is merely a technicality, and that essentially all "natural" systems are ergodic.

3.3 Canonical ensemble

3.3.1 Definition of the canonical ensemble

So we have made progress understanding what energy, volume and particle number correspond to. Still, we are lacking an understanding of temperature and entropy. After all, temperature is the notion that defines an equilibrium state. We hence bring a system into contact with a heat bath and will assume that the joint system – so the system plus the heat bath – are described by a micro canonical ensemble. The Hamiltonian function of the composite system is

$$H(\gamma,\gamma_B) = H(\gamma) + H_B(\gamma_B) + V(\gamma,\gamma_B), \tag{3.33}$$

with the obvious interpretation of the terms. The interaction term V allows for an exchange of energy, macroscopically speaking for an exchange of heat. But it is sufficient to allow for very small perturbations of the operator $H + H_B$. We expect also from thermostatics that the equilibrium value does not depend on the specifics of how the heat contact has been made. When computing the micro canonical ensemble, we hence set – in an approximation – just

$$V = 0. \tag{3.34}$$

This is surely an approximation, as the system becomes clearly non-ergodic when the two parts are not in contact with one another. But it should be clear that one can think of sequences of systems, which are coupled less and less, each of which being ergodic. So this approximation is less ridiculous as one might think at first (besides, it is not so easy to overcome this. In quantum theory, we have just published new work in the Physical Review Letters on perturbed systems, in 2012).

For observables that do not depend on the coordinates of the heat bath, we hence get

$$\begin{aligned}\langle f\rangle_E &= Z^{-1}\int d\gamma d\gamma_B \delta(H(\gamma)+H_B(\gamma_B)-E)f(\gamma)\\ &= Z^{-1}\int d\gamma f(\gamma) d\gamma_B \delta\left(H_B(\gamma_B)-(E-H(\gamma))\right)\\ &= Z^{-1}\int d\gamma f(\gamma)\omega_B(E-H(\gamma)),\end{aligned} \tag{3.35}$$

where Z stands for the same expression as above, with f replaced by 1. Also

$$\omega_B(E_B) = \int d\gamma_B \delta(H_B(\gamma_B)-E_B) \tag{3.36}$$

is the micro-canonical density of states of the bath. We therefore find that expectation values are determined by a density that is no longer concentrated on an energy surface alone.

We note another thing: The only property of the heat bath that matters is the micro-canonical density of states. If we take the heat bath to be an ideal gas, so in this statistical description N independent particles of mass m in a container Ω with volume V), we can explicitly determine this quantity. We have

$$\begin{aligned}\omega_B(E-H(\gamma)) &= \int d\gamma_B \delta(H_B(\gamma_B)-(E-H(\gamma)))\\ &= \int_\Omega d^{3N}q \int d^{3N}p\delta\left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}-(E-H(\gamma))\right). \quad (3.37)\end{aligned}$$

The first integral gives V, the second the surface of a $3N$-dimension hyper ball with radius

$$(2m(E-H(\gamma)))^{1/2}. \quad (3.38)$$

Calling $\nu_d R^{d-1}$ the surface of a d-dimensional ball of radius R, we get

$$\begin{aligned}\omega_B(E-H(\gamma)) &= (2m)^{3N/2-1}V^N\nu_{3N}(E-H(\gamma))^{3N/2-1}\\ &= c(E-H(\gamma))^{3N/2-1}, \quad (3.39)\end{aligned}$$

with a suitable constant $c>0$. For very small N, this will hardly be a heat bath, so we have to consider the limit of large particle numbers. We therefore consider $N\to\infty$ and let the energy E of the system and bath proportionally grow with N, so $E=NE_1$. For large N, the energy of the small system itself will be negligible anyway, and we want to keep a finite energy density for the bath.

From thermodynamical considerations on the ideal gas we know that $U_B=fRT/2$, where here $f=3$ (which originates from the three degrees of freedom of movement). The particle number N is here the actual particle number, and not an abstract "Stoffmenge" as is common in thermodynamics. The unit $k=R/\mathrm{mol}$ is then the Boltzmann constant. We will come back to that later. So we get

$$E_1=U_B/N=\frac{3}{2}kT \quad (3.40)$$

$$\begin{aligned}\langle f\rangle_E &= Z^{-1}\int d\gamma f(\gamma)c(E-H(\gamma))^{3N/2-1}\\ &= Z^{-1}\int d\gamma f(\gamma)\left(1-\frac{H(\gamma)}{NE_1}\right)^{3N/2-1}. \quad (3.41)\end{aligned}$$

Since we know that

$$e^{-x} = \lim_{n\to\infty} \left(1 - \frac{x}{n}\right)^n , \tag{3.42}$$

for $N \to \infty$, we get

$$\begin{aligned} \langle f \rangle_\beta &:= \lim_{N\to\infty} \langle f \rangle_{NE_1} = Z^{-1} \int d\gamma f(\gamma) e^{-\frac{3H(\gamma)}{2E_1}} \\ &= Z^{-1} d\gamma f(\gamma) e^{-\beta H(\gamma)}, \end{aligned} \tag{3.43}$$

with

$$\beta = \frac{3}{2E_1} = \frac{1}{kT}. \tag{3.44}$$

This is important enough to deserve a box:

Canonical ensemble: The canonical expectation value of f at the inverse temperature $\beta > 0$ is given by

$$\langle f \rangle_\beta = \int d\gamma \rho_\beta(\gamma) f(\gamma), \tag{3.45}$$

with the canonical ensemble being the distribution

$$\rho_\beta(\gamma) = Z^{-1} e^{-\beta H(\gamma)}. \tag{3.46}$$

The normalisation is provided by the canonical partition function defined as

$$Z = \int d\gamma e^{-\beta H(\gamma)}. \tag{3.47}$$

3.3.2 Equivalence of ensembles

At this point, we have a good reason to be confused: We have just derived two different ensembles, apparently quite different ones, that claim to describe equilibrium situations well. This seems a paradoxical situation. Which one is the correct one? After all, from thermodynamics we know that temperature is defined by the property that the state of two systems is not changed when bringing two bodies at the same temperature together.

At the same time, it is also clear that the two ensembles must be different: Note that the canonical distribution is nowhere zero in phase space, whereas the micro-canonical one is zero except on the energy shell.

This paradox can be resolved by acknowledging that in the regime where the two situations described here are supposed to capture thermodynamical systems in equilibrium, they are practically identical anyway. This observation is called the equivalence of ensembles. This becomes a mathematical statement if one formulates a precise thermodynamic limit of $N \to \infty$ and $V \to \infty$ at E/N being fixed or β being fixed. The actual rigorous proofs that are available are actually quite hairy, however, and the ones commonly stated in text books not quite satisfactory and sometimes even wrong.

For this course, we take a pragmatic approach and rather show that for large systems, the canonical distribution is very much concentrated around an energy surface. This is an instance of the effect known in mathematics as concentration of measure. Let us be specific and look at the variance of energy observables in the canonical ensemble, i.e.,

$$\begin{aligned}\langle H^2\rangle_\beta - \langle H\rangle_\beta^2 &= \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial\beta}\right)^2 \\ &= \frac{\partial}{\partial\beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right). \qquad (3.48)\end{aligned}$$

Note, after all, that

$$U = \langle H\rangle_\beta. \qquad (3.49)$$

This gives

$$\begin{aligned}\langle H^2\rangle_\beta - \langle H\rangle_\beta^2 &= -\frac{\partial U}{\partial\beta} = kT^2\frac{\partial U}{\partial T} = kT^3\frac{\partial S}{\partial U}\frac{\partial U}{\partial T} \\ &= kT^3\frac{\partial S}{\partial T} \\ &= kT^2 C_V, \qquad (3.50)\end{aligned}$$

where all derivatives are done at fixed $V, \mathbf{N}, \ldots$. Now C_V is an extensive quantity, linear in the particle number N. The variance hence diverges as $N \to \infty$. However, this is not the interesting quantity, but rather the energy density per particle. For this, we get for its variance

$$\left(\left\langle\left(\frac{H}{N}\right)^2\right\rangle_\beta - \left\langle\frac{H}{N}\right\rangle_\beta^2\right)^{1/2} = \left(\frac{kT^2C_V}{N^2}\right)^{1/2} \sim \frac{1}{\sqrt{N}}, \qquad (3.51)$$

for large N. The relative deviations of the energy density hence converges to zero for large N. The fluctuations of the order $N^{-1/2}$ is also characteristic for fluctuations in central limit theorems, where independent random variables are being added. The value of the energy per particle is the canonical energy expectation value $\langle H\rangle_\beta$: Hence, since fluctuations can be neglected for large N, the canonical ensemble of inverse temperature β is equivalent with the micro canonical ensemble with energy $U = \langle H\rangle_\beta$.

3.3.3 Revisiting thermodynamic potentials

We have already been doing a good job with refining our "dictionary" for translating statistical concepts into thermodynamical ones. The volume V was easy, this is pretty much the same in thermodynamics as in statistical physics. The energy was a bit trickier, but we now get in what way E and U are the same thing. The temperature T is more subtle, but we have just looked at that.

We are not quite there yet, however. In order to have complete knowledge about a thermodynamical system, we have to know a thermodynamic potential, as we have learned earlier in the course. We know how to compute the inner energy as a function of T, V, and N, from the formula $U = \langle H\rangle_\beta$. After all, V and N are already parameters of the Hamiltonian function. Still, as we surely remember, $U(T,V,N)$ is not quite a thermodynamic potential: It depends on the wrong variables.

A thermodynamic potential that depends on just these variables, however, is the free energy. We know that, on the one hand,

$$\begin{aligned} U &= F + TS = F - T\frac{\partial F}{\partial T} \\ &= F + \beta\frac{\partial F}{\partial \beta} = \frac{\partial}{\partial\beta}(\beta F). \end{aligned} \tag{3.52}$$

On the other hand, exploiting our new knowledge on statistical physics,

$$\begin{aligned} \langle H\rangle_\beta &= \frac{\int d\gamma H e^{-\beta H(\gamma)}}{\int d\gamma e^{-\beta H(\gamma)}} \\ &= \frac{\partial}{\partial\beta}\ln\int d\gamma e^{-\beta H(\gamma)} \\ &= -\frac{\partial}{\partial\beta}\ln Z(\beta,V,N). \end{aligned} \tag{3.53}$$

If we are to identify the left hand sides of the two sets of equations, we have to set

$$F(T,V,N) = -kT\ln\int d\gamma e^{-\frac{H(\gamma)}{kT}} + c_0(V,N), \tag{3.54}$$

where the additional term c_0 does not depend on the temperature T. In order to understand this term better, let us compare F for the ideal gas with the expression for $\ln Z$. This gives

$$\begin{aligned} Z &= \left(\int_{\mathbf{q}_i\in\Omega} d^{3N}q\right)\left(\int d^{3N}pe^{-\frac{\beta}{2m}\sum_{i=1}^{3N}p_i^2}\right) \\ &= V^N\left(\int dpe^{-\frac{\beta}{2m}p^2}\right)^{3N} \\ &= V^N\left(\frac{2\pi m}{\beta}\right)^{3N/2}. \end{aligned} \tag{3.55}$$

That is to say,

$$-\frac{1}{\beta}\ln Z = NkT\left(-\frac{3}{2}\ln T - \ln V + \text{const}\right). \tag{3.56}$$

This we can compare with our expression known from thermodynamics,

$$F(T,V,N) = NRT\left(-\frac{f}{2}\ln T - \ln V + \ln N + \text{const}'\right). \tag{3.57}$$

Here, we have taken for simplicity logarithms of dimensionless expressions, hence the constants still depend on our choice of units. The prefactors are again the same, identifying again N with the “Stoffmenge” in the above way, and setting $f = 3$.

So, meditating over this, we see that the dependence in temperature is correct, after having set $f = 3$. The dependence on the volume is also fine. But, in the expression derived from statistical physics, the term $\ln N$ is lacking. We can hence set

$$c_0 = c_0(N) = -N\ln N \sim -\ln(N!). \tag{3.58}$$

This is perfectly acceptable, given that the above term c_0 does not depend on the temperature. Still, it is a bit of an ad hoc insertion, identifying expressions in statistical physics and thermodynamics. Frankly, classical statistical physics is unable to give a satisfactory explanation to this. In this framework, we simply have to add it in order to render the free energy an extensive function of V and N. Therefore, it comes as no surprise that it was already added by Gibbs in the early descriptions of the field. We will come back to this and will properly derive this in the framework of quantum statistical mechanics.

Now we are essentially there. The other thermodynamic functions we get from this. For example, we have

$$S = -\frac{\partial F}{\partial T} = k\beta^2 \frac{\partial}{\partial \beta}\left(-\frac{1}{\beta}\ln Z\right), \tag{3.59}$$

but it should be clear that once we have access to a thermodynamical potential, we can derive any thermodynamic quantity of the system.

3.4 Remarks on the ensembles of classical statistical mechanics

3.4.1 Gibbs' variational principle

Remember that we had defined the free energy as the Legendre transform of the inner energy, i.e., as $\inf\{U - T_B S\}$, where T_B was treated as a parameter. The infimum was supposed to be taken at all equilibrium values for given values of the control parameters. In the last subsection, we have both derived the inner energy as well as the entropy as functionals over the canonical density ρ_β.

But surely, it also makes sense to think of a corresponding expression in which the infimum is not taken over all macroscopic equilibrium states, but rather over all microscopic states, i.e., all densities ρ. We therefore consider

$$\hat{f}(H) := \inf\left\{\int d\gamma \rho(\gamma) H(\gamma) - \frac{1}{\beta}\hat{S}(\rho)\right\}, \tag{3.60}$$

$$\hat{S}(\rho) := \int d\gamma \hat{s}(\rho(\gamma)), \tag{3.61}$$

where the infimum is taken over all positive integrable functions $\rho : \Gamma \to \mathbb{R}$ with

$$\int d\gamma \rho(\gamma) = 1, \tag{3.62}$$

and the function $\hat{s}$ is given by the function

$$\hat{s}(t) = \begin{cases} -t\ln t & \text{for}\, t > 0, \\ 0 & \text{for}\, t = 0, \\ -\infty & \text{for}\, t < 0. \end{cases} \tag{3.63}$$

Here, we have left out the Boltzmann constant in the definition, so

$$S = k\hat{S}(\rho_\beta). \tag{3.64}$$

If we insert ρ for the canonical ensemble ρ_β, then the above expression just becomes $F(T,V,N)$ again. Indeed, we again have a Legendre transform: The set of density functions forms an infinite dimensional vector space, in which concepts like convexity of sets and functions are defined as before. In this sense, the functional

$$H \mapsto -\hat{F} \tag{3.65}$$

is the Legendre transform of the functional

$$\rho \mapsto \hat{S}(\rho). \tag{3.66}$$

Surely, $-\hat{F}$ is convex, and hence $\hat{F}$ is concave.

Let us now try to find the actual infimum in Eq. (3.60). To start with, we have

$$\begin{aligned} & \lambda\hat{S}(\rho_1) + (1-\lambda)\hat{S}(\rho_2) - \hat{S}(\lambda\rho_1 + (1-\lambda)\rho_2) \qquad (3.67)\\ = & \int d\gamma \, (\lambda\hat{s}(\rho_1(\gamma)) + (1-\lambda)\hat{s}(\rho_2(\gamma)) - \hat{s}(\lambda\rho_1(\gamma) + (1-\lambda)\rho_2(\gamma)) \geq 0, \end{aligned}$$

because of the concavity of $\hat{s}$. That is to say, $\hat{S}$ is concave. In fact, it is even strictly concave (since $\hat{s}$ is strictly concave, the integral can be zero only if for almost all γ we have that $\rho_1(\gamma) = \rho_2(\gamma)$.). Since the first integral is affine in ρ, we have to find the infimum over a strictly convace function. This means that this infimum can be attained at most in a single point. In order to identify this point, we make use of differential calculus. We consider curves $\epsilon \mapsto \rho_\epsilon$ for an ϵ in a small region around the origin, and assume that ρ_0 is the extremum of the expression

$$\int d\gamma \rho_\epsilon H - \beta^{-1}\hat{S}(\rho_\epsilon) \tag{3.68}$$

That means that the first derivative to ϵ must disappear at $\epsilon = 0$, so

$$\begin{aligned} 0 &= \int d\gamma \rho_0'(\gamma) H(\gamma) - \beta^{-1} \int d\gamma \hat{s}'(\rho(\gamma))\rho_0'(\gamma) \\ &= \int d\gamma \rho_0'(\gamma) \left(H(\gamma) + \frac{1}{\beta}\ln \rho_0(\gamma) + \frac{1}{\beta} \right). \qquad (3.69) \end{aligned}$$

Here,

$$\rho_\epsilon' = \frac{\partial \rho}{\partial \epsilon}, \tag{3.70}$$

and ρ_0' is except from the condition

$$\int d\gamma \rho_0'(\gamma) = \frac{d}{d\epsilon}\int d\gamma \rho_\epsilon(\gamma) = 0 \tag{3.71}$$

an arbitrary integrable function. Hence, the expression in the bracket of Eq. (3.69) has to be a constant function. For the point ρ_0 of the extremum one gets the condition

$$\rho_0(\gamma) = ce^{-\beta H(\gamma)}, \tag{3.72}$$

with some constant c that is to be determined by

$$\int d\gamma \rho_0(\gamma) = 1. \tag{3.73}$$

Canonical ensemble as minimiser of the free energy: The unique infimum of the free energy is taken at the canonical ensemble ρ_β.

