

Partition function

In physics, a partition function describes the statistical properties of a system in thermodynamic equilibrium. Partition functions are functions of the thermodynamic state variables, such as the temperature and volume. Most of the aggregate thermodynamic variables of the system, such as the total energy, free energy, entropy, and pressure, can be expressed in terms of the partition function or its derivatives. The partition function is dimensionless, it is a pure number. Each partition function is constructed to represent a particular statistical ensemble (which, in turn, corresponds to a particular free energy). The most common statistical ensembles have named partition functions. The canonical partition function applies to a canonical ensemble, in which the system is allowed to exchange heat with the environment at fixed temperature, volume, and number of particles. The grand canonical partition function applies to a grand canonical ensemble, in which the system can exchange both heat and particles with the environment, at fixed temperature, volume, and chemical potential.

It may not be obvious why the partition function, as we have defined it above, is an important quantity. First, consider what goes into it. The partition function is a function of the temperature T and the microstate energies E_1, E_2, E_3 , etc. The microstate energies are determined by other thermodynamic variables, such as the number of particles and the volume, as well as microscopic quantities like the mass of the constituent particles. This dependence on microscopic variables is the central point of statistical mechanics. With a model of the microscopic constituents of a system, one can calculate the microstate energies, and thus the partition function, which will then allow us to calculate all the other thermodynamic properties of the system.

The partition function can be related to thermodynamic properties because it has a very important statistical meaning. The probability P_s that the system occupies microstate s is

$$P_s = 1/Z e^{-\beta E_s}$$

Thus, as shown above, the partition function plays the role of a normalizing constant (note that it does *not* depend on s), ensuring that the probabilities sum up to one:

$$\sum P_s = \sum 1/Z e^{-\beta E_s} = 1/Z \times Z = 1$$

This is the reason for calling Z the "partition function": it encodes how the probabilities are partitioned among the different microstates, based on their individual energies. The letter Z stands for the German word *Zustandssumme*, "sum over states". The usefulness of the partition function stems from the fact that it can be used to relate macroscopic thermodynamic quantities to the microscopic details of a system through the derivatives of its partition function. Finding the partition function is also equivalent to performing a Laplace transform of the density of states function from the energy domain to the β domain, and the inverse Laplace transform of the partition function reclaims the state density function of energies.

4. Two-level systems

4.1 Introduction

Two-level systems, that is systems with essentially only two energy levels are important kind of systems, as at low enough temperatures, only the two lowest energy levels will be involved. Especially important are solids where each atom has two levels with different energies depending on whether the electron of the atom has spin up or down.

We consider a set of N distinguishable "atoms" each with two energy levels. The atoms in a solid are of course identical but we can distinguish them, as they are located in fixed places in the crystal lattice. The energy of these two levels are ε_0 and ε_1 . It is easy to write down the partition function for an atom

$$Z = e^{-\varepsilon_0/k_B T} + e^{-\varepsilon_1/k_B T} = e^{-\varepsilon_0/k_B T} (1 + e^{-\varepsilon/k_B T}) = Z_0 \cdot Z_{term}$$

where ε is the energy difference between the two levels. We have written the partition sum as a product of a zero-point factor and a "thermal" factor. This is handy as in most physical connections we will have the logarithm of the partition sum and we will then get a sum of two terms: one giving the zero-point contribution, the other giving the thermal contribution.

At thermal dynamical equilibrium we then have the occupation numbers in the two levels

$$n_0 = \frac{N}{Z} e^{-\varepsilon_0/k_B T} = \frac{N}{1 + e^{-\varepsilon/k_B T}}$$

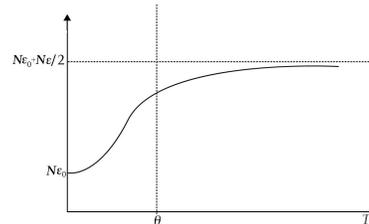
$$n_1 = \frac{N}{Z} e^{-\varepsilon_1/k_B T} = \frac{N e^{-\varepsilon/k_B T}}{1 + e^{-\varepsilon/k_B T}}$$

We see that at very low temperatures almost all the particles are in the ground state while at high temperatures there is essentially the *same* number of particles in the two levels. The transition between these two extreme situations occurs very roughly when $k_B T \approx \varepsilon$ or $T \approx \theta = \varepsilon/k_B$, the so-called *scale temperature* θ that is an important quantity.

