

A short overview of statistical thermodynamics

Our course will mostly concern the thermodynamic properties of polymeric systems (single polymer molecules which in many cases can be considered as systems large enough to apply thermodynamics to on a single molecule level), polymer solutions, polymer blends etc. The course is a bit short, and it may happen that we will not be able to touch some important topics concerning the systems' dynamics, e.g. the viscoelasticity of polymer melts and/or rubber-like materials. The level of difficulty we adopt is "as simple as possible but not simpler": in the cases when the result follows by a relatively straightforward calculation, this will be presented in detail; in the case a simple calculation delivers only a rough description, this will also be discussed in detail, and the results needing for a complicated theory will be simply told about.

The thermodynamical properties of polymer systems will follow from their statistical description on some intermediate level of coarse-graining, where the exact chemical structure of the molecules under investigation hardly plays a role, but the fact that these are long, flexible, complex molecules (not merely interacting point particles) is of importance.

In this first lecture we refresh some basics (or fundamentals) of statistical thermodynamics, being a universal theory of large and complex systems. The classical thermodynamics is a phenomenological theory (i.e. is based on formalization of our everyday experience and on immense amount of experimental observations), and starts from a few postulates, called Laws of Thermodynamics, and numbered from zeroth to the third. The corresponding systems within the thermodynamical description are described by a set of *state variables*, like volume, pressure, temperature, energy, etc. describing the system as a whole (i.e. being collective variables if the level of description taking into account single particles building the system is accepted).

The *zeroth law* postulates the existence of a specific state of a physical system called its thermodynamical equilibrium. Roughly speaking, equilibrium is the state the system adopts in the course of time when leaved to itself, without any action from the outside. Being at the state of equilibrium, the system does not leave it spontaneously. The two systems are at equilibrium with each other if their state does not change when these systems are brought into a contact with each other. If two systems are at equilibrium with some third one, they are also in equilibrium with each other. This property allows for the introduction of the first important non-mechanical quantity: the *temperature* (which will be always denoted by T). If two systems are at equilibrium, they definitely have the same temperature. While two systems with the same temperature may be at equilibrium with each other or not, the two systems at different temperatures cannot be at equilibrium: If these systems would be brought into contact, something will change until their temperatures would be equal to each other.

Each physical system is characterized by its most important physical quantity, the *energy*. The (internal) energy U of a thermodynamic system can be changed in two ways. First, one can perform the work on this system by changing its volume, switching on an electric field, etc. Second, the energy can be changed

by cooling or heating the system. This means that the energy can be transferred from the exterior to the system in the form of work or heat. An infinitesimal change of energy dU of the system is thus

$$dU = \delta A + \delta Q$$

with δA being the performed work, and δQ the transferred heat. The difference between the exact differential d and an infinitesimal change δ stresses the fact that U is the property of the system fully determined by its state variables, while the work A and the heat Q depend on the process which is performed with the system, i.e. on how exactly the *protocol* of changes look like, is it performed slowly or fast, etc. The equation above is a differential formulation of the *first law* of thermodynamics, which is simply a law of energy conservation.

Now imagine, a system is prepared out of equilibrium, and we wait until it equilibrates. How do we know that it does? There exists a universal state variable, the *entropy* S , which possesses the following property: It continuously grows as long as the system is evolving to its equilibrium state, and reaches its maximum when the system is at equilibrium. This means that for a system let to itself (isolated)

$$dS \geq 0.$$

This is one of the formulations for the *second law* of thermodynamics. If the system is not isolated, and the heat transfer is possible one always has

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

The equality sign here corresponds to slow, quasistatic processes, in which the system is in some equilibrium state at any time. In this case the infinitesimal heat can be expressed via the change of the state variable S : $\delta Q = TdS$.

The *third law* governs the behavior of the entropy at extremely low temperatures and states that at $T = 0$ the entropy vanishes, $S = 0$.

The state variables at equilibrium can be subdivided into two classes: the intensive and the extensive ones. The extensive variables are proportional to the system size; if two systems are brought together, the *extensive variable* characterizing the composite will be the sum of the extensive variables of its parts: thus the volume, the number of particles, but also the entropy and energy are extensive. On the contrary, the temperature or the pressure in each part of the system are the same. Temperature and pressure are *intensive variables*.

The infinitesimal work δA can also be expressed via differential form in changes of the state variables of the system. If this work is of mechanical nature (as it will be mostly be in this course), i.e. the work performed by some mechanical force $f(x)$, we know that $A = \int_{x_1}^{x_2} f(x)dx$, and therefore

$$\delta A = f dx.$$

Here we have to define, whether the force we exert on the system or the force the system exerts is counted: they differ by sign. The energy of the system may grow if we exert the force and the system resists (consider an example of a spring), in this case we will consider the work positive.