We have seen a similar statement before, needless to say. But now we have extended this result to an infimum over all densities allowed by a microscopic classical theory, and not merely about thermodynamic properties. The minimum free energy is assumed for the micro canonical ensemble, quite a remarkable result.

3.4.2 Equipartition theorem

Let $f : \Gamma \to \mathbb{R}$ be an arbitrary differentiable function. We first have a look at

$$\tilde{f}(\gamma) = f(\gamma)e^{-\beta H(\gamma)} \tag{3.74}$$

as a function of the momentum coordinates $\{p_j\}$. If we assume that f does not grow for $p_j \to \pm\infty$ not so fast that it compensates the exponential factor, then we get

$$\int d\gamma \frac{\partial}{\partial p_j} \left(f(\gamma)e^{-\beta H(\gamma)} \right) = \int d\gamma' \left(\tilde{f}_{p_j \to \infty} - \tilde{f}_{p_j \to -\infty} \right) = 0, \tag{3.75}$$

where $d\gamma'$ denotes the integration over all variables except p_j. After division by the partition function Z, we get

$$0 = Z^{-1} \int d\gamma \left(\frac{\partial f}{\partial p_j} - \beta f \frac{\partial H}{\partial p_j} \right) e^{-\beta H} = \left\langle \frac{\partial f}{\partial p_j} \right\rangle_\beta - \beta \left\langle f \frac{\partial H}{\partial p_j} \right\rangle_\beta . \tag{3.76}$$

A convenient, but by now means the only, choice is to take for f simple another momentum coordinate p_i. Then we have the following statement:

Equipartition theorem:

$$\left\langle p_i \frac{\partial H}{\partial p_j} \right\rangle_\beta = \frac{1}{\beta}\delta_{i,j}. \tag{3.77}$$

Usually, the Hamiltonian is of the form

$$H(p,q) = \sum_{i=1}^{N} \left(\frac{1}{2m_i} p_i^2 + V(q) \right). \tag{3.78}$$

Then

$$\frac{1}{2} p_i \frac{\partial H}{\partial p_i} \tag{3.79}$$

is just the i-th contribution in the sum leading to the kinetic energy. We can hence conclude the following. This result specifically is often referred to as equipartition theorem.

Equipartition theorem applied to the expectation value of the kinetic energy: Each of the n degrees of freedom contributes $kT/2$ to the canonical expectation value of the kinetic energy.

Having this insight in mind, we can give the inner energy of the ideal gas without any calculation: Since the particles do not interact, the expectation value of the Hamiltonian is just the expectation value of the kinetic energy itself. For each particle, three momentum coordinates contribute. That is to say,

$$\langle H \rangle_\beta = \frac{3}{2} NkT. \tag{3.80}$$

So we have finally found a good reason for the choice of $f = 3$ that was possibly more mysterious before.

But we can go much further than that. We can say something even on the inner energy of gases consisting of particles having some structure. Let us consider a gas made out of molecules that are shaped like an O_2 molecule. The specifics are not so important: But rather the fact that two angular momentum angles contribute (but not a third, from the symmetry of the molecule). This means that per molecule, we have $3 + 2 = 5$ degrees of freedom. This gives us the inner energy

$$\langle H \rangle_\beta = \frac{5}{2} NkT. \tag{3.81}$$

It should be clear from this that this is a simple, but quite powerful insight. For a molecule for which the constituents are not in alined on a line, such as a H_2 O water molecule, we have

$$\langle H \rangle_\beta = \frac{6}{2} NkT, \tag{3.82}$$

and so on. In general, we have for f degrees of freedom

$$\langle H \rangle_\beta = \frac{f}{2} NkT, \tag{3.83}$$

which is exactly the formula encountered before.

3.4.3 Virial expansion

For ideal gases, we could always compute the partition functions: This is, needless to say, due to the fact that particles do not interact. If the Hamiltonian is of the form

$$H(\gamma) = \sum_{j=1}^{N} h(\gamma_j), \tag{3.84}$$

where γ_j denotes the phase space coordinates of the j-th particle, then, say, the canonical partition function is just the N-th power of the partition function of each particle. This is a radical simplification, to say the least. The free energy, for example, can in this way computed to be

$$F = -NkT \log \int d\gamma_1 e^{-\beta H(\gamma_1)}. \tag{3.85}$$

This trick, however, no longer works for particles that interact. Unfortunately, this is the generic situation: All particles interact to some extent. Fortunately, in turn, we can go a long way in case this interaction is weak.

Let us consider a gas with two-particle interaction potential Φ, so the Hamiltonian is given by

$$H(\gamma) = \sum_{j=1}^{N} \frac{\mathbf{p}_j^2}{2m} + \sum_{i<j} \Phi(|\mathbf{q}_i - \mathbf{q}_j|). \tag{3.86}$$

This potential Φ we get from a microscopic model. A good model for interactions between molecules constitutes the Lennard Jones potential: It is given by

$$\Phi(r) = \frac{c_1}{r^{12}} - \frac{c_2}{r^6} \tag{3.87}$$

for $r > 0$. The r^{-6} comes from induced dipole-dipole attractive interactions, whereas the r^{-12} reflects a sharp repulsion. This is no typo: There is really a power of 12 in the denominator.

The canonical partition function becomes

$$\begin{aligned} Z &= \int d^{3N}p e^{-\sum_{j=1}^N \beta \mathbf{p}_j^2/(2m)} \int_{\mathbf{q}_j \in \Omega} d^{3N}q e^{-\beta \sum_{i<j} \Phi(|\mathbf{q}_i - \mathbf{q}_j|)} \\ &= Z_{\text{ideal}} \left(\frac{1}{V^N} \int d^{3N}q \prod_{i<j} e^{-\beta\Phi(|\mathbf{q}_i - \mathbf{q}_j|)} \right) \\ &= Z_{\text{ideal}} Z_{\text{pot}}. \end{aligned} \tag{3.88}$$

Here, Z_{ideal} is the corresponding expression for the ideal gas, the one we would get for $\Phi = 0$. Z_{pot} reflects the term arising from the potential energy.

Of course, all the misery and trouble is now in computing this additional term Z_{pot}, as we already know how to compute the former. It is clear that the product runs over $\binom{N}{2}$ terms. Now, each of these terms is almost exactly equal to one – unless the particles are really close to each other. Remember that we are thinking of macroscopic containers here, so the typical distance between particles is of that order of magnitude, whereas the above deviation from unity becomes relevant only in case the particles become as close as 10^{-10}m. So there are many orders of magnitude between these scales.

To reflect this insight, let us write

$$f(r) = e^{-\beta\Phi(r)} - 1. \tag{3.89}$$

In this way, we get

$$Z_{\text{pot}} = \frac{1}{V^N} \int d^{3N}q \prod_{i<j} (1 + f(|\mathbf{q}_i - \mathbf{q}_j|)) \tag{3.90}$$

If we expand this product, we get the irritating number of $2^{N(N-1)/2}$ terms. Each term is essentially characterised by the knowledge whether for a given pair (i, j) the number 1 contributes, or a factor $f(|\mathbf{q}_i - \mathbf{q}_j|)$.

If the interaction is weak, and very dilute, then it is a good approximation to neglect this potential altogether, and we are back to the ideal gas. This corresponds to $Z_{\text{pot}} = 1$.

- In the next best approximation, we assume that at each instance in time, at most two particles interact with each other. This is often still a remarkably good approximation, since the probability for three-body collisions can be neglected. Of these terms, we have $\binom{N}{2}$ many, and each contributes

  $$V^{-N+(N-2)}\int d^{3N}\mathbf{q}_1 d^{3N}\mathbf{q}_2 f(|\mathbf{q}_1-\mathbf{q}_2|). \tag{3.91}$$

  In the double integral, we substitute

  $$\begin{aligned}\mathbf{q} &= \mathbf{q}_1-\mathbf{q}_2, &(3.92)\\ \mathbf{Q} &= (\mathbf{q}_1+\mathbf{q}_2)/2, &(3.93)\end{aligned}$$

- Now, since, in integration only terms contribute for which $\mathbf{q}_1\approx\mathbf{q}_2$, we hardly make an error by integrating $\mathbf{Q}$ over the entire volume.

- Similarly, we can integrate $\mathbf{q}$ over $\mathbb{R}^3$.

- Then, we can set $N(N-1)\approx N^2$.

The sum of terms containing f then becomes

$$\frac{N^2}{2V}\int d\mathbf{q} f(|\mathbf{q}|). \tag{3.94}$$

This quantity we treat as a small quantity. In this approximation, we hence get

$$\begin{aligned}F &= -\frac{1}{\beta}\log Z\\ &\approx F_{\text{ideal}}-\frac{1}{\beta}\log\left(1+\frac{N^2}{2V}\int d\mathbf{q} f(|\mathbf{q}|)\right)\\ &\approx F_{\text{ideal}}-\frac{N^2}{2\beta V}\int d\mathbf{q} f(|\mathbf{q}|). &(3.95)\end{aligned}$$

Defining

$$B(T)=\frac{1}{2}\int d\mathbf{q} f(|\mathbf{q}|)=\frac{1}{2}\int d\mathbf{q}\left(e^{-\beta\Phi(|\mathbf{q}|)}-1\right), \tag{3.96}$$

we finally get the following expression for the pressure.

Pressure in virial expansion:

$$
\begin{aligned}
p &= -\frac{\partial F}{\partial V} \approx \frac{NkT}{V} + \frac{N^2kT}{V^2}B(T) \\
&= \frac{NkT}{V}\left(1 + \frac{N}{V}B(T)\right). \qquad (3.97)
\end{aligned}
$$

Since N/V is just the particle density, this is the beginning of an expansion of the pressure in terms of powers of the particle density. $B(T)$ is in this light also called second virial coefficient. The first virial coefficient is then simply 1. Since one can easily measure the pressure as a function of the particle density and the temperature, one can easily determine $B(T)$ also experimentally. More elaborate derivations also produce higher order terms in this expansion.

Chapter 4

Elements of quantum statistical physics

4.1 Review of the structural elements of quantum mechanics

We have seen that the classical description reaches its limits every once in a while and that the encountered paradoxes that a classical description could not resolve. This is no surprise, given that the fundamental theory that captures the dynamics of microscopic particles is quantum mechanics, not classical mechanics. Any serious attempt to derive the laws of equilibrium thermodynamics from microscopic laws hence must in one way or the other resort to a quantum mechanical description. In this chapter, we lay out the basics of such a quantum mechanical description. We begin with a review of the structural elements of quantum mechanics as such, and then turn to the specific topic of quantum statistical mechanics.

4.1.1 Hilbert spaces

In classical mechanics, each type of particles was associated a phase space Γ. In quantum theory, we associate with systems a Hilbert space $\mathcal{H}$. This is a vector space over $\mathbb{C}$, that is, for $|\psi\rangle, |\phi\rangle \in \mathcal{H}$, and $\lambda \in \mathbb{C}$, we also have that

$$|\psi\rangle + |\phi\rangle \in \mathcal{H}, \tag{4.1}$$

$$\lambda|\psi\rangle \in \mathcal{H}. \tag{4.2}$$

Hilbert space elements are also referred to as "kets" in the Dirac notation. There also is a scalar product $\langle\phi|\psi\rangle \in \mathbb{C}$ which is additive in each component and which satisfies

$$\lambda\langle\phi|\psi\rangle = \langle\lambda^*\phi|\psi\rangle = \langle\phi|\lambda\psi\rangle. \tag{4.3}$$

The scalar product also induces a norm

$$\||\psi\rangle\|^2 = \langle\psi|\psi\rangle \geq 0. \tag{4.4}$$

We find

$$\langle\phi|\psi\rangle^* = \langle\psi|\phi\rangle, \tag{4.5}$$

and hence the Cauchy-Schwarz inequality

$$|\langle\phi|\psi\rangle| \leq \||\phi\rangle\| \, \||\psi\rangle\| \tag{4.6}$$

is satisfied. Cauchy sequences with respect to this norm in $\mathcal{H}$ are convergent.

A sequence $\{|\psi_i\rangle\}_{i=1}^d$ is called an orthonormal basis, if

$$\langle\psi_i|\psi_j\rangle = \delta_{i,j} \tag{4.7}$$

and if every vector $|\psi\rangle$ can be written as a norm convergence sequence

$$|\psi\rangle = \sum_i \alpha_i|\psi_i\rangle. \tag{4.8}$$

The components in turn are given by

$$\alpha_j = \langle\psi_j|\psi\rangle. \tag{4.9}$$

The number d of elements of this basis is the same for each basis and is called the dimension of the Hilbert space. This can be finite or infinite. Examples of finite-dimensional Hilbert spaces are the Hilbert spaces of a single spin-1/2 degree of freedom,

$$\mathcal{H} = \text{span}\{|0\rangle, |1\rangle\} \simeq \mathbb{C}^2, \tag{4.10}$$

where $|0\rangle$ is associated with "spin down" and $|1\rangle$ with "spin up". Other finite-dimensional Hilbert spaces are

$$\mathcal{H} = \text{span}\{|0\rangle, \ldots, |d-1\rangle\}, \tag{4.11}$$

of d-level systems. Position degrees of freedom are not associated with finite-dimensional Hilbert spaces, but rather infinite-dimensional ones. The familiar Hilbert spaces of a position degree of freedom of a spinless particle is

$$\mathcal{H} = \mathcal{L}^2(\mathbb{R}) = \left\{\psi : \mathbb{R} \to \mathbb{C} : \|\psi\|^2 := \int dx|\psi(x)|^2 < \infty\right\}, \tag{4.12}$$

the Lebesgues square integrable functions.

4.1.2 Observables

Quantities that are captured by functions in phase space in classical mechanics become linear operators on $\mathcal{H}$ in quantum mechanics. That is to say, they become operators $A : \mathcal{H} \to \mathcal{H}$ with

$$A(\lambda|\phi\rangle + \mu|\psi\rangle = \lambda A|\phi\rangle + \mu A|\psi\rangle, \tag{4.13}$$

for $|\psi\rangle, |\phi\rangle \in \mathcal{H}$ and $\lambda, \mu \in cc$. An operator is called bounded if there exists a constant $\infty > c > 0$ such that

$$\|A|\phi\rangle\| \leq c\||\phi\rangle\|. \tag{4.14}$$

This set of bounded operators is usually called $\mathcal{B}(\mathcal{H})$. For operators $A \in \mathcal{B}(\mathcal{H})$ one can define the adjoint operator $A^\dagger$ with

$$\langle\phi|A^\dagger|\psi\rangle = \langle A\phi|\psi\rangle. \tag{4.15}$$

An operator is called Hermitian, if

$$A = A^\dagger. \tag{4.16}$$

Observables: The observables in quantum theory correspond to Hermitian linear operators $A = A^\dagger$. If a system is prepared in a pure state with state vector $|\psi\rangle$, then the expectation value of A is given by

$$\langle A\rangle = \langle\psi|A|\psi\rangle. \tag{4.17}$$

Examples for spin-1/2 systems of observables are the Pauli operators

$$\begin{aligned}
\sigma_X &= |0\rangle\langle 1| + |1\rangle\langle 0|, && (4.18)\\
\sigma_Y &= -i|0\rangle\langle 1| + i|1\rangle\langle 0|, && (4.19)\\
\sigma_Z &= |0\rangle\langle 0| - |1\rangle\langle 1|. && (4.20)
\end{aligned}$$

It is easy to see that they are Hermitian. In Stern-Gerlach-type devices, they can be measured. An operator is called positive (or positive semi-definite), if

$$\langle\psi|A|\psi\rangle \geq 0 \tag{4.21}$$

for all $|\psi\rangle \in \mathcal{H}$. This is equivalent with stating that all eigenvalues of A are non-negative. Positive operators are by definition Hermitian, so the concept of positivity does not make any sense for non-Hermitian operators. Hermitian operators have real eigenvalues. Observable quantities are associated with Hermitian operators, which are also called observables.