In this case we can directly write down the internal energy

$$E = n_0 \varepsilon_0 + n_1 \varepsilon_1 = N \frac{\varepsilon_0 e^{-\varepsilon_0/k_B T} + \varepsilon_1 e^{-\varepsilon_1/k_B T}}{e^{-\varepsilon_0/k_B T} + e^{-\varepsilon_1/k_B T}} = N \varepsilon_0 + \frac{N \varepsilon e^{-\theta/T}}{1 + e^{-\theta/T}}$$

The internal energy is a monotonous increasing function of temperature that starts from $E(0) = N \varepsilon_0$ and asymptotically approaches $E(0) + N \varepsilon / 2$ at high temperatures.



Exercise. Compute the internal energy by using the formula $E = -N \frac{\partial \ln Z}{\partial \beta}$ and check that you get the same result as above.

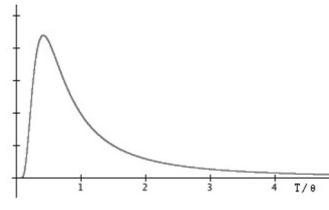
When we now know the internal energy as a function of temperature we can easily compute the heat capacity of the system as a function of temperature.

Exercise: Use the graph above to make a sketch of how the heat capacity depends on temperature.

We have

$$c = \frac{dE}{dT} = Nk_B \frac{(\theta/T)^2 e^{-\theta/T}}{(1 + e^{-\theta/T})^2}$$

The result is somewhat unexpected. The heat capacity has a maximum of order Nk_B at a temperature that is approximately the scale temperature (more precisely for $T \approx 0.417 \cdot \theta$). At low temperatures the heat capacity approaches zero quite fast, like $T^{-2}e^{-\theta/T}$. At high temperatures the heat capacity also goes to zero like T^{-2} . This behaviour is typical for a two-level system and is called a *Schottky anomaly*. That the heat capacity goes to zero as the temperature goes to zero is universal for any system. As we have seen this is required unless the entropy becomes singular (infinite).



We can understand the heat capacity curve by qualitative reasoning. At low temperatures the distance between the energy levels is so large that it is very difficult to excite thermally the particles from the ground state, this implies a small heat capacity. As the temperature then approaches the scale temperature it is easy to excite the particles and you get a large heat capacity. At higher temperatures we have essentially the same number of particles in the levels and that situation does not change very much as we increase the temperature. This means that the system does not increase very much its internal energy when the temperature increases: the heat capacity will be small again.

We could now compute the entropy from

$$S = Nk_B \ln Z + E/T$$

but instead we will use another method that further on will be quite useful.

Suppose that we study the internal energy $E = E(S, V, N)$. For the differential we have

$$dE = TdS - pdV + \mu dN$$

The internal energy is a function of the entropy, a quantity that is difficult to measure. We would like to change the functional dependence to for instance temperature T . We write

$$\begin{aligned} dE &= TdS + SdT - SdT - pdV + \mu dN = \\ &= d(TS) - SdT - pdV + \mu dN \end{aligned}$$

Move the TS -term to the left side

$$d(E - TS) = -SdT - pdV + \mu dN$$

Introduce a new function of state for energy, $F = E - TS$, for which we evidently have

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

something that tells us that $F = F(T, V, N)$, all variables are now easily measurable quantities. The function F is called *Helmholtz' free energy*.