If we consider a fluid system, the force acting on it is defined by the pressure, to increase the energy of the system we have to work against this force, i.e. decrease the system's volume, the corresponding work differential is

$$\delta A = -pdV$$

One can also change the energy of the system adding or removing particles. If the energy change per particle added is μ , the corresponding change is equal to μdN . The intensive property μ of the system is called its *chemical potential*.

Using the differential form of the first law together with heat and work differentials at equilibrium gives us the Gibbs' fundamental equation

$$dU = -pdV + \mu dN + \dots + TdS.$$

This describes the change of the internal energy of the system when the volume, number of particles, etc., and the entropy of the system are changed. These state variables are called the *natural variables* of the internal energy which therefore is a function $U = U(V, N, \dots, S)$. All natural variables of the internal energy are extensive ones. In a fluid single-component system $U = U(V, N, S)$ if we are not interested in electric or magnetic effects, so that $dU = -pdV + \mu dN + TdS$.

It is important to note that the form simplifies if some natural variable is kept fixed, thus, if $V = \text{const}$ (isochoric process) no mechanical work is performed, and only the two terms stay in the last form, if $S = \text{const}$ (adiabatic, or isentropic process) only the first two stay, etc.

The Gibbs' fundamental equation shows that if the internal energy as a function of its natural variables is known, the intensive variables of states can be obtained by taking its derivatives:

$$p = -\frac{\partial U}{\partial V}, \quad \mu = \frac{\partial U}{\partial N}, \quad \dots, \quad T = \frac{\partial U}{\partial S}.$$

Many experiments are performed at isothermal conditions, i.e. the temperature is well-controlled and kept constant. To describe such cases it is nicer to use a *thermodynamic potential* other than the internal energy, the one with temperature as a natural variable. Such a thermodynamic potential is called the *free energy* and is given by

$$F = U - TS.$$

It is easy to check (by building a differential) that

$$dF = -pdV + \mu dN + \dots - SdT,$$

so that

$$p = -\frac{\partial F}{\partial V}, \quad \mu = \frac{\partial F}{\partial N}, \quad \dots, \quad S = -\frac{\partial F}{\partial T}.$$

From the properties of the internal energy and of the entropy it follows that at equilibrium the free energy reaches its *minimum*.

The thermodynamic state of a system is defined uniquely by the values of the corresponding state variables. While the physical meaning of the volume, number of particles, etc. is clear, the entropy needs some interpretation. Such interpretation is given within *statistical physics*. Let us imagine that state variables are fixed and the thermodynamic state of the system (called in statistical physics its *macrostate*) is well-defined. We can assume that all such variables are the functions of positions and velocities of particles the system consists of. We have however fixed only a couple of collective variables, and an immense number of mechanical variables defining the microstate are undefined: a single macrostate is realized by many microstates of the system. The entropy of the system in a given macrostate is then connected with the number W of microstates corresponding to the macrostate under consideration,

$$S = k_B \ln W \quad (1)$$

with $k_B = 1.38 \cdot 10^{-23}$ J/K being the Boltzmann constant. The full (and relatively simple) description of the situation can be given on the quantum level, which explains the appearance of the Planck's constant in many quantitative equations even on the classical level; if we don't want to know the full truth, we can consider the situation on a purely classical level using coarse-graining. Here we have to abandon the idea to calculate W exactly. We can however introduce some (relatively arbitrary) raster according to which different microstates are distinguished, and count how many different states the system does have, and how this number changes if the external conditions change.

In many *model* systems (called athermal in the slang of polymer physics) in a relevant domain of parameters the mechanical energy in a microstate does not change considerably with the system's configuration. The total kinetic energy in a classical system is anyhow a function of temperature only, and therefore for such systems one can assume

$$F = \text{const} - TS \quad (2)$$

where in calculating S only the number of different spatial arrangements of particles has to be estimated (leading to the so-called configurational entropy). An example of such an athermal system is an ideal gas. The particles in the ideal gas don't interact, that means in our model they don't feel each other's presence at all.

To assess S we can subdivide the whole (three-dimensional) space into small cubic cells with side a , for a system of volume V the number of such cells will be $M = V/a^3$. How many configurations do exist which correspond to different arrangements of N particles among these M cells? Each particle has exactly M possibilities to be placed in one of the cells. These possibilities are simply combined: if one particle has M possibilities, for two particles there are M^2 , and for N particles these are M^N such possibilities. If the particles are indistinguishable, we have to divide this result by $N! = N(N-1)(N-2) \dots 1$ (to be

discussed later), but now this indistinguishability does not play any role (it will be absorbed in the additive constant).