It is often to represent operators (and vectors and dual vectors) in their matrix form. One picks a basis and represents the operators in this basis. This is strictly speaking an isomorphism. But often, the operators and their matrix forms are identified. For a basis $\{|\psi_k\rangle\}$, one gets the components

$$A_{j,k} = \langle\psi_j|A|\psi_k\rangle. \tag{4.22}$$

For example, for the spin-1/2 system one can take the basis $\{|0\rangle, |1\rangle\}$, and then represent the Pauli operators as Pauli matrices

$$\sigma_X = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \tag{4.23}$$

$$\sigma_Y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \tag{4.24}$$

$$\sigma_Z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \tag{4.25}$$

In general, the identity operator becomes

$$\mathbb{1} = \sum_j |\psi_j\rangle\langle\psi_j|. \tag{4.26}$$

The operations on matrices are defined in terms of the components. So

$$(AB)_{j,k} = \sum_l A_{j,l}B_{l,k}, \tag{4.27}$$

so one encounters the familiar matrix product. Also, one obviously has that

$$\mathrm{tr}(AB) = \sum_{j,k} A_{j,k}B_{k,j} = \mathrm{tr}(BA), \tag{4.28}$$

for the trace

$$\mathrm{tr}(A) = \sum_j A_{j,j} = \langle\psi_j|A|\psi_j\rangle. \tag{4.29}$$

In fact, the trace is cyclic, and for arbitrary A, B, C, one has that

$$\mathrm{tr}(ABC) = \mathrm{tr}(CAB) = \mathrm{tr}(BCA). \tag{4.30}$$

In fact, we will see that the trace plays an important role when computing expectation values. The analogue of expectation values

$$\langle f \rangle_\rho = \int d\gamma \rho(\gamma) f(\gamma) \tag{4.31}$$

in classical physics becomes

$$\langle A \rangle_\rho = \mathrm{tr}(\rho A) \tag{4.32}$$

for density operators ρ in quantum physics. What does that mean? For that purpose, we will revisit the concept of a density operator, so a general quantum state, in the next subsection.

4.1.3 Density operators and expectation values

Let us imagine we have a single spin, associated with a Hilbert space $\mathcal{H} \simeq \mathbb{C}^2$. We now throw a coin. In case of heads, we prepare the spin in $|0\rangle$, in case of tails, we prepare it in $|1\rangle$. That is to say, with the classical probability $1/2$ we have $|0\rangle$, and with classical probability $1/2$ we get $|1\rangle$. How do we capture this situation? Can we describe the system by a state vector

$$|+\rangle = (|0\rangle + |1\rangle)/\sqrt{2}? \tag{4.33}$$

Not quite. This is easy to see: In case of a σ_x measurement, we would always get the same outcome. But this is different from the situation we encounter here. In fact, when we make a measurement of σ_x, we would get both outcomes with equal probability. Or

$$|-\rangle = (|0\rangle - |1\rangle)/\sqrt{2}? \tag{4.34}$$

Again, this will not work, for the same reason. In fact, no state vector is associated with such a situation, and for that, we need to generalize our concept of a quantum state slightly: to density operators. This is, however, the most general quantum state in standard quantum mechanics, and we will not have to generalize it any further.

In fact, the above situation is an instance of the situation where we prepare with probability p_j, $j = 1, \ldots, n$, a system in a state vector $|\psi_i\rangle$. Since we encounter a probability distribution, we have

$$\sum_{j=1}^{n} p_j = 1. \tag{4.35}$$

Such a situation is sometimes referred to as a mixed ensemble. How do we incorporate that?

Density operator of a pure state: A pure state associated with a state vector $|\psi\rangle \in \mathcal{H}$ from some Hilbert space $\mathcal{H}$ is given by the density operator

$$\rho = |\psi\rangle\langle\psi|. \tag{4.36}$$

We immediately find some properties of such an operator: We obviously have that

$$\rho = \rho^\dagger. \tag{4.37}$$

Then,

$$\mathrm{tr}(\rho) = 1. \tag{4.38}$$

Finally, we have that

$$\rho \geq 0, \tag{4.39}$$

which means that all of its eigenvalues are non-negative, which is clearly the case, as all the eigenvalues are given by 0 or 1, clearly non-negative numbers. We also have the property that

$$\mathrm{tr}(\rho^2) = \mathrm{tr}(|\psi\rangle\langle\psi|\psi\rangle\langle\psi|) = \mathrm{tr}(|\psi\rangle\langle\psi|) = \mathrm{tr}(\rho) = 1. \tag{4.40}$$

How to we compute expectation values from such a density operator? Well, we know that for an observable

$$\langle A\rangle = \langle\psi|A|\psi\rangle. \tag{4.41}$$

This we can equally well (although at this instance in time this may look unnecessarily complicated, but we will see the point in a second) write as

$$\langle A\rangle = \langle\psi|A|\psi\rangle = \mathrm{tr}(A|\psi\rangle\langle\psi|) = \mathrm{tr}(A\rho). \tag{4.42}$$

We have hence made use of one of the above rules, and have written expectation values as a trace of the observable, multiplied with the density operator.

A general density operator is just extended by linearity from this definition.

Density operator of a mixed ensemble: Consider the situation of preparing $|\psi_j\rangle$, $j = 1, \ldots, n$ with probability p_j. This is associated with a density operator

$$\rho = \sum_{j=1}^{n} p_j |\psi_j\rangle\langle\psi_j|. \tag{4.43}$$

How do we compute expectation values from that? We have for observables A that

$$\langle A\rangle = \sum_{j=1}^{n} p_j \langle\psi_j|A|\psi_j\rangle, \tag{4.44}$$

from the very definition of a mixed ensemble. This we can, however, also write as

$$\begin{aligned} \langle A\rangle &= \sum_{j=1}^{n} p_j \mathrm{tr}(A|\psi_j\rangle\langle\psi_j|) \\ &= \mathrm{tr}\left(A\sum_{j=1}^{n} p_j|\psi_j\rangle\langle\psi_j|\right) \\ &= \mathrm{tr}(A\rho). \end{aligned} \tag{4.45}$$

So again, expectation values are just computable as the trace of the density operator multiplied with the observable.

We now once more investigate properties of such a density operator: We find that again,

$$\rho = \rho^\dagger. \tag{4.46}$$

In the same fashion as before, since now

$$\sum_{j=1}^{n} p_j = 1, \tag{4.47}$$

we also have that

$$\mathrm{tr}(\rho) = 1. \tag{4.48}$$

Finally, we have that

$$\rho \geq 0, \tag{4.49}$$

since all of the probabilities are positive, and a sum of positive operators is positive. These are exactly the same properties as above, except from one that is now missing. We no longer have

$$\mathrm{tr}(\rho^2) = 1. \tag{4.50}$$

In fact, this property is replaced by

$$\begin{aligned} \mathrm{tr}(\rho^2) &= \mathrm{tr}\left(\sum_{j=1}^{n} p_j|\psi_j\rangle\langle\psi_j|\right)\left(\sum_{k=1}^{n} p_k|\psi_k\rangle\langle\psi_k|\right) \\ &= \sum_{j,k=1}^{n} p_j p_k \mathrm{tr}(|\psi_j\rangle\langle\psi_j|\psi_k\rangle\langle\psi_k|) \\ &\leq 1, \end{aligned} \tag{4.51}$$

where we have bounded the scalar products between two arbitrary state vectors. We have now arrived at the most general concept of a state in (standard) quantum mechanics. This is surely worth a box:

Density operators: General states of quantum systems with Hilbert space $\mathcal{H}$ are given by density operators ρ. Their properties are

$$\rho = \rho^\dagger \text{ (Hermicity)}, \tag{4.52}$$

$$\rho \geq 0 \text{ (Positivity)}, \tag{4.53}$$

$$\mathrm{tr}(\rho) = 1 \text{ (Normalization)}. \tag{4.54}$$

Pure states are those density operators for which

$$\mathrm{tr}(\rho) = 1, \tag{4.55}$$

those can be represented by state vectors $|\psi\rangle \in \mathcal{H}$ as

$$\rho = |\psi\rangle\langle\psi|. \tag{4.56}$$

Otherwise, if $\mathrm{tr}(\rho^2) < 1$, the state is called mixed. For observables, expectation values are computed as

$$\langle A\rangle = \mathrm{tr}(A\rho). \tag{4.57}$$

This is a good moment to discuss a number of examples. Let us go back to our initial situation discussed at the beginning of the chapter, of preparing $|0\rangle$ or $|1\rangle$ with equal probability. We can now easily associate this with a density operator

$$\rho = \frac{1}{2}|0\rangle\langle 0| + \frac{1}{2}|1\rangle\langle 1|. \tag{4.58}$$

We can write this in matrix form – remember that operators and their matrix representation are identified with each other throughout the script

$$\rho = \begin{bmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{bmatrix}. \tag{4.59}$$

We have that

$$\mathrm{tr}(\rho^2) = \frac{1}{4} + \frac{1}{4} = \frac{1}{2} < 1. \tag{4.60}$$

This in fact the minimum value $\mathrm{tr}(\rho^2)$ can take for a system with $\mathcal{H} \simeq \mathbb{C}^2$. The pure state $\rho = |0\rangle\langle 0|$ in turn is represented as

$$\rho = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}, \tag{4.61}$$

obviously satisfying $\mathrm{tr}(\rho) = 1$. Generally, if we have probabilities p_0 and p_1 to prepare $|0\rangle\rangle$ and $|1\rangle$, we have the density operator

$$\rho = \begin{bmatrix} p_0 & 0 \\ 0 & p_1 \end{bmatrix}. \tag{4.62}$$

But of course, we are not forced to take the standard basis. The situation of having prepared $|+\rangle$ and $|-\rangle$ with equal probabilities is captured as

$$\rho = \frac{1}{2}|+\rangle\langle +| + \frac{1}{2}|-\rangle\langle -|. \tag{4.63}$$

This is

$$\begin{aligned} \rho &= \frac{1}{4}\left((|0\rangle + |1\rangle)(\langle 0| + \langle 1|)\right) + \frac{1}{4}\left((|0\rangle - |1\rangle)(\langle 0| - \langle 1|)\right) \\ &= \frac{1}{2}|0\rangle\langle 0| + \frac{1}{2}|1\rangle\langle 1|, \end{aligned} \tag{4.64}$$

with matrix representation

$$\rho = \begin{bmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{bmatrix}. \tag{4.65}$$

Eh, wait a minute? Was this not the matrix representation of the ensemble consisting of $|0\rangle$ and $|1\rangle$? So we are faced here with the irritating situation that two different mixed ensembles are described by the same density operator. Let us face it: There are many different ways of preparing the same density operator! Since all expectation values of observables are computed as

$$\langle A\rangle = \mathrm{tr}(A\rho), \tag{4.66}$$

we get exactly same same value for all observables in case of

$$\rho = \sum_{j=1}^{n} p_j |\psi_j\rangle\langle\psi_j| = \sum_{k=1}^{m} q_k |\phi_k\rangle\langle\phi_k|, \tag{4.67}$$

even if all of the probabilities $\{p_j\}$ and $\{q_k\}$ as well as all state vectors $\{|\psi_j\rangle\}$ and $\{|\phi_k\rangle\}$ are different. In fact, now even $n = m$ has to hold. What matters for all outcomes in all experiments is the density operator, not the mixed ensemble we have started with.

The situation is hence quite subtle: Yes, a density operator is a concept that allows to introduce the concept of classical probability distributions into quantum mechanics. We have to have a way of incorporating probabilistic preparation, where we do one thing with some probability and another with another. In statistical physics, we will encounter such a situation frequently, where density operators are ubiquitous, to say the least.

But no, once we arrive at a given density operator, there is no way to reconstruct the mixed ensemble that can be held responsible for the density operator. In retrospect, there always would have been infinitely many other ways of preparing the same density operator (unless it is a pure state). Sometimes, people use notions of the kind, "the system is in some pure state vector $|\psi_j\rangle$, $j = 1, \dots, n$, we simply do not know which one". Such reasoning is not quite precise and can be plain wrong, in which case it is referred to as preferred ensemble fallacy.

4.1.4 Time evolution

Now that we have understood what a density operator is, the rest will be a piece of cake. How do density operators evolve in time? Well, this equation is just inherited from the Schroedinger equation by linearity. Since it was von-Neumann who first described this situation well, it is called von-Neumann equation. But really, it is just the ordinary Schroedinger equation written for density operators. There is no new physics happening here.

Von Neumann equation: Density operators of physical systems described by Hamiltonians H evolve in time according to

$$i\hbar\frac{d}{dt}\rho(t) = [H, \rho(t)]. \tag{4.68}$$

So together with the initial condition at $\rho(0)$, this differential equation fully specifies the density operator at a later time, exactly as the Schroedinger equation does for state vectors. Is this equation mysterious? Not at all: Let us write

$$\rho(t) = \sum_{j=1}^{n} p_j |\psi_j(t)\rangle\langle\psi_j(t)|, \tag{4.69}$$

then

$$\begin{aligned} i\hbar\frac{d}{dt}\rho(t) &= i\hbar\sum_{j=1}^{n} p_j \frac{d}{dt}|\psi_j(t)\rangle\langle\psi_j(t)| \\ &= i\hbar\sum_{j=1}^{n} p_j \left(\left(\frac{d}{dt}|\psi_j(t)\rangle\right)\langle\psi_j(t)| + \langle\psi_j(t)|\left(\frac{d}{dt}\langle\psi_j(t)|\right)\right) \\ &= \sum_{j=1}^{n} p_j \left(H|\psi_j(t)\rangle\langle\psi(t)| - |\psi_j(t)\rangle\langle\psi(t)|H\right) \\ &= [H, \rho(t)]. \end{aligned} \tag{4.70}$$

Of course we can again write the non-differential form of time evolution:

Time evolution in terms of the time evolution operator: We have that

$$\rho(t) = U_t \rho(0) U_t^\dagger, \tag{4.71}$$

with $U_t = e^{-iHt}$ being the time evolution operator for times $t \geq 0$.

4.1.5 Composite systems

The last ingredient that we still need is the concept of a composite quantum system. If we have a system that is composed of two spins, we already encounter a composite system. Of a particle that has three motional degrees of freedom. Or a particle with a spin. These are simple examples. But obviously, in statistical physics we have the situation in mind where we have very many similar or identical systems at hand. The mathematical object that reflects this situation is the one of the tensor product.

Let us first have a look at the situation for two parts only, corresponding to Hilbert spaces $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$, where $\mathcal{H}_1$ and $\mathcal{H}_2$ are the Hilbert spaces of the two parts, respectively. The way to define the tensor product is as follows. We first consider the vectors, the "pure tensors",

$$|\psi_1\rangle \otimes |\psi_2\rangle \in \mathcal{H}, \tag{4.72}$$

for which $|\psi_1\rangle \in \mathcal{H}_1$ and $|\psi_2\rangle \in \mathcal{H}_2$. Since $\mathcal{H}$ is a vector space, it of course contains all linear combinations of such vectors, and as a Hilbert space also the norm limits. The scalar product, and hence the norm, only have to be defined on these pure tensors, as

$$\langle\phi_1| \otimes \langle\phi_2|\psi_1\rangle \otimes |\psi_2\rangle = \langle\phi_1|\psi_1\rangle\langle\phi_2|\psi_2\rangle. \tag{4.73}$$

This defines the tensor product. When A_1 and A_2 are linear operators on $\mathcal{H}_1$ and $\mathcal{H}_2$, then one has

$$(A_1 \otimes A_2)|\psi_1\rangle \otimes |\psi_2\rangle = (A_1|\psi_1\rangle) \otimes (A_2|\psi_2\rangle), \tag{4.74}$$

defined a tensor product of linear operators, by considering the linear extension. Of course,

$$(A_1 \otimes A_2)(B_1 \otimes B_2) = (A_1 B_1) \otimes (A_2 B_2). \tag{4.75}$$

We remember that parts were considered statistically independent, if the density was of the form

$$\rho(\gamma_1, \gamma_2) = \rho_1(\gamma_1)\rho_2(\gamma_2). \tag{4.76}$$

The quantum mechanical analogue is a state of the form

$$\rho = \rho_1 \otimes \rho_2. \tag{4.77}$$

We give this situation a box:

Product states: Product states are states of the form

$$\rho = \rho_1 \otimes \rho_2. \tag{4.78}$$

They reflect an independent preparation of two parts.

Of course, we cannot only consider the composition of parts. We always have the option to only look at a part. Classically, we know what that means. That was related to the marginal distribution, reflecting “disregarding” a part. We had that the marginal distribution was given by

$$(R_1\rho)(\gamma_1) = \int d\gamma_2 \rho(\gamma_1, \gamma_2). \tag{4.79}$$

Of course, if the distribution of the total system was pointlike and we “knew everthing of the system”, the same was true for any marginal distribution. This is actually quite intuitive.

