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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 intertwining 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.

## 1.2 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 (1839-1903) 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 countless 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  $v_{z,\text{lid}}$  lead to

$$mv_z = mv'_z + Mv_{z,\text{lid}}, \quad (1.1)$$

$$\frac{1}{2}mv_z^2 = \frac{1}{2}mv_z'^2 + \frac{1}{2}Mv_{z,\text{lid}}^2, \quad (1.2)$$

where  $V$  is the velocity of the lid, which implies that

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

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

$$MV = 2mv_z. \quad (1.4)$$

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

$$F = \frac{N}{V}Am\langle v_z^2 \rangle. \quad (1.5)$$

The pressure is hence

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

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

$$p = \frac{c}{V}, \quad (1.7)$$

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 demon

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 demon 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 demon closes the gate. Surely this is not so easy, and requires a lot of knowledge of the precise situation at hand. The demon being a demon, this is a piece of cake for him. We assume that the demon knows exactly what he (are demons 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.

### 1.4.4 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 genuinely 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.