Now let us take our Eq.(1), calculate $S = k_B \ln M^N = k_B N \ln M = k_B N (\ln V - 3 \ln a)$, and insert this in our Eq.(2):

$$F = \frac{\text{const} + 3k_B N T \ln a}{\text{const}} - k_B T N \ln V.$$

Now we can obtain the equation of state of the ideal gas using the relation $p = -\partial F / \partial V$ and get

$$p = \frac{k_B T N}{V},$$

the one you have definitely learn about at school.

Now we know *how* the method works. To understand, *why* it works, one has to learn statistical physics, unfortunately not the topic of this course. It is important to know, that the corresponding force (pressure) is, within the approach adopted, mathematically fully due to the configurational entropy; therefore the corresponding force is called an *entropic force*. A characteristic feature of all entropic forces is the fact that the force is proportional to temperature.

Now let us consider a more complicated example, the so-called lattice gas model. This is used to describe the molecular repulsion in real gases; within this simple model particles are considered as small solid bodies characterized by some *excluded volume*, which is impenetrable for other particles. This model is also athermal. To describe this situation we can also use a lattice model, now it is reasonable to take a equal to the particle size, and assume that each cell can be only occupied by a single particle. A discussion of the number of configurations shows that the first particle can occupy each of M cells, the second one each of the free $M - 1$ cells, the third one each of the still free $M - 2$, so that

$$W = M(M - 1)(M - 2) \dots (M - N + 1) = \frac{M!}{N!}.$$

It is important to note that what we count is the number of physically different configurations of the system. Let us for example consider a situation with 3 possible positions and exactly one particle. There are three physically different configurations:

X O O

O X O

O O X

where X denotes the particle and O the empty place. On the other hand the expression above gives us $W = 6$ possibilities. These differ by the numbering of the empty places. Physically these empty cells *have* to be considered as indistinguishable (the physical situation does not depend on how they are numbered). Therefore it is necessary to divide the result by the factorial of the number of "holes". This leads to the expression we will continuously use for different models:

$$W = \frac{M!}{N! (M - N)!}$$

To understand this expression we mention that there are exactly $M!$ different ways to number the cells; $N!$ ways to number the occupied cells and $(M - N)!$ ways to number the empty cells. The number of physically different situations is the total number of possibilities divided by the corresponding number of possibilities which cannot be distinguished (this we will train in our first tutorial).

Thus, the entropy of the lattice gas is

$$S = k_B \ln W = k_B (\ln M! - \ln N! - \ln(M - N)!)$$

Now we will derive a simple approximation for the logarithm of a factorial, $\ln N!$. Let us consider $\ln N! = \ln 1 + \ln 2 + \dots + \ln N$. Using the definition of the Riemann's integral sum, we can approximate the sum by the integral:

$$\sum_{n=1}^N \ln n \approx \int_1^N \ln n \, dn$$

where (in the last expression) n is now considered as a continuous variable. The corresponding integral can be explicitly calculated: $\int \ln x \, dx = x \ln x - x$ and therefore

$$\sum_{n=1}^N \ln n \approx N \ln N - N + 1.$$

For $N \gg 1$ we can use the approximation $\ln N! \approx N \ln N - N$. There exists a much better approximation, the Stirling formula, which will be continuously used during the whole course:

$$\ln N! = \left(N + \frac{1}{2}\right) \ln N - N + \ln(\sqrt{2\pi}).$$

The difference with our simple approximation is the appearance of the additional term $\ln N/2$ and of $\ln(\sqrt{2\pi}) \approx 0.919$ instead of unity in the term which does not depend on N .

Using our simple approximation $\ln N! \approx N \ln N - N + 1$ (and neglecting last contribution as small compared to N -dependent ones) we get

$$\begin{aligned} S &= k_B (M \ln M - M - N \ln N + N - (M - N) \ln(M - N) + M - N) \\ &= k_B (M \ln M - N \ln N - (M - N) \ln(M - N)), \end{aligned}$$

and use it in our $F = -TS$ expression. We can moreover take $M = V/a^3$, and calculate the free energy as a function of the volume, particle number and temperature, and then, say, obtain the pressure of this model of the hard-core gas. Let us denote $\Phi = N/M$ the volume fraction occupied by the molecules, and rewrite everything using this volume fraction. We get: $N = \Phi M$, $M - N = (1 - \Phi)M$ and therefore

$$\begin{aligned} F &= -k_B T M [\ln M - \Phi (\ln \Phi + \ln M) - (1 - \Phi) (\ln(1 - \Phi) + \ln M)] \\ &= k_B T M [\Phi \ln \Phi + (1 - \Phi) \ln(1 - \Phi)]. \end{aligned}$$

Getting the pressure, and investigating its limiting behavior for a rarified gas and for very dense one is now left for a tutorial.