Of course, we can also quantum mechanically define the analogue of the marginal distribution, called the reduced state: If is defined as

$$\mathrm{tr}\,((R_1\rho)A) = \mathrm{tr}(\rho(A \otimes \mathbb{1})), \tag{4.80}$$

for observables A that are only supported on the first tensor factor. $R_1\rho$ is called the reduced state or reduced density operator. In matrix components, one has

$$(R_1\rho)_{j,k} = \sum_n \rho_{j,n;k,n}. \tag{4.81}$$

So one fixes a basis in the part one disregards, and takes the partial trace over this basis. The specific choice of basis does not matter. As such, this is a very straightforward procedure. There is only one subtlety encountered here: Even if a joint system is in a pure state, the reduced state does not have to be!

Entangled pure states: Pure states that have the property that reduced states are mixed are called entangled pure states.

This is quite remarkable. So even if we had a pure preparation and know that a joint system is in a pure state, there is no way one can consistently assign a state vector to any of the parts. For example, consider two spins, in a pure state $\rho = |\psi\rangle\langle\psi|$ with

$$|\psi\rangle = \frac{1}{\sqrt{2}} (|0,0\rangle + |1,1\rangle.) \,. \tag{4.82}$$

Then

$$R_1\rho = \frac{1}{2}|0\rangle\langle 0| + \frac{1}{2}|1\rangle\langle 1|. \tag{4.83}$$

So in fact, the reduced state is not only mixed, but in fact maximally mixed. We come back to that remarkable feature later. Entanglement manifests itself in correlations that are in a sense "stronger" than classically attainable. Also, the proof that quantum mechanics cannot be captured as a classical statistical theory is based on entangled states of this kind.

4.1.6 A translation table

We are now in the position to recapitulate what we have learned. In this subsection, we summarise the state concepts in classical and quantum statistical mechanics, which have been and will be used from now on. Of course, this table is not only applicable to our statistical physics concept at hand: It generally summarises the relevant concepts in classical and quantum physics.

	Classical physics	Quantum physics
Configuration space	Phase space Γ, e.g., $\Gamma = \mathbb{R}^{6N}$	Hilbert space $\mathcal{H}$ e.g., $\mathcal{H} = \mathcal{L}^2(\mathbb{R}^{3N})$
Coordinates	Canonical coords. $\mathbf{p}_1, \ldots, \mathbf{q}_N$	Orthonormal basis
State	Density function $\rho \geq 0$, $\int d\gamma \rho(\gamma) = 1$	Density operator $\rho \geq 0$, $\mathrm{tr}(\rho) = 1$
Property	Function $f : \Gamma \to \mathbb{R}$	Hermitian operator $A = A^\dagger$
Expectation value	Integral of a function $\langle f \rangle_\rho = \int d\gamma f(\gamma)\rho(\gamma)$	Trace of an operator $\langle A \rangle_\rho = \mathrm{tr}(\rho A)$
Pure states	$\rho(\gamma) = \delta(\gamma - \gamma_0)$	$\rho = \|\psi\rangle\langle\psi\|$
One particle	$\Gamma = \{\mathbf{p}, \mathbf{q}) : \mathbf{p}, \mathbf{q} \in \mathbb{R}^3\}$	$\mathcal{H} = \mathcal{L}^2(\mathbb{R}^3)$
Composition	$\Gamma = \Gamma_1 \times \Gamma_2$	$\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$
Observable on one part	$f(\gamma_1, \gamma_2) = f_1(\gamma_1)$	$A(\|\phi_1\rangle \otimes \|\phi_1\rangle) = (A_1\|\phi_1\rangle) \otimes \|\phi_2\rangle$ $A = A_1 \otimes \mathbb{1}$
Product observable	$(f_1 \times f_2)(\gamma_1, \gamma_2) = f_1(\gamma_1) f_2(\gamma_2)$	$(A_1 \otimes A_2)(\|\phi_1\rangle \otimes \|\phi_1\rangle)$ $= (A_1\|\phi_1\rangle) \otimes A_2\|\phi_2\rangle$
Independent prep.	$\rho(\gamma_1, \gamma_2) = \rho_1(\gamma_1)\rho_2(\gamma_2)$	$\rho = \rho_1 \otimes \rho_2$
Reduced description	Marginal distribution $\rho_1(\gamma_1) = \int d\gamma_2 \rho(\gamma_1, \gamma_2)$	Reduced state $\rho_1 = \mathrm{tr}_2(\rho)$
Hamiltonian	Hamiltonian function	Hamilton operator
Dynamics	$\dot{\rho}_t = \{\rho_t, H\}$ $\dot{p}_i = -\frac{\partial H}{\partial q_i}, \dot{q}_i = \frac{\partial H}{\partial p_i}$ $\rho_t(\gamma) = \rho(\mathcal{F}_{-t}(\gamma))$	$\dot{\rho}_t = i[\rho, H]$ $i\dot{\|}\psi\rangle(t)\rangle = H\|\psi(t)\rangle$ $U_t = e^{-iHt}$
Independent dynamics	$H(\gamma_1, \gamma_2) = H_1(\gamma_1) + H_2(\gamma_2)$	$H = H_1 \otimes \mathbb{1} + \mathbb{1} \otimes H_2$

This translation table should be quite helpful from now on, when we look at further implications and applications of quantum and classical statistical physics.

4.2 Quantum mechanical ensembles

4.2.1 Microcanonical ensemble

This will be quick: We have all the tools at hand. In fact, we will define the micro canonical ensemble just in the analogous way compared to the classical situation. We write the spectral decomposition of the Hamilton operator as

$$H = \sum_{j=1}^{n} E_j |E_j\rangle\langle E_j|, \tag{4.84}$$

assuming that the spectrum of the Hamiltonian has no continuous parts; otherwise, one has to replace this expression by spectral projectors.

Microcanonical ensemble: For $E > 0$ and $\epsilon > 0$, the micro canonical ensemble is given by

$$\rho(E) = Z(E)^{-1} \sum_{E-\epsilon \leq E_j \leq E} |E_j\rangle\langle E_j|. \tag{4.85}$$

$Z(E)$ is called the micro canonical partition function.

4.2.2 Canonical ensemble

Similarly, we can define the canonical ensemble, belonging to situations at some given inverse temperature $\beta > 0$.

Canonical ensemble: For $\beta > 0$, the canonical ensemble is given by

$$\rho_\beta = Z^{-1} e^{-\beta H}. \tag{4.86}$$

This state is also called thermal state or Gibbs state. Here,

$$Z = \mathrm{tr}(e^{-\beta H}) \tag{4.87}$$

is the canonical partition function.

We encounter here a matrix function. Generally, for a Hermitian matrix A, we can diagonalise it as

$$A = UDU^\dagger, \tag{4.88}$$

with U unitary and D being diagonal and real. For a real-valued function $f : \mathbb{R} \to \mathbb{R}$, we can now define

$$f(A) = Uf(D)U^\dagger. \tag{4.89}$$

In terms of the above spectral decomposition of H, the canonical ensemble hence becomes

$$\rho = Z^{-1} \sum_j e^{-\beta E_j} |E_j\rangle\langle E_j|, \tag{4.90}$$

and

$$Z = \sum_j e^{-\beta E_j}. \tag{4.91}$$

This expression looks very similar to the classical one.

Both ensembles are invariant under time evolution, since any matrix function of H clearly commutes with H. We have for the canonial ensemble

$$e^{-iHt} \rho_\beta e^{iHt} = \rho_\beta, \tag{4.92}$$

and the same expression for the micro canonical ensemble. They are hence preserved in time.

We are also already in the position to formulate the main equation that allows to derive thermostatic properties from microscopic ensembles. We can identify the free energy with

$$F = -\frac{1}{\beta} \log \operatorname{tr}(e^{-\beta H}), \tag{4.93}$$

from which can can deduce all thermostatic properties.

4.2.3 Gibbs variational principle revisited

Let us introduce the functionals

$$\begin{aligned} F(H) &= -\frac{1}{\beta} \log \operatorname{tr}(e^{-\beta H}), & (4.94) \\ \tilde{S}(\rho) &= -\operatorname{tr}(\rho \log \rho). & (4.95) \end{aligned}$$

Here, again, this is to be read as a matrix function. In analogy with the classical case, we expect an expression like

$$F(H) = \inf_{\rho} \left\{ \mathrm{tr}(\rho H) - \frac{1}{\beta} \tilde{S}(\rho) \right\}. \tag{4.96}$$

And indeed, as before, the Gibbs or thermal state of the canonical ensemble assumes that minimum:

Quantum mechanical Gibbs variational principle: Among all states, the Gibbs state ρ_β of the canonical ensemble minimises $\mathrm{tr}(\rho H) - \tilde{S}(\rho)/\beta$.

So as before, the canonical ensemble minimises the expression for the free energy. This was already true for classical densities, and we encountered a similar formula in the thermodynamic setting. In a similar before, we indeed find that the above pair is a pair of Legendre transforms, so we have

$$\tilde{S}(\rho) = \beta \inf_{H} \left\{ \mathrm{tr}(\rho H) - F(H) \right\}. \tag{4.97}$$

4.2.4 Von Neumann entropy

Let us spend some time with the entropy as such the entropy we just encountered, referred to as von Neumann entropy. Clearly, if we write the spectral decomposition of a state ρ as

$$\rho = \sum_j p_j |\psi_j\rangle\psi_j|, \tag{4.98}$$

we find that the entropy can be written as follows:

Von Neumann entropy:

$$\tilde{S}(\rho) = \mathrm{tr}(\rho \log \rho) = -\sum_j p_j \log(p_j). \tag{4.99}$$

In other words, the von Neumann entropy is nothing but the information theoretic Shannon entropy for the eigenvalues of ρ. We will come back to that point later. The function

$$x \mapsto -x \log x \tag{4.100}$$

is concave, and indeed, even the von-Neumann entropy S is even concave on states. For pure states ρ, only one of the $\{p_j\}$ equals to one, while all other values are zero, so without loss of generality $p_1 = 1$, $p_j = 0$ for $j > 1$. Hence, for pure states ρ, the entropy vanishes,

$$\tilde{S}(\rho) = 0. \tag{4.101}$$

For all other states, one has $S(\rho) > 0$. This is easy to see: From $S(\rho) > 0$ it follows that all spectral values must be $p_j \in \{0, 1\}$. Because of

$$\sum_j p_j = 1, \tag{4.102}$$

however, only exactly one eigenvalue can be equal to 1. As mentioned before, the entropy is also concave, so for any states ρ_1, ρ_2 and any $\lambda \in [0, 1]$, one has that

$$\tilde{S}(\lambda\rho_1 + (1-\lambda)\rho_2) \geq \lambda\tilde{S}(\rho_1) + (1-\lambda)S(\rho_2). \tag{4.103}$$

In other words, we have the following: Mixing, so convex combination of two states, can only enlargen the entropy, compared to the weighted sum of the entropies of the parts.

How does the von Neumann entropy behave under tensor products? Let us assume we have a state $\rho^{(1)} \otimes \rho^{(2)}$, reflecting totally independent preparations. Then it is easy to see that

$$\tilde{S}(\rho^{(1)} \otimes \rho^{(2)}) = \tilde{S}(\rho^{(1)}) + \tilde{S}(\rho^{(2)}). \tag{4.104}$$

That is, the von Neumann entropy is additive, or an extensive quantity. In fact, also the free energy is an additive quantity. If the parts do not interact, so if the Hamiltonian is of the form

$$H = H_1 \otimes \mathbb{1} + \mathbb{1} \otimes H_2, \tag{4.105}$$

then

$$e^{-\beta H} = e^{-\beta H_1} \otimes e^{-\beta H_2}, \tag{4.106}$$

and therefore,

$$\begin{aligned} F(H_1 \otimes \mathbb{1} + \mathbb{1} \otimes H_2) &= -\frac{1}{\beta} \log \left(\mathrm{tr} e^{-\beta H_1} \mathrm{tr} e^{-\beta H_2} \right) \\ &= F(H_1) + F(H_2). \end{aligned} \tag{4.107}$$

In a way, one can say the following. This is not meant to be a rigorous statement, but rather a general guideline.

Statistical physics of uncoupled systems: “The statistical physics of uncoupled systems is in many ways essentially that of single systems, up to simple sums and products.”

Finally, there is another thing one can show: If ρ_{β_1} and ρ_{β_2} are two Gibbs states of the canonical ensemble, with $\beta_2 > \beta_1$, then

$$\tilde{S}(\rho_1) > \tilde{S}(\rho_2). \tag{4.108}$$

In other words, the von Neumann entropy is a monotonous function in the temperature. This is again a manifestation of the von Neumann entropy quantifying mixedness: If a state is pure, it has vanishing entropy. The higher the temperature becomes, the “more mixed” is the state.

4.3 Third law of thermodynamics

Although this may be a bit late, we for a moment go back to thermodynamics. This, however, for a good reason. Before we entered the quantum description, there was hardly a way to motivate this last law of thermodynamics. Now there is. We remember that the (thermodynamic) entropy was only determined after fixing the absolute temperature scale up to an additive constant. This was an undesesirable feature: In fact, it was in these additive constants that gave information about whether a system in a reaction would consume or deliver energy. In the context of phenomelological thermodynamics – so actually independent of statistical physics – the question emerged what happens at low temperatures with the entropy. Nernst postulated, that for

$$T \to 0 \tag{4.109}$$

the entropy converges to a constant value which is independent of all intensive state variables (such as the pressure p). This postulate is usually called the third law of thermodynamics. As a convention, one can set this constant value to zero, and this is usually done. In this way, one has eliminated the last arbitrary aspect from the concept of the absolute entropy:

Third law of thermodynamics: For $T \to 0$ the absolute entropy converges to 0.

Nernst would not have suggested that based on classical mechanics. In fact, for the ideal gas, S converges for $T \to 0$ to $-\infty$ rather than to 0. For $\beta \to \infty$ the function $\gamma \mapsto e^{-\beta H(\gamma)}$ is more and more concentrated to the points in which H takes its absolute minimum $\lambda_{\min}$. Since the canonical ensemble is normalized, it actually does not matter at which point this minimum is assumed. All γ, for which

$$H(\gamma) > \lambda_{\min} + \epsilon \tag{4.110}$$

for some $\epsilon > 0$ are suppressed at least by a factor of $e^{-\beta\epsilon}$. In the region of small $H(\gamma)$, where the canonical ensemble ρ_β is focused, all of the function values $\log \rho_\beta(\gamma)$ are large as well. Hence, the integral diverges to $-\infty$. Hence, within the validity of classical mechanics, the third law of thermodynamics is not valid.

How is the situation in a quantum mechanical description? There is one thing that makes us certain that the situation is different here: We have

$$\tilde{S}(\rho) \geq 0 \tag{4.111}$$

for all states ρ. Hence, the entropy cannot diverge to $-\infty$. Since we already know that the von Neumann entropy is monotonous, we find that it converges to a finite value. But let us check whether really

$$\lim_{\beta\to\infty} \tilde{S}(\rho_\beta) = 0 \tag{4.112}$$

holds true. For that purpose, we have to again look at ρ_β for large β.

Again, of course, only the lower energy values matter. Let us write

$$H = \sum_j E_j P_j, \tag{4.113}$$

for $E_0 < E_1 < E_2 < \dots$, where P_j are the projections onto the eigenspaces with eigenvalue E_j. If the space is degenerate, then this is captured by this projector, and the respective projector is no longer one-dimensional. In these terms, we can write the canonical ensemble

$$\begin{aligned} \rho_\beta &= \frac{\sum_j e^{-\beta(E_j - E_0)P_j}}{\sum_j e^{-\beta(E_j-E_0)}\mathrm{tr}(P_j)} \\ &= \mathcal{N}\left(P_0 + e^{-\beta(E_1-E_0)}\sum_{j\geq 1} e^{-\beta(E_j-E_1)}P_j\right), \end{aligned} \tag{4.114}$$

with $\mathcal{N}$ denoting normalization. The sum in the last expression converges for all β and is a monotone falling function of β .Together with $e^{-\beta(E_1-E_0)}$ the second term goes to zero, exponentially quickly. The same happens for the normalization $\mathcal{N}$, so that

$$\lim_{\beta\to\infty} \rho_\beta = \frac{P_0}{\mathrm{tr}(P_0)} = \rho_\infty. \tag{4.115}$$

Therefore,

$$\lim_{\beta\to\infty} \tilde{S}(\rho_\beta) = \tilde{S}(\rho_\infty) = \log \mathrm{tr}(P_0). \tag{4.116}$$

Now $\mathrm{tr}(P_0)$ is just the degeneracy of the ground state of H. Usually, this ground state is non-degenerate, so that indeed,

$$\lim_{\beta\to\infty} \tilde{S}(\rho_\beta) = 0. \tag{4.117}$$

But even if the ground state is degenerate, the degeneracy is usually small, and does not grow linearly with the system size. In the thermodynamic limit, the entropy density hence still goes to zero.

Chapter 5

Applications of quantum statistical physics

We now turn to first applications of quantum statistical physics. We will first have a look at one of the simplest quantum systems: The quantum harmonic oscillator. We will then turn to the situation of having many coupled oscillators, and encounter the anyway interesting concept of decoupling oscillators. A big proportion of the chapter will be spent with discussing bosons and fermions, so indistinguishable quantum many-body systems. We assume a basic knowledge of bosonic and sermonic systems already, but not too much.

5.1 Harmonic systems

5.1.1 Statistical mechanics of single harmonic oscillators

Harmonic systems are ubiquitous in physics, surely in theoretical physics. This is true for two reasons:

a) Many problems can be modelled by harmonic oscillators. This is true for the mechanical motion of a micro-cantilever or a mirror in opto-mechanics, the motion of ions in a trap, of motions of ions in a crystal structure in condensed matter physics. It is also true for discrete versions of free fields and many other systems. This is no surprise: To first approximation, one can often take the Hamiltonian to be quadratic in positions and momenta, and couplings to be linear. Non-linearities can then be treated as a perturbation.

b) The other reason is that they can be exactly solved. This is a merit that should not be underestimated. To be fair, most of what is published concerns both (i) what is genuinely interesting and (ii) what can be actually treated. Since harmonic systems can be studied in all generality, one can often answer quite elaborate questions for these systems and hence use them as a kind of "theoretical laboratory".

Quantum harmonic oscillator: The Hamiltonian of a harmonic oscillator is given by

$$H = \frac{1}{2m} P^2 + \frac{D}{2} Q^2, \tag{5.1}$$

where P and Q are the operators of momentum and position, $m > 0$ is the mass and $D > 0$ the spring constant.

It is not difficult to see that this oscillator can always be brought into the normal form

$$H = \frac{\omega}{2}(P^2 + Q^2), \tag{5.2}$$

where $\omega = (D/m)^{1/2} > 0$ is its frequency. This can be done by means of a unitary transformation, we will get back to that. We already know how the Hamiltonian looks like in the energy eigenbasis, it is

$$H = \sum_{n=0}^{\infty} E_n |E_n\rangle\langle E_n|, \tag{5.3}$$

where

$$E_n = \left(n + \frac{1}{2}\right)\omega. \tag{5.4}$$

The ground state energy is $E_0 = \omega/2$, while the spectrum is not bounded from above. Taking this knowledge into account, it is not difficult to compute the partition function of the quantum canonical ensemble. It is

$$\begin{aligned} Z &= \operatorname{tr}(e^{-\beta H}) = \sum_{n=0}^{\infty} e^{-\beta\omega(n+1/2)} \\ &= \frac{e^{-\beta\omega/2}}{1 - e^{-\beta\omega}} \\ &= \frac{1}{2\sinh(\beta\omega/2)}. \end{aligned} \tag{5.5}$$

This was easy! For comparison, let us also compute the classical partition function of a harmonic oscillator. Also here we could have considered the simplified Hamiltonian as in Eq. (5.2), only that now, of course, the classical instance is now taken. But let us keep the mass and the spring constant for a moment. We have

$$\begin{aligned} Z &= \int d\gamma e^{-\beta H} \\ &= \int dp \int dq \exp\left(-\beta\left(\frac{p^2}{2m} + \frac{D}{2}q^2\right)\right) \\ &= \left(\frac{2\pi m}{\beta}\right)^{1/2}\left(\frac{2\pi}{\beta D}\right)^{1/2} = \frac{2\pi}{\beta\omega}. \end{aligned} \tag{5.6}$$

Remember that we have taken $\hbar = 1$, remember, and in the quantum mechanical description, we should have replaced ω by $\hbar\omega$ in SI-units, we have to divide the classical partition function by h such that it corresponds to the quantum mechanical one at high temperatures. From this, we can compute the thermodynamical potentials and functions. We rather state the results here, for

$$F = -\frac{1}{\beta}\log Z, \tag{5.7}$$

$$U = \langle H\rangle_\beta = \frac{\partial}{\partial\beta}\log Z, \tag{5.8}$$

$$\tag{5.9}$$

as well as S and C:

Quantum	Classical
$F = \frac{1}{\beta}\log 2\sinh(\beta\omega/2)$	$F = \frac{1}{\beta}\log(\beta\omega)$
$U = \frac{\omega}{2} + \frac{\omega}{e^{\beta\omega}-1}$	$U = \frac{1}{\beta}$
$S = k\frac{\beta}{\omega}2\coth(\beta\omega/2) - k\log(2\sinh(\beta\omega/2))$	$S = k - k\log(\omega)$
$C = k\left(\frac{\beta\omega}{2\sinh(\beta\omega/2)}\right)^2$	$C = k$

We see that we need at least $\beta\omega \approx 1$, hence $kT \approx \hbar\omega$ such that the motional degrees of freedom contribute to the thermodynamics. Below that temperature, they do not contribute significantly and are “frozen in”, as one says. In fact, we have already implicitly made use of that fact earlier when counting degrees of freedom.

5.1.2 Many uncoupled oscillators

So far so good. In statistical physics, one is, however, usually less interested in studying the properties of a single harmonic oscillator. Bur rather of many of them. This might sound scarier than it is: If they are not coupled at all, then we are already there. The Hamiltonian of many uncoupled oscillators is

$$H = \sum_j H_j = \sum_j \frac{\omega_j}{2}(P_j^2 + Q_j^2), \tag{5.10}$$

defined on the Hilbert space $\otimes_j \mathcal{H}_j$. Therefore, we partition function factors,

$$Z = \prod_j Z_j \tag{5.11}$$

and hence we get

$$F = \sum_j F_j, \tag{5.12}$$

$$U = \sum_j U_j, \tag{5.13}$$

$$S = \sum_j S_j. \tag{5.14}$$

Hence, the thermodynamics of many oscillators can be reduced to the thermodynamics of a single harmonic oscillator: We just have to take the sum in a last step. So there is nothing more to say. We already know the thermodynamics of many uncoupled oscillators.

5.1.3 Coupled oscillators and symplectic transformations

But this is not quite the situation one usually encounters yet. Often, the constituents are coupled, even though only slightly. Think of ions in a lattice structure of a crystal structure. Surely, the motions will to a good approximation be harmonic. But neglect couplings altogether would be ridiculous. After all, the ions are in a crystal structure. Let us hence consider Hamiltonians of the general form

$$H = \sum_{j,k=1}^{m} \left(A_{j,k} P_j P_k + D_{j,k} Q_j Q_k \right). \tag{5.15}$$

The matrices $A, B \in \mathbb{R}^{m\times m}$ are Hermitian (and hence symmetric, as they are real), $A = A^T$, $B = B^T$. The main diagonal elements take the above role, but the off-diagonal elements reflect couplings. How can we capture them? This seems like an impossible task.

It is not. In fact, it is very easy to relate this case again to the case of uncoupled harmonic oscillators. The key insight is that harmonic systems can always be decoupled. Let us think of the vector of position and momentum operators

$$\mathbf{R} = (Q_1, \dots, Q_m, P_1, \dots, P_m)^T \tag{5.16}$$

We can now transform the Hamiltonian to a new form: This can be done by canonical transformation, so by linear transformations from one set of coordinates to a new one, while keeping the canonical commutation relations invariant:

$$\begin{aligned} [Q_j, P_k] &= i\delta_{j,k}, && (5.17)\\ [P_j, P_k] &= 0, && (5.18)\\ [Q_j, Q_k] &= 0, && (5.19) \end{aligned}$$

for $j, k = 1, \dots, m$. Here, we have again set $\hbar = 1$. We can hence think of linear transformations transformations

$$\mathbf{R} \mapsto S\mathbf{R} = \mathbf{R}' = (Q_1', \dots, Q_m', P_1', \dots, P_m')^T, \tag{5.20}$$

with $S \in \mathbb{R}^{m\times m}$. The obvious question now is: What are the allowed matrices S, such that the commutation relations between position and momentum operators are respected? Let us define the skew symmetric matrix

$$\sigma = \begin{bmatrix} 0 & \mathbb{1}_m \\ -\mathbb{1}_m & 0 \end{bmatrix}. \tag{5.21}$$

Now, a moment of thought reveals the following:

Symplectic transformations: The linear transformations $\mathbf{R} \mapsto S\mathbf{R}$ that preserve the canonical commutation relations are exactly those corresponding to matrices $S \in \mathbb{R}^{m\times m}$ that satisfy

$$S\sigma S^T = \sigma. \tag{5.22}$$

These matrices form a group, the real symplectic group $Sp(2m, \mathbb{R})$.

What are these symplectic transformations? The are the canonical transformations, as they appear also in classical physics. Still, what elements are contained in it? Let us consider the situation of a single harmonic oscillator first, so $Sp(2,\mathbb{R})$. Clearly, any rotation

$$\left[\begin{array}{c} Q_1' \\ P_1' \end{array}\right] = \left[\begin{array}{cc} \cos(\theta) & -\sin(\theta) \\ \sin(\theta) & \cos(\theta) \end{array}\right], \tag{5.23}$$

with $\theta \in [0, 2\pi)$ is a symplectic transformation: The canonical commutation relations between the new position and momentum operator are the same one as before. Such operations are called “passive”, in that they preserve the number of excitations.

But the symplectic group contains also other elements: One can also “squeeze” the coordinates: One can stretch the position variables and compress the momentum ones and the other way around. For our oscillator, this means that

$$\left[\begin{array}{c} Q_1' \\ P_1' \end{array}\right] = \left[\begin{array}{cc} x & 0 \\ 0 & 1/x \end{array}\right] \tag{5.24}$$

for $x \in \mathbb{R}\backslash\{0\}$ is an allowed map of this kind, as one can easily verify. Such operations are called “active”, as the number of excitations is not preserved. For a single oscillator, this is also it: The symplectic group is generated by such elements.

For a larger number of modes things are more complicated: It is still true that squeezers are the only non-passive transformations, but the passive ones are more than simple rotations. In fact, if $O \in O(m)$ is an orthogonal map, then

$$O \oplus O \in Sp(2m, \mathbb{R}). \tag{5.25}$$

But there are more than those as well. In fact, the passive subgroup is isomorphic to $U(m)$, for the group theory experts in the audience. A homework here: Can you, with these tools, decouple the above general Hamiltonian defined in Eq. (5.15)?

5.1.4 Quantum statistics of the harmonic chain

But let us rather turn to an important example, the linear harmonic chain. Such a harmonic chain is a model for phonons of a solid body in the condensed matter context. Here, we allow for $N+2$ chain units, of which the left and the right ones cannot move and are fixed. We also consider only the motion in one direction, so only longitudinal motion. If Q_j and P_j are the positions and momenta of the j-th oscillator, then the Hamiltonian can be written as follows.

Hamiltonian of the harmonic chain:

$$H = \sum_{j=0}^{N} \left(\frac{P_j^2}{2m} + \frac{D}{2} (Q_j - Q_{j+1})^2 \right), \; P_0 = 0, \; Q_0 = Q_{N+1} = 0. \quad (5.26)$$

We expect wave solutions, but since the ends are fixed, the amplitude of the wave is forced to zero at the boundary. We can hence have a good guess of the above symplectic transformation. We take

$$Q_j = \sqrt{\frac{2}{N+1}} \sum_{k=1}^{N} \sin\left(\pi \frac{jk}{N+1}\right) Q'_k, \quad (5.27)$$

$$P_j = \sqrt{\frac{2}{N+1}} \sum_{k=1}^{N} \sin\left(\pi \frac{jk}{N+1}\right) P'_k. \quad (5.28)$$

In order to check that this really amounts to a symplectic transformation, we use the discrete orthogonality

$$\sum_{j=1}^{N} \sin\left(\pi \frac{jk}{N+1}\right) \sin\left(\pi \frac{jl}{N+1}\right) = \frac{N+1}{2} \delta_{l,k}. \quad (5.29)$$

This equality can be simply deduced from the real part of the orthogonality relations of the Fourier transform

$$\sum_{j=0}^{2N+1} e^{\pi ijk/(N+1)} e^{\pm \pi ijl/(N+1)} = \sum_{j=0}^{2N+1} e^{2\pi i \frac{j(k\pm l)}{2N+2}} = 2(N+1) \left\{ \begin{array}{ll} \delta_{k,0}\delta_{l,0} & +, \\ \delta_{k,l} & -, \end{array} \right. \quad (5.30)$$

for $0 \leq k, l \leq N$. Indeed, this is a passive symplectic transformation of the form as in Eq. (5.25). With $m = N + 2$, we have applied the same orthogonal transformation to the position and momentum coordinate, and this transformation hence corresponds to an element in $Sp(2(N+2), \mathbb{R})$. What is more, the kinetic part involving the momentum coordinates will remain the same: After all, the coupling matrix is simply an identity matrix which is left unchanged by this orthogonal transformation. The coupling in the position coordinates, however, now becomes

$$\sum_{j=0}^{N}(Q_j - Q_{j+1})^2 = \sum_{k=1}^{N} 4\sin^2\left(\frac{\pi}{2}\frac{k}{N+1}\right) {Q'_k}^2. \tag{5.31}$$

This is an uncoupled system! Let us digest for a moment what this means: We have transformed a system that is coupled to one that reflects the physics of simple harmonic oscillators. Hence, all we know on statistical mechanics will be applicable, quite an exciting state of affairs.

In this way, we hence have an uncoupled set of harmonic oscillators with frequencies

$$\omega_k = 2\sqrt{\frac{D}{m}}\sin\left(\frac{\pi}{2}\frac{k}{N+1}\right) = \Omega\sin\left(\frac{\pi}{2}\frac{k}{N+1}\right) \tag{5.32}$$

for $1 \leq k \leq N$, introducing

$$\Omega = 2\sqrt{\frac{D}{m}}. \tag{5.33}$$

So the harmonic oscillators are uncoupled, but all – except from some double degeneracies – have a different frequency now, which is sine modulated. One finde that they become dense for large N, so they better and better approximate a continuum function.

In this light of this observation, it makes sense to think of a "density if states" g, such that $g(\omega)$ denotes how many frequencies are around ω in the thermodynamic limit $N \to \infty$. We first compute the total number $N(\omega)$ of frequencies which are $\leq \omega$, for some ω. This gives

$$N(\omega) = \sum_{k:\omega_k \leq \omega} 1 \approx \int_{\Omega\sin\left(\frac{\pi}{2}\frac{k}{N+1}\right)\leq\omega} dk = (N+1)\frac{2}{\pi}\arcsin\left(\frac{\omega}{\Omega}\right). \tag{5.34}$$

The density of states it the derivative of this expression to ω. This exact derivative would be a sum of δ-distributions. We hence first take the thermodynamic limit and then take the derivative. There are good reasons for that, and this can also be made rigorous. This leads to the definition

$$g(\omega) = \frac{d}{d\omega}\lim_{N\to\infty}\frac{N(\omega)}{N} = \frac{2}{\pi\sqrt{\Omega^2 - \omega^2}}. \tag{5.35}$$

This density of states is in a sense an intensive variable and estimates the value $Ng(\omega)\Delta\omega$ for the number of eigenfrequencies in the interval $\Delta\omega$ at ω. For small values of ω the function g becomes constant. At the value $\omega = \Omega$, when neighboring chain elements oscillate in opposite directions, g diverges.

Just in the same way as a system of finitely many oscillators the values ω_k determine the partition function and the thermodynamical functions, the function g contains it in the thermodynamical limit. For the energy density, for example, we get

$$u(\beta) = \lim_{N\to\infty} \langle H\rangle_\beta = \int_0^\Omega d\omega g(\omega) U(\beta\omega), \tag{5.36}$$

where U is the expression derived above, so

$$U = \frac{\omega}{2} + \frac{\omega}{e^{\beta\omega}-1}. \tag{5.37}$$

Such formulas are also true in more general contexts, and also in higher dimensions, except that the function g needs to be altered then. Specifically, for d dimensions, one gets

$$\int d\omega g(\omega) = kd. \tag{5.38}$$

5.2 Bosons and fermions

5.2.1 Statistics in quantum theory

We now turn to quantum gases consisting of identical particles. There is a lot to say about identical particles in quantum mechanics, needless to say. Given that the course on advanced quantum mechanics is held at the same time, however, we will skip all the introduction and will jump right into the middle of the discussion. The presumably simplest quantum system of N particles is composed of N non-interacting members. Their Hamiltonian is given by

$$H = \sum_{j=1}^N \frac{P_j^2}{2m}, \tag{5.39}$$

where P_j denotes the momentum operator of the particle labelled j. Now systems consisting of N identical quantum systems come in two flavours. Bose systems and Fermi systems. The eigenfunctions of a Bose system are those eigenfunctions of H that are symmetric under interchange of the coordinates of any pair of particles. The eigenfunctions of Fermi systems are anti-symmetric, in contrast. Examples of Bose systems are phonons, photons, and so on. Examples for fermions are electrons. We will not get too much into detail here, as this is something surely covered in the other course. We will discuss the situation of ideal Bose and Fermi gases, however, as far as their implications for quantum statistical mechanics are concerned, however.

5.2.2 Ideal quantum gases in the micro-canonical ensemble

We start with the micro-canonical ensemble for the ideal Bose gas. We fix the energy interval $[E-\epsilon, E]$ for some energy $E > 0$ (and some $\epsilon > 0$). In order to get the partition function of this ensemble, we simply have to count. The energy eigenvalues of an ideal system is a sum of single-particle energies, often referred to as energy levels. They are given by

$$E_p = \frac{p^2}{2m}, \tag{5.40}$$

where $p = |\mathbf{P}|$ is the momentum eigenvalue of the single particle,

$$\mathbf{p} = \frac{2\pi\hbar}{L}\mathbf{n}, \tag{5.41}$$

for which $\mathbf{n} \in \mathbb{Z}^3$ and L is the cube root of the volume of the system,

$$L = V^{1/3}. \tag{5.42}$$

In the limit of a large volume, it is possible to treat the possible values of $\mathbf{p}$ as a continuum. The sum over $\mathbf{p}$ is then replaced by an integral,

$$\sum_{\mathbf{p}} \mapsto \frac{V}{h^3}\int d^3p, \tag{5.43}$$

where $h = 2\pi\hbar$. We now recapitulate what we have learnt in the other course on second quantization: A basis state vector in second quantised form is defined by the occupation numbers $\{n_{\mathbf{p}}\}$, so by the numbers of particles $n_{\mathbf{p}}$ that have momentum $\mathbf{p}$. The total energy E and the total number of particles are given by

$$\begin{aligned} E &= \sum_{\mathbf{p}} E_{\mathbf{p}} n_{\mathbf{p}}, & (5.44)\\ N &= \sum_{\mathbf{p}} n_{\mathbf{p}}. & (5.45) \end{aligned}$$

For spinless bosons and fermions – so particles that have no further internal degree of freedom – these numbers uniquely define the basis state of the system. The allowed values are

$$n_{\mathbf{p}} = \begin{cases} 0, 1, 2, \dots, & \text{for bosons,} \\ 0, 1, & \text{for fermions} \end{cases}. \tag{5.46}$$

For massless particles, state vectors can also be superpositions of such basis states, otherwise, a particle number super-selection rule is in action. Do you know what this is? If not, ask me.

We now turn to the computation of the partition function, so $Z(E)$. In the limit of large V, we can proceed as follows. The energy levels then form a continuum. We can devide the spectrum hence into groups of levels that contain $c_1, c_2, \dots$ energy levels, each group having an average energy E_j. The occupation number of the j-th cell, denoted as n_j is the sum over all $n_{\mathbf{p}}$ over all levels in that cell. Let us denote with $W(n_1, n_2, \dots)$ the number of basis states of the system corresponding to the set of occupation numbers $(n_1, n_2, \dots)$. Then the partition function of the micro-canonical ensemble is given by

$$Z(E) = \sum W(n_1, n_2, \dots), \tag{5.47}$$

where the sum of performed over all configurations that satisfy both

$$E = \sum_j E_j n_j, \tag{5.48}$$

$$N = \sum_j n_j. \tag{5.49}$$

To find $W(n_1, n_2, \dots)$ for a Bose gas and a Fermi gas it is sufficient to identify the collection of all w_j, $j = 1, 2, \dots$, so the number of ways in which the n_j particles can be assigned to the j-th cell. Because then we simply have

$$W(n_1, n_2, \dots) = \prod_j w_j. \tag{5.50}$$

We have boiled down the problem to a combinatorical one, therefore.

For bosons, each level can be occupied by any number of particles, in principle even all particles, as it happens in perfect Bose-Einstein condensation. We find that

$$w_j = \frac{(n_j + c_j - 1)!}{n_j!(c_j - 1)!}. \tag{5.51}$$

Therefore,

$$W(n_1, n_2, \dots) = \prod_j \frac{(n_j + c_j - 1)!}{n_j!(c_j - 1)!}. \tag{5.52}$$

For fermions, the number of particles in each of the c_j subcells in the j-th cell is either 0 or 1. Therefore, w_j is given by the number of ways in which n_j items can be chosen from c_j things, so

$$w_j = \frac{c_j!}{n_j!(c_j - n_j)!}. \tag{5.53}$$

Again,

$$W(n_1, n_2, \dots) = \prod_j \frac{c_j!}{n_j!(c_j - n_j)!}. \tag{5.54}$$

We are not quite there, however. In order to get the partition function, we need to sum this expression over all those entries that satisfy both Eq. (5.48) and (5.49). In an exact fashion, this is not an easy task. Fortunately, this can simply be done in a very good approximation. One takes $W(\bar{n}_1, \bar{n}_2, \dots)$, where $(\bar{n}_1, \bar{n}_2, \dots)$ are the numbers that solve the problem of maximizing

$$W(\bar{n}_1, \bar{n}_2, \dots), \tag{5.55}$$

subject to the conditions

$$E = \sum_j E_j \bar{n}_j, \tag{5.56}$$

$$N = \sum_j \bar{n}_j. \tag{5.57}$$

This is again an optimisation problem that we can solve with the machinery of Lagrange multipliers that we have discussed before. The computation is straightforward and not too interesting. We state the results here: We find

$$\bar{n}_j = \frac{c_j}{z^{-1} e^{\beta E_j} - 1} \tag{5.58}$$

for bosons and

$$\bar{n}_j = \frac{c_j}{z^{-1} e^{\beta E_j} + 1} \tag{5.59}$$

for fermions. We can derive from this that

$$\bar{n}_{\mathbf{p}} = \frac{1}{z^{-1} e^{\beta E_{\mathbf{p}}} - 1} \tag{5.60}$$

for bosons and

$$\bar{n}_{\mathbf{p}} = \frac{1}{z^{-1} e^{\beta E_{\mathbf{p}}} + 1} \tag{5.61}$$

for fermions. Here, the parameters $z, \beta \in \mathbb{R}$ are two Lagrange parameters determined from

$$E = \sum_{\mathbf{p}} E_{\mathbf{p}} \bar{n}_{\mathbf{p}}, \tag{5.62}$$

$$N = \sum_{\mathbf{p}} \bar{n}_{\mathbf{p}}. \tag{5.63}$$

5.2.3 Bose and Fermi gases in the grand canonical ensemble

In principle, this is the solution to the problem. It is easier to progress, however, in a different picture, namely by referring to the grand canonical ensemble. This is yet another ensemble, and yet one that is equivalent to the known ones in the same sense as the micro-canonical ensemble and the canonical one are equivalent. Let us first state the canonical partition function again. In this second-quantised picture, this may not be entirely straightforward.

Canonical partition function of the ideal Bose and Fermi gas: For both fermions and bosons,

$$Z = \sum e^{-\beta \sum_{\mathbf{p}} E_{\mathbf{p}} n_{\mathbf{p}}}, \tag{5.64}$$

where the sum is performed over all $\{n_{\mathbf{p}}\}$ for which

$$\sum_{\mathbf{p}} n_{\mathbf{p}} = N. \tag{5.65}$$

For a Bose gas, $n_{\mathbf{p}} = 0, 1, 2, \ldots$, for a Fermi gas $n_{\mathbf{p}} = 0, 1$.

This is one condition less compared to the micro-canonical ensemble. Still, the condition in Eq. (5.65) makes things a bit awkward. This is by we consider the grand canonical partition function. It is defined as follows.

Grand canonical ensemble: The grand canonical ensemble is

$$\rho = \frac{1}{G} e^{-\beta(H-\mu N)} \tag{5.66}$$

and has the partition function

$$G = \mathrm{tr}(e^{-\beta(H-\mu N)}). \tag{5.67}$$

Expectation values of observables A are obtained as

$$\langle A \rangle = \frac{1}{G} \mathrm{tr}(A e^{-\beta(H-\mu N)}). \tag{5.68}$$

The grand canonical ensemble hence goes one step further and considers the particle number not as a fixed number, but one rather holds the expected particle number fixed. In a similar way as the canonical ensemble emerged from a description of a system in contact to a heat bath, we now also have a particle bath. The expected particle number is

$$\langle N\rangle = z\frac{\partial}{\partial z}\log(G). \tag{5.69}$$

Here, we have set

$$\log(z) = \mu\beta. \tag{5.70}$$

z is called the fugacity, and μ the chemical potential. So both take the same role, roughly speaking. In the same way,

$$U = \langle H\rangle. \tag{5.71}$$

Again, we can identify a quantity that can be identified with the respective thermodynamic potential as

$$\tilde{J}(T,V,\mu) = -\frac{1}{\beta}\log G. \tag{5.72}$$

As before, this is not "the same" as the thermodynamic potential J in thermodynamics, but can be identified in the same way as we have done before. One therefore also finds

$$pV = kT\log(G). \tag{5.73}$$

In this way, one gets the following expression for the ideal Bose and Fermi gas:

Grand canonical partition function of the ideal Bose and Fermi gas:

$$\begin{aligned} G &= \sum_{N=0}^{\infty}\sum_{\{n_{\mathbf{p}}:\sum n_{\mathbf{p}}=N\}} z^N e^{-\beta\sum_{\mathbf{p}}E_{\mathbf{p}}n_{\mathbf{p}}} \\ &= \sum_{N=0}^{\infty}\sum_{\{n_{\mathbf{p}}:\sum n_{\mathbf{p}}=N\}} e^{-\beta(\sum_{\mathbf{p}}E_{\mathbf{p}}n_{\mathbf{p}}-\mu N)}. \end{aligned} \tag{5.74}$$

Again, both z and μ take a role of a Lagrange parameter, just in a different disguise. Eq. (5.74) is the same as

$$G = \sum_{N=0}^{\infty} \sum_{\{n_{\mathbf{p}}:\sum n_{\mathbf{p}}=N\}} \prod_{\mathbf{p}} \left(ze^{-\beta E_{\mathbf{p}}}\right)^{n_{\mathbf{p}}}. \tag{5.75}$$

Again, the occupations are as given for Bose and Fermi gases. This is an easier expression, however: We find that the double summation is equivalent to summing each $n_{\mathbf{p}}$ independently. We therefore find

$$G = \prod_{\mathbf{p}} \left(\sum_{n} (ze^{-\beta E_{\mathbf{p}}})^n \right) = \prod_{\mathbf{p}} \left(\sum_{n} (e^{-\beta(E_{\mathbf{p}}-\mu)})^n \right), \tag{5.76}$$

where again the sum extends over $n = 0, 1, 2, \ldots$ for the Bose gas and $n = 0, 1$ for the Fermi gas. The result is as follows:

$$G = \prod_{\mathbf{p}} \frac{1}{1 - ze^{-\beta E_{\mathbf{p}}}} = \prod_{\mathbf{p}} \frac{1}{1 - e^{-\beta(E_{\mathbf{p}}-\mu)}} \tag{5.77}$$

for the Bose gas and

$$G = \prod_{\mathbf{p}} (1 + ze^{-\beta E_{\mathbf{p}}}) = \prod_{\mathbf{p}} (1 + e^{-\beta(E_{\mathbf{p}}-\mu)}) \tag{5.78}$$

for the Fermi gas. The equations of state are

$$\frac{pV}{kT} = \log G = -\sum_{\mathbf{p}} \log(1 - ze^{-\beta E_{\mathbf{p}}}) \tag{5.79}$$

for the Bose gas and

$$\frac{pV}{kT} = \log G = \sum_{\mathbf{p}} \log(1 + ze^{-\beta E_{\mathbf{p}}}) \tag{5.80}$$

for the Fermi gas. From this, we can eliminate the Lagrange parameter z with the help of the equations

$$\langle N \rangle = z\frac{\partial}{\partial z} \log G = \sum_{\mathbf{p}} \frac{ze^{-\beta E_{\mathbf{p}}}}{1 - ze^{-\beta E_{\mathbf{p}}}} \tag{5.81}$$

for bosons and

$$\langle N \rangle = z\frac{\partial}{\partial z} \log G = \sum_{\mathbf{p}} \frac{ze^{-\beta E_{\mathbf{p}}}}{1 + ze^{-\beta E_{\mathbf{p}}}} \tag{5.82}$$

for fermions. The average occupation numbers are

$$\langle n_{\mathbf{p}} \rangle = -\frac{1}{\beta} \frac{\partial}{\partial E_p} \log G = \frac{z e^{-\beta E_{\mathbf{p}}}}{1 \mp z e^{-\beta E_{\mathbf{p}}}} = \frac{e^{-\beta(E_{\mathbf{p}}-\mu)}}{1 \mp e^{-\beta(E_{\mathbf{p}}-\mu)}}, \tag{5.83}$$

where the minus sign is for bosons and the plus sign for fermions. We hence get

$$N = \sum_{\mathbf{p}} \langle n_{\mathbf{p}} \rangle. \tag{5.84}$$

We now progress, hopefully in a not too elliptic style, by looking at the limit of large V and performing the continuum limit. Hence, sums become integrals, as explained above. The value $z \geq 0$, the fugacity is non-negative. Again, it is related to the chemical potential as $\log(z) = \mu/(kT)$.

Performing the continuum limit, we get for ideal fermions the following equation of state.

$$\frac{pV}{kT} = \frac{4\pi}{h^3} \int_0^\infty dp p^2 \log(1 + z e^{-\beta p^2/(2m)}), \tag{5.85}$$

$$\frac{1}{v} = \frac{4\pi}{h^3} \int_0^\infty dp p^2 \left(z^{-1} e^{\beta p^2/(2m)} + 1 \right)^{-1}, \tag{5.86}$$

where $v = V/N$. This can also be written as

$$\frac{pV}{kT} = \frac{1}{\lambda^3} f_{5/2}(z), \tag{5.87}$$

$$\frac{1}{v} = \frac{1}{\lambda^3} f_{3/2}(z), \tag{5.88}$$

where

$$\lambda = \left(2\pi\hbar^2\right)^{1/2} \tag{5.89}$$

is the thermal wavelength and

$$f_{5/2} = \frac{4}{\sqrt{\pi}} \int_0^\infty dx x^2 \log(1 + z e^{-x^2}), \tag{5.90}$$

$$f_{3/2} = z \frac{\partial}{\partial z} f_{5/2}(z). \tag{5.91}$$

The thermal wavelength is called like that since it is of the order of the de Broglie wavelength of a particle with mass m and energy kT.

For the ideal Bose gas, things are slightly messier, as the sums over $\mathbf{p}$ in the equations of state diverge as $z \to 1$, since the single term corresponding to $\mathbf{p} = 0$ diverges. Thus, the term corresponding to $\mathbf{p} = 0$ may be as important as the entire sum. We split off the terms reflecting $\mathbf{p} = 0$, therefore, when we compute the equation of state. This gives

$$\begin{aligned} \frac{pV}{kT} &= \frac{4\pi}{h^3}\int_0^\infty dpp^2 \log(1 - ze^{-\beta p^2/(2m)}) - \frac{1}{V}\log(1-z), && (5.92) \\ \frac{1}{v} &= \frac{4\pi}{h^3}\int_0^\infty dpp^2 \left(z^{-1}e^{\beta p^2/(2m)} - 1\right)^{-1} + \frac{1}{V}\frac{z}{1-z}, && (5.93) \end{aligned}$$

where again $v = V/N$. This can again be written as

$$\begin{aligned} \frac{pV}{kT} &= \frac{1}{\lambda^3} g_{5/2}(z) - \frac{1}{V}\log(1-z), && (5.94) \\ \frac{1}{v} &= \frac{1}{\lambda^3} g_{2/3}(z) + \frac{1}{V}\frac{z}{1-z}. && (5.95) \end{aligned}$$

Here now

$$\begin{aligned} g_{5/2} &= -\frac{4}{\sqrt{\pi}}\int_0^\infty dxx^2 \log(1 - ze^{-x^2}), && (5.96) \\ g_{2/3} &= z\frac{\partial}{\partial z} g_{5/2}(z). && (5.97) \end{aligned}$$

We have that the quantity $z/(1-z)$ is the average occupation number $\langle n_0 \rangle$ for the single particle level,

$$\langle n_0 \rangle = \frac{z}{1-z}. \tag{5.98}$$

This term contributes if $\langle n_0 \rangle / V$ is a non-negligible number, so if a non-zero fraction of the particles occupy a level with $\mathbf{p} = 0$. Such a macroscopic occupation of the ground state is called Bose-Einstein-condensation. We now compute the inner energy from this:

$$U = -\frac{\partial}{\partial \beta}\log G, \tag{5.99}$$

and since $\log G = pV/(kT)$, we get

$$\frac{U}{V} = \frac{3}{2}\frac{kT}{\lambda^3} f_{5/2}(z), \tag{5.100}$$

for fermions and

$$\frac{U}{V} = \frac{3}{2}\frac{kT}{\lambda^3} g_{5/2}(z), \tag{5.101}$$

for bosons. Eliminating z gives

$$U = \frac{3}{2}pV. \tag{5.102}$$

5.2.4 Fermi gases at high temperatures and low densities

Let us have a slightly more detailed look at the equation

$$\frac{\lambda^3}{v} = f_{3/2}(z), \tag{5.103}$$

where again $v = V/N$. The function $f_{3/2} : \mathbb{R}^+ \to \mathbb{R}$ is a monotone increasing function of z. For small z, one finds a power series expansion

$$f_{3/2}(z) = z - \frac{z^2}{2^{3/2}} + O(z^3). \tag{5.104}$$

For large z, one finds with slightly heavier machinery that

$$f_{3/2}(z) = \frac{4}{3\sqrt{\pi}} \left((\log(z))^{3/2} + \frac{\pi^2}{8} (\log(z))^{-1/2} + O(z^{-1}). \right) \tag{5.105}$$

For high temperatures and low densities, one should expect

$$\lambda^3/v \ll 1 \tag{5.106}$$

to be true. Then quantum effects should be rather negligible. We find

$$\frac{\lambda^3}{v} \approx z - \frac{z^2}{2^{3/2}}. \tag{5.107}$$

The equation of state then becomes

$$\frac{pv}{kT} = \frac{v}{\lambda^3} \left(z - \frac{z^2}{2^{5/2}} + O(z^3) \right) = 1 + \frac{1}{2^{5/2}} \frac{\lambda^3}{v} + o(v^{-1}). \tag{5.108}$$

This has the form of a virial expansion. Again, we find a correction to the expression for the classical ideal gas. But this time, the correction is not due to molecular interactions, but rather due to quantum effects. The additional pressure is sometimes also referred to as Fermi pressure.

5.2.5 Low temperatures and high densities

For

$$\lambda^3/v \gg 1, \tag{5.109}$$

one finds that the de Broglie wavelength of a particle is much greater than the average particle separation. Thus quantum effects will become most important. This holds true in particular for the Pauli principle. Close to zero temperature, we have

$$\frac{1}{v}\left(\frac{2\pi\hbar^2}{mkT}\right)^{3/2} \approx \frac{4}{3\sqrt{\pi}}(\log(z))^{3/2}, \tag{5.110}$$

so

$$z \approx e^{\beta E_F}, \tag{5.111}$$

where

$$E_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2}{v}\right)^{2/3} \tag{5.112}$$

is the Fermi energy. In order to assess its physical significance, let us have a look at $\langle n_{\mathbf{p}} \rangle$ near zero temperature. We have

$$\langle n_{\mathbf{p}} \rangle \approx \frac{1}{e^{\beta(E_{\mathbf{p}}-E_F)}+1}. \tag{5.113}$$

If now $E_{\mathbf{p}} < E_F$, then the exponential in the denominator vanishes as $T \to 0$ or as $\beta \to \infty$. Then

$$\langle n_{\mathbf{p}} \rangle \approx 1. \tag{5.114}$$

Otherwise, $\langle n_{\mathbf{p}} \rangle \approx 0$. In fact, at exactly zero temperature, one has

$$\langle n_{\mathbf{p}} \rangle = \begin{cases} 1, & E_{\mathbf{p}} \leq E_F, \\ 0, & E_{\mathbf{p}} < E_F. \end{cases} \tag{5.115}$$

The interpretation of this should be rather obvious: The fermions try to occupy the levels with the lowest energy. Due to the Pauli principle, they cannot all occupy the same, so the fill up the levels up to the Fermi energy. This “jump” is also called the Fermi surface. So E_F is the single particle energy below which there are exactly N levels. In momentum space, one obtains a sphere, the Fermi sphere.

At non-zero temperature, this Fermi surface is “melting”, and is no longer discontinuous. To obtain a correction, let us perform an expansion in kT/E_F. Let us define the Fermi temperature by $kT_F = E_F$. Then low temperatures and high densities mean $T \ll T_F$. In this domain, the gas is called degenerate, as the particles try to occupy the lowest levels. The average occupation number is

$$\langle n_{\mathbf{p}} \rangle = \frac{1}{e^{\beta(E_{\mathbf{p}}-\log(z))}+1} = \frac{1}{e^{\beta(E_{\mathbf{p}}-\mu)}+1}. \tag{5.116}$$

From this point on, one can derive all thermodynamic properties, although we will not go too much into detail here. For example one gets the expansion

$$p = \frac{2}{5}\frac{E_F}{v}\left(1 + \frac{5\pi^2}{12}\left(\frac{kT}{E_F}\right)^2 + o(T^2)\right). \tag{5.117}$$

A lot of interesting physics emerges from the statistical physics of non-interacting fermions. For example, the theory of white dwarf stars can be pushed quite far with only the tools that we have just encountered. To go too much into detail would be beyond the scope of our course, but feel invited to have a look in the literature on that.

5.2.6 Bose-Einstein condensation

We finally have a brief look at the situation of bosons at low temperatures. Again, we already know the equation of state for an ideal Bose gas of N particles of mass m contained in a volume V. In order to render this expression useful, we must identify the fugacity as a function of the temperature and the specific volume by solving the above equation of state, i.e.,

$$\frac{1}{v} = \frac{1}{\lambda^3} g_{2/3}(z) + \frac{1}{V}\frac{z}{1-z}, \tag{5.118}$$

where again $v = V/N$ and $\lambda = (2\pi\hbar^2/(mkT))^{1/2}$. In order to accomplish this task, we have to have a close look at the function $g_{2/3} : [0,1] \to \mathbb{R}$. For real values between 0 and 1, $g_{2/3}(z)$ is bounded, and a positive, monotone increasing function of z. For small z, a power series expansion delivers

$$g_{2/3}(z) = z + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + o(z^3). \tag{5.119}$$

At $z = 1$ the derivative diverges, but it value is finite,

$$g_{2/3}(1) = \zeta(3/2) = 2.612\ldots, \tag{5.120}$$

where ζ is the Riemann zeta function. Therefore, for all values $z \in [0,1]$, we have that

$$g_{2/3}(z) \leq \zeta(3/2). \tag{5.121}$$

Now let us rewrite the above equation of state as

$$\lambda^3 \frac{\langle n_0 \rangle}{V} = \frac{\lambda^3}{v} - g_{2/3}(z). \tag{5.122}$$

This means that

$$\frac{\langle n_0 \rangle}{v} > 0 \tag{5.123}$$

whenever the temperature and the specific volume are such that

$$\frac{\lambda^3}{v} > g_{2/3}(1). \tag{5.124}$$

Bose-Einstein condensation: For $\lambda^3/v > g_{2/3}(1)$, a finite fraction $\langle n_0 \rangle / v$ occupies the level with

$$\mathbf{p} = 0. \tag{5.125}$$

This phenomenon is called Bose-Einstein condensation.

So for low temperatures and if the densities are right, a macroscopic fraction of all bosons accumulate in the lowest energy level. This is a quite intriguing phenomenon. In order to study it experimentally, one of the problems is to cool down the bosonic gases sufficiently, and to understand the impact of interactions, which will be weak, but cannot be truly neglected at such small temperatures. Of course, the study of cold atomic bosonic gases has in the meantime become a big field of research in its own right, and interest has exploded since the Nobel prize was given to protagonists who were involved in experimentally generating the first Bose-Einstein condensate. If there is time, we will say more about this at the end of the course.

Chapter 6

Lattice models and phase transitions

Lattice models are quite ubiquitous in physics. We have already encountered such lattice models when we had a look at a coupled harmonic system. It should be clear that there are many instances of such models. Here, one thinks of having a graph $G = (V, E)$ given, with a quantum or a classical degree of freedom per lattice site. This graph could reflect a cubic lattice, or a simple line – such as in the case of the simple harmonic chain above. Or a more sophisticated lattice, such as a Kagome lattice, or a triagonal lattice. It should be clear that in particular in the condensed-matter context, such lattice models are everywhere. Also, for systems of cold atoms in optical lattices one encounters such lattice models: The lattice is then the one given by the laser light itself. Interactions are usually local. This means that systems directly interact only with finitely many neighbours, such as nearest neighbours.

Local Hamiltonians: A local Hamiltonian is a Hamiltonian on a lattice defined by a graph $G = (V, E)$. Interactions are finite-ranged in the sense that there exists an r such that whenever $j, k \in V$ with

$$\mathrm{dist}(j, k) > r \tag{6.1}$$

then the two constituents do not interact.

This is a somewhat sophisticated way of putting it. For practical purposes, one is usually interested in cubic lattices of some dimension D, and nearest-neighbor interactions, for which $r = 1$. One then often writes $\langle j,k\rangle$ for nearest neighbors in the lattice, that is, for sites $j,k \in V$ for which

$$\mathrm{dist}(j,k) = 1. \tag{6.2}$$

One distinguishes then periodic boundary conditions from open boundary conditions. For periodic boundary conditions, one has $V = \mathbb{Z}_L^D$, that is, one considers the sites in each dimension modulo N. For open boundary conditions, the sites at the boundary are only coupled to neighbours in the interior. For such local interactions, a common translationally invariant quantum Hamiltonian with open boundary conditions then looks as follows.

Hamiltonian with nearest-neighbor interaction in a cubic lattice: With V being the cubic lattice, the Hamiltonian is of the form

$$H = \sum_{j\in V} h_j + \sum_{\langle j,k\rangle} v_{j,k}. \tag{6.3}$$

Each of the terms h_j are the same then, respectively, only translates of each other, and supported on sites j only. In case of $v_{j,k}$, again all terms are either translates of each other, or appropriately rotated instances. Again, it is always the same Hamiltonian term, only the support is different. Of course, it is a small step to accommodate also more complicated periodicities: We can think of elementary cells in a crystal structure and have not a fully translationally invariant Hamiltonian. In condensed matter physics, one often encounters such Hamiltonians.

Now there is an intricate feature about such lattice models: They are easy to describe. We have just done so: For a translationally invariant model, it is sufficient to give the on-site term h_j for some j and the coupling term $v_{j,k}$ for some j,k. That is it! These are only very, very few numbers. Yet, it is usually very difficult to grasp properties of such models. They can exhibit a very sophisticated behaviour, and can show phase transitions, topological order, string order, and so on. And of course, this is all a property of the Hamiltonian. Still, these intricate properties are in a way an emergent property. Still today, a lot of research is dedicated to finding out properties from such lattice models.

6.1 Classical lattice models

6.1.1 Classical Ising model

We start by discussing classical lattice models. Here, each degree of freedom per site in V is a classical degree of freedom. The most famous model of that kind is the Ising model, where each site is associated with a classical spin degree of freedom. In fact, it is the simplest mathematical model of ferromagnetism in statistical mechanics that already shows very important features of the phenomenon. It has also been used to describe the behaviour of lattice gases, binary alloys melting of DNA, and other situations. The Ising model was invented by Wilhelm Lenz, who gave this model as a problem to be solved to Ising, who indeed presented the solution for the one-dimensional situation given below. To be fair, this is a very simple problem. The big breakthrough was the exact solution for the two-dimensional case given by Onsager. We will only have the time to hint at that. In the Ising model, the underlying lattice is

$$V = L^{\times D}, \tag{6.4}$$

so L in one dimension, $L \times L$ in two dimensions, and so on. At each site, there is a spin that can take the values $s_j \in \{+1, -1\}$. A configuration is hence a collection of all values

$$s = (s_1, \dots, s_{L^D}). \tag{6.5}$$

$s = (-1, -1, \dots, -1)$ is a configuration in which all spins are pointing downwards, for $s = (1, 1, \dots, 1)$ all are going up.

Hamiltonian of the Ising model: For $J, B \in \mathbb{R}$, the Hamiltonian is

$$H(s) = -J \sum_{\langle j,k \rangle} s_j s_k - B \sum_j s_j. \tag{6.6}$$

This is a model for spins in a solid-state system: J is the magnetic interaction energy between nearest-neighbour spins in the lattice. B reflects an external magnetic field. This is usually written as μB with a chemical potential μ, but this we have absorbed in our definition of B to keep the discussion simpler. In this model, both positive and negative values for J make sense. If

- $J > 0$, the interaction is called ferromagnetic,

- $J < 0$, the interaction is called antiferromagnetic,
- $J = 0$, the spins are noninteracting.

We will also subsequently freely move between different boundary conditions; but it should be clear that for each dimension, one can consider all boundary conditions separately. At this point, we are in the position to formulate the partition function of the classical canonical ensemble for inverse temperature $\beta > 0$,

$$Z = \sum_s \exp\left(\beta J \sum_{\langle j,k\rangle} s_j s_k + \beta B \sum_j s_j\right). \tag{6.7}$$

Here, the sum s is the sum over all 2^{L^D} many configurations of the spins in the lattice. Clearly, this is a daunting sum, and it is not easy to perform naively. In 1D and in 2D, one can still solve the model exactly. In 1D, this is a very easy task, in 2D not so much. But already at this level, we can roughly grasp what is going on here. At low temperatures, we expect the lattice to be ordered. As we increase the temperature, at some point the order should disappear and the spins should become randomly oriented.

6.1.2 Absence of a phase transition in the 1D Ising model

For our discussion in 1D, let us pick periodic boundary conditions. This does not alter the problem compared to open boundary conditions here, but the notation becomes a bit simpler. We hence consider spins on a ring, with sites $(1, \ldots, L)$. We identify $s_{j+N} = s_j$. The Hamiltonian is hence

$$H(s) = -J \sum_{j=1}^{L} s_j s_{j+1} - B \sum_{j=1}^{L} s_j. \tag{6.8}$$

Again, the partition function in the canonical ensemble becomes

$$Z = \sum_{s_1=\pm 1} \cdots \sum_{s_L=\pm 1} \exp\left(\beta \sum_{j=1}^{L}\left(J s_j s_{j+1} + \frac{1}{2}B(s_j + s_{j+1})\right)\right), \tag{6.9}$$

where we have used that

$$\sum_{j=1}^{L} s_j = \frac{1}{2}\sum_{j=1}^{L}(s_j + s_{j+1}) \tag{6.10}$$

for a periodic lattice. At this point, it seems infeasible to perform the sum over all configurations. We can, however, introduce a trick of a transfer operator. In fact, this trick is quite magic: Be astonished by the simplicity of it. This amounts to reordering the sum in a way such that the entire expression can be written as a matrix power of a transfer operator. In modern terms, one could also say that the tensor network describing this can be efficiently contracted. The trick is as follows. Let us introduce a 2×2-matrix, called the transfer matrix,

$$P = \left(\begin{array}{cc} e^{\beta(J+B)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-B)} \end{array} \right). \tag{6.11}$$

We identify the matrix elements with a kernel of a quadratic form over $(+1, -1)$, so the elements of this matrix are

$$\begin{aligned} \langle +1|P|+1\rangle &= e^{\beta(J+B)}, & (6.12)\\ \langle +1|P|-1\rangle &= \langle -1|P|+1\rangle = e^{-\beta J}, & (6.13)\\ \langle -1|P|-1\rangle &= e^{\beta(J-B)}. & (6.14) \end{aligned}$$

That is to say, we have

$$\langle s_j|P|s_k\rangle = e^{\beta(J s_j s_{j+1} + \frac{1}{2}B(s_j+s_{j+1})}. \tag{6.15}$$

In this way, can write the partition function as

$$Z = \sum_{s_1=\pm 1} \cdots \sum_{s_L=\pm 1} \langle s_1|P|s_2\rangle\langle s_2|P|s_3\rangle \dots \langle s_L|P|s_1\rangle. \tag{6.16}$$

At first glance, it seems as if we had not gained much by this reformulation. But we have. We can now perform the sum over each term explicitly, using the completeness relation. We get

$$Z = \sum_{s_1=\pm 1} \langle s_1|P^L|s_1\rangle = \mathrm{tr}(P^L). \tag{6.17}$$

So we can reduce the entire sum to a single sum, so to a trace of the transfer matrix. But this is easy. If we denote the largest and the smallest eigenvalues of the symmetric matrix with λ_+ and λ_-, respectively (remember they are real for symmetric matrices), then one finds

$$Z = \lambda_+^L + \lambda_-^L = \lambda_+^L \left(1 + \left(\frac{\lambda_-}{\lambda_+}\right)^L\right). \tag{6.18}$$

We can easily find these eigenvalues explicitly,

$$\lambda_{\pm 1} = e^{\beta J}\left(\cosh(\beta B) \pm \left(\cosh^2(\beta B) - 2^{-2\beta J}\sinh(2\beta J)\right)^{1/2}\right); \tag{6.19}$$

after all, do not forget that P is a simple 2×2 matrix where we can simply solve the equation involving the characteristic polynomial. In the limit $L \to$, only the largest eigenvalue λ_+ contributes to thermodynamic quantities. For example, the free energy per site is in the thermodynamic limit

$$\lim_{L\to\infty} \frac{\beta}{L} \log Z = -\beta \log(\lambda_+). \tag{6.20}$$

Here, we have used that

$$\lim_{L\to\infty} \left(\frac{\lambda_-}{\lambda_+}\right)^L = 0. \tag{6.21}$$

Hence, the free energy per site is

$$f = -L - k\log\left(\cosh(\beta B) + \left(\cosh^2(\beta B) - 2^{-2\beta J}\sinh(2\beta J)\right)^{1/2}\right). \tag{6.22}$$

The order parameter is given by the magnetisation

$$m = \frac{1}{L}\sum_{j=1}^{L} s_j. \tag{6.23}$$

One finds

$$\langle m \rangle = -\left(\frac{\partial f}{\partial B}\right)_T = \frac{\sinh(\beta B)}{(\cosh^2(\beta B) - 2e^{-2\beta J}\sinh(2\beta J))^{1/2}}. \tag{6.24}$$

We see that this model cannot exhibit a phase transition, since when $B \to 0$, the order parameter also goes to zero. That is to say, no spontaneous non-zero value of the order parameter is possible. The reason is that there are for each site not enough neighbours in order to enforce some kind of order. The equivalent 2D model, in fact, does exhibit a phase transition.

6.1.3 Existence of a phase transition in the 2D Ising model

We will now see that the same model in 2D does exhibit a phase transition. This can again be exactly solved with more elaborate methods. We will first have a look at a high-level argument, however. This high level argument will show that there in fact exists a phase transition, but not quite at what point.

To keep the discussion simple, let us set $B = 0$: We anyway want to see a spontaneous non-zero value of the order parameter at a vanishing field. We also pick now open boundary conditions, this again to keep the discussion as simple as possible. The Hamiltonian is hence nothing but

$$H(s) = -J \sum_{\langle j,k \rangle} s_j s_k, \tag{6.25}$$

for configurations $s = (s_1, \ldots, s_{L^2}) \in \{-1, 1\}^{\times 2}$. The neighbours of each site are the four sites that are immediately adjacent to each site, so again nearest neighbours only. As we know, the probability that the system takes some configuration s is given by

$$p(s) = \frac{1}{Z} e^{-\beta H(s)}. \tag{6.26}$$

We consider the case of low temperatures, so the limit $\beta \to \infty$, and state that with high probability, the magnetisation

$$m = \frac{1}{L^2} \sum_{j=1}^{L} s_j \tag{6.27}$$

takes values close to $+1$ or -1. This means that all spins then point to the same direction, spontaneously. "Spontaneous" here means, as is common in physics, that the state emerging has less symmetry that the original problem, which is perfectly symmetric under exchange of $+1$ and -1. In many fields of physics, such as in quantum field theory, one encounters such spontaneously broken symmetries all the time, even if in a slightly different sense.

The basic argument will be that the spins that are in the minority (meaning, the spins not taking the most probable value) are enclosed by a contour which separates $+1$ values from -1 values. Such a contour costs energy and is hence improbable. We will have a closer look at this idea in the following.

Let us first define properly what we think a contour is. A contour C is a line running on the lines of the lattice, which does not cross itself, and which is either closed or which ends on the boundary of the lattice. The length of the contour we denote as $l(C)$. The inner of the contour C is defined as the enclosed surface, if C is closed, or the smaller of the two areas, if C ends at the boundaries and hence cuts the lattice into two parts. We denote this enclosed area with $f(C)$. With this convention, of course we have

$$f(C) = l(C)^2. \tag{6.28}$$

We will also need the number $n(l, L)$ of contours of a given length l. It is not so easy to compute this number, it is a combinatorical problem. Still, this number can somewhat crudely be upper bounded by

$$n(l, L) \leq (L+1)^2 4 3^{l-1}. \tag{6.29}$$

The factor $(L+1)^2$ reflects the choice of the starting point. The factor 4 originates from the freedom of choosing the initial direction. And the factor 3^{l-1} stands for the choice of a direction for the rest of the pieces, respecting the fact that one cannot go back. This is of course not very tight. To start with, not for all lattice sites all 4 initial directions are possible. Also, after a few steps, other directions will be restricted. Still, it is obviously an upper bound, and it will be sufficient for our purposes.

Now we have to bring the concept of a contour together with the spin configurations. For that we define what it means that a contour C fits to a configuration s. We say that C fits to s if C separates $+1$ from -1 everywhere, and if all boundary values in the inner of C have the same value. For a given contour C, the probability $p(C)$ that this contour fits is then

$$p(C) = \frac{\sum_{s,\text{ fits}} e^{\beta J \sum_{\langle j,k\rangle} s_j s_k}}{\sum_s e^{\beta J \sum_{\langle j,k\rangle} s_j s_k}}. \tag{6.30}$$

We now come to an important observation: To each configuration $\tilde{s}$ of the nominator there is a configuration in the nominator s with energy

$$H(\tilde{s}) = 2Jl(C) + H(s), \tag{6.31}$$

which one gets by altering the sign of all spins in the inner of C. In this way, one also alters the interaction terms along the contour line from $-J$ to J, while all other contributions stay the same. This procedure amounts to a change of the interaction energy of $\pm JL(C)$. We can hence single out these terms in the above some, and write

$$p(C) = e^{-2\beta Jl(C)} \frac{\sum_{s,\text{ fits}} e^{\beta J \sum_{\langle j,k\rangle} s_j s_k}}{\sum_{s,\text{ fits}} e^{\beta J \sum_{\langle j,k\rangle} s_j s_k} + \text{further terms}} \leq e^{-2\beta Jl(C)}. \tag{6.32}$$

Here, we have used that the exponential function delivers always positive terms. Up to now, the problem is symmetric under an interchange of + and −. For every spin configuration, however, there is at least one spin that is not contained in a fitting contour. Also, according to our convention, no lines of different contours may cross each other and hence there must be at least one site that is not in the inner of a fitting contour. In case there are several spins for a given configuration that are not contained in a fitting contour, then these spins must have the same value: Otherwise, there would be a separating contour between them and one of the spins would be in the inner of this contour. That is to say, we can assign each spin configuration in this way a $+$ or a $-$, called the "outer spin". In this way, we have broken the symmetry between $+$ and $-$ and will from now on look at only configurations with outer spin $+$. We will now show that for small temperatures, these configurations will only have a few $-$ spins. We will therefore consider the quantity

$$N_-(s) = \#\{j : s_j = -1\}, \tag{6.33}$$

the number of spins that have in the configuration s the value $-$. Every $-$ spin has to be contained in a contour, since $+$ spins can only be outside of a contour. We can hence bound the number of $-$ spins by the sum of the areas of all fitting contours. Again the bound is very crude, since contours may be contained within another and hence, for an exact count, some areas have to be counted with a negative sign. But for our purposes, this bound will be tight enough. We get

$$N_-(s) \leq \sum_{C,\text{fits to } s} f(C) \leq \sum_{C,\text{fits to } s} l(C)^2. \tag{6.34}$$

We will now look at the canonical expectation value of N_-, only considering configurations with outer spin $+$. Again, by this we break the symmetry. We get

$$\begin{aligned} \langle N_- \rangle &\leq \frac{1}{2Z} \sum_{s,+} \left(\sum_{C,\text{fits to } s} l(C)^2 \right) e^{-\beta H(s)} \\ &= \frac{1}{2Z} \sum_{C} l(C)^2 \sum_{s,\text{fits to } C,+} e^{-\beta H(s)} \\ &= \sum_{C} l(C)^2 p(C). \end{aligned} \tag{6.35}$$

Remember that $p(C)$ is the probability that the contour C fits to a configuration. The factor $1/2$ is obtained since we only consider configurations with outer spin $+$. We now put in out bounds derived above and get

$$\begin{aligned}
\langle N_- \rangle &\leq \frac{1}{4}\sum_{C} l(C)^2 e^{-\beta J l(C)} \\
&= \frac{1}{4}\sum_{l} l^2 e^{-2\beta J l} n(j,L) \\
&\leq \frac{1}{3}(L+1)^2 \sum_{l=2}^{\infty} l^2 e^{-\beta J l} 3^l \\
&\leq \frac{1}{3}(L+1)^2 \sum_{l=0}^{\infty} l^2 (e^{-2\beta J} 3)^l . \qquad (6.36)
\end{aligned}$$

This sum is convergent if $3e^{-2\beta J} < 1$ or

$$\beta > \log(3)/(2J), \qquad (6.37)$$

as one can show by twice differentiating the geometric sum. In particular, the sum goes to 0 if $e^{-2\beta J}$ goes to 0, hence $\beta \to \infty$. For the probability that an arbitrary spin is in the state $-$, we get

$$\left\langle \frac{N_-}{L^2} \right\rangle_+ \to 0 \qquad (6.38)$$

for $\beta \to \infty$. Of course we can repeat the calculation with outer spin $-$. One gets in an analogous fashion that the number of $+$ spins is small. In particular, the expectation value for N_- (and of N_+) depends continuously of β, hence also at finite temperatures, with high probability one gets only configurations for which almost all spins take the same value, so either all $+$ or all $-$.

6.1.4 Classical mean field approaches

As we have already mentioned, in 2D the model can be exactly solved, and a closed form of the partition function is known. We will not get into the details of this Onsager solution, however, at this point. Instead, we will pursue a line of thought that gives rise to surprisingly accurate results, in particular for high-dimensional systems (there also is a good reason for that). In this subsection, we will have a look at mean field approaches. The mean field idea is a simple one: One considers each spin to be subject to a "mean field" generated by all of the neighboring ones. Of course, this mean field will again depend on the solution of the problem. The trick is that one takes this mean field as a parameter of the problem, solves the now uncoupled problem, and then asks for self-consistency. We will see how this goes by having another look at the Ising model.

We replace the Hamiltonian of the Ising model in arbitrary dimension (do no longer 1D or 2D) by

$$H(s) = -\frac{1}{2}\sum_j \nu J\langle s\rangle s_j - B\sum_j s_j, \tag{6.39}$$

where ν is the number of nearest-neighbors in the lattice (so the sites with $\mathrm{dist}(j,k) = 1$) and $\langle s\rangle = \langle s_j\rangle$ for each j is the average spin per site. That is, the Hamiltonian can be written as

$$H(s) = -\sum_j E(J,B)s_j, \tag{6.40}$$

where

$$E(J,B) := \frac{1}{2}\nu J\langle s\rangle + B. \tag{6.41}$$

As explained above, we have an uncoupled system, one that we can simply solve – at the expense that the expectation value $\langle s\rangle$ is contained in the expression, which must be determined in a self-consistent manner. The partition function can now be written as

$$Z = \left(\sum_{s_1=\pm 1} e^{\beta E(J,B)s_1}\right)^N = (2\cosh(\beta E))^N. \tag{6.42}$$

We have singled out here s_1, but could have taken any other spin as well, as we encounter a completely uncoupled problem. The free energy per site is then

$$f = -kT\lim_{N\to\infty}\left(\frac{1}{N}\log(Z)\right) = -kT\log(2\cosh(\beta E)) \tag{6.43}$$

The expected magnetization is then

$$\langle m\rangle = \frac{\sum_{s_1=\pm 1} s_1 e^{\beta E s_1}}{\sum_{s_1=\pm 1} e^{\beta E s_1}} = \tanh(\beta E) = \tanh\left(\beta(\frac{1}{2}\nu J\langle s\rangle + B)\right). \tag{6.44}$$

The magnetization is the order parameter for the spin lattice. If $B = 0$, then the magnetization will be zero for the high-temperature paramagnetic phase of the lattice. The spins are just randomly ordered. For low temperatures, in contrast, it will be non-zero when the spins have spontaneously aligned.

We will now determine the critical temperature at which the lattice starts to become ordered when the temperature is lowered. We start from the expression of $\langle s\rangle$ for the case of $B = 0$. We then get

$$\langle s\rangle = \tanh\left(\frac{1}{2}\beta\nu J\langle s\rangle\right) = \tanh\left(\frac{\nu J\langle s\rangle}{2kT}\right). \tag{6.45}$$

We now must solve this equation for $\langle s\rangle$. There are many ways of doing this. A particularly appealing way is to do it "graphically", and plots $\langle s\rangle \mapsto \langle s\rangle$ versus

$$\langle s\rangle \mapsto \tanh\left(\alpha\langle s\rangle\right), \tag{6.46}$$

calling

$$\alpha := \frac{\nu J}{2kT}. \tag{6.47}$$

The solution will then correspond to the intersections of the two graphs. Now there are two quite different regimes:

- For $\alpha < 1$ there is only one crossing point at $\langle s\rangle = 0$.
- For $\alpha > 1$ there are now three crossing points: One at $\langle s\rangle = 0$ and one each at $\langle s\rangle = \pm s_0$.

The free energy per site in various cases is

$$f = \left\{\begin{array}{cl} -kT\log(2), & \text{if } \langle s\rangle = 0, \\ -kT\log(2\cosh(\beta\nu J s_0/2)), & \text{if } \langle s\rangle = s_0. \end{array}\right. \tag{6.48}$$

Thus the values $\langle s\rangle = \pm s_0$ describe possible states of thermodynamic equilibrium situations since they minimize the free energy. The transition point (the critical point) is at $\alpha = 1$, and hence when

$$\nu J/(2kT) = 1. \tag{6.49}$$

The critical temperature is therefore

$$T_c = \nu J/(2k). \tag{6.50}$$

Mean field theory hence predicts a phase transition for a D-dimensional cubic lattice. This prediction is wrong in 1D, as we already know, and correct in 2D. It is expected to be good in case of a large number of neighbors, so for a large dimension. This indeed turns out to be true.

6.2 Quantum lattice models

We now turn to quantum lattice models. Again, the Hamiltonian is of the form

$$H = \sum_{j \in V} h_j + \sum_{\langle j,k \rangle} v_{j,k}, \tag{6.51}$$

but now both the on-site terms h_j as well as the nearest-neighbor couplings $v_{j,k}$ are operators with a small support. As mentioned before, quantum lattice models are ubiquitous in physics, in particular in the condensed matter context. We will only have time to have a look at some paradigmatic models.

6.2.1 Bose-Hubbard model and other quantum lattice models

Some of the most studied instances of quantum lattice models of the kind that we have in mind are the quantum versions and generalizations of the Ising model discussed in the last section. Here one has at each lattice site a $\mathbb{C}^2$-spin degree of freedom (or more generally, a higher spin, but let us not get into detail here). A prototypical and actually exactly solvable model of this sort is the XY model with a transverse magnetic field.

Hamilton operator of the XY model:

$$H = -\frac{1}{2} \sum_{j=1}^{n} \left(\frac{1+\gamma}{4} (\sigma_X)_j (\sigma_X)_{j+1} + \frac{1-\gamma}{4} (\sigma_Y)_j (\sigma_Y)_{j+1} \right) - \frac{\lambda}{2} \sum_{j=1}^{n} (\sigma_Z)_j. \tag{6.52}$$

Here, γ is the anisotropy parameter, and λ the external magnetic field.

For $\gamma = 1$, one indeed gets the quantum Ising model, so the natural quantum version of the classical Ising model. We will later have a glimpse at how this can be exactly solved. The Heisenberg model is another simple model of this kind which is frequently studied (but which is generally no longer exactly solvable),

$$H = -\frac{1}{2} \sum_{j=1}^{n} ((\sigma_X)_j (\sigma_X)_{j+1} + (\sigma_Y)_j (\sigma_Y)_{j+1} + (\sigma_Z)_j (\sigma_Z)_{j+1}) - \frac{\lambda}{2} \sum_{j=1}^{n} (\sigma_Z)_j. \tag{6.53}$$

Another important instance of a quantum lattice model of this kind is the Bose Hubbard model.

Hamilton operator of the Bose-Hubbard model: In one dimension, we have

$$H = -J \sum_{j=1}^{L} \left(b_j^\dagger b_{j+1} + b_{j+1}^\dagger b_j \right) + \frac{U}{2} \sum_{j=1}^{L} n_j (n_j - 1) - \mu \sum_{i=1}^{L} n_j, \quad (6.54)$$

with $n_i = b_j^\dagger b_j$.

Here, $\{b_j\}$ are the bosonic annihilation operators, on sites $1, \ldots, L$. U governs the on-site interaction, while J determines the strength of the tunneling, the "hopping" to a nearest neighbor.

6.2.2 Quantum phase transitions at zero temperature

6.2.3 Fermionic chains and phase transitions of second order

Chapter 7

Open systems and non-equilibrium

7.1 Open systems

7.2 Decoherence and emergence of classicality

7.3 Markovian open systems

7.4 Fluctuation theorems