But we have also

$$dF = \frac{\partial F}{\partial T} dT + \frac{\partial F}{\partial V} dV + \frac{\partial F}{\partial N} dN$$

If we identify terms we get

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

We can now rewrite

$$S = Nk_B \ln Z + E/T \quad \Rightarrow \quad F = E - TS = -Nk_B T \ln Z$$

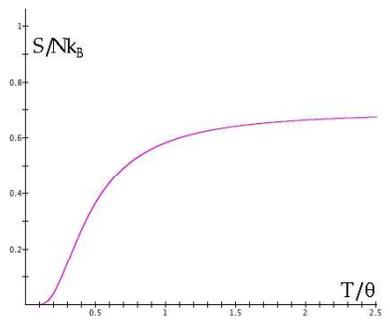
Inserting the expression for Z we get

$$F = N\epsilon_0 + Nk_B T \ln(1 + e^{-\theta/T})$$

that after derivation with respect to temperature gives

$$S = -\frac{\partial F}{\partial T} = Nk_B \left[\ln(1 + e^{-\theta/T}) + \frac{(\theta/T)e^{-\theta/T}}{1 + e^{-\theta/T}} \right]$$

The entropy goes to zero for small temperatures, as it should, at absolute zero the system has no degrees of freedom (only one possible microstate). At high temperatures the entropy approaches the $S = Nk_B \ln 2$ something that is easy to see is correct.



Exercise. Why is this limit correct?

*4.2. Interlude

In chemistry we are often interested in having a function of state for the energy that depends on pressure instead of volume. In chemical reactions the pressure is normally constant. This is easily fixed:

$$\begin{aligned}dF &= -SdT - pdV + \mu dN = \\ &= -SdT - pdV - Vdp + Vdp + \mu dN = \\ &= -SdT - d(pV) + Vdp + \mu dN\end{aligned}$$

This gives

$$dG = d(F + pV) = -SdT + Vdp + \mu dN$$

with a new function of state

$$G = G(T, p, N) = F + pV = E - TS + pV, \text{ Gibb's energy.}$$

For this function we have the partial derivatives

$$\frac{\partial G}{\partial T} = -S \quad \frac{\partial G}{\partial p} = V \quad \frac{\partial G}{\partial N} = \mu$$

Another function of state that is used in chemistry is the *enthalpy*, H . We start from

$$\begin{aligned}dE &= TdS - pdV + \mu dN = TdS - pdV - Vdp + Vdp + \mu dN = \\ &= TdS - d(pV) + Vdp + \mu dN\end{aligned}$$

This implies

$$dH = d(E + pV) = TdS + Vdp + \mu dN$$

with

$$\begin{aligned}\frac{\partial H}{\partial S} &= T \quad \frac{\partial H}{\partial p} = V \quad \frac{\partial H}{\partial N} = \mu \\ H &= H(S, p, N)\end{aligned}$$

These transformations to get a suitable function of state are called *canonical transformations*.

4.3. Magnetic solids

The electron has spin 1/2 that gives it a magnetic moment z-component μ . The electron behaves as a small magnet. You can also have a magnetic moment because of the orbital movement of the electron in the atom. Finally you can also have a magnetic moment due to a spinning nucleus. The electron spin and the orbital movement result in a magnetic moment of order the *Bohr magneton*

$$\mu_B = \frac{e\hbar}{2m} \approx 0.93 \cdot 10^{-23} \text{ J/T}$$

The magnetic moment of the nucleus is of order the *nuclear magneton*

$$\mu_N = \frac{e\hbar}{2M_p} \approx 5.05 \cdot 10^{-27} \text{ J/T}$$

If we put an atom or nucleus that has a magnetic moment in a magnetic field in the z direction (or rather define the direction of the magnetic field as the z -axis) one of the two (essentially degenerate) energy levels to be displaced upwards by μB , the other one is displaced downwards by μB . The energy difference between the levels is then $2\mu B$. We use the results from our two-level model. We want each atom to be essentially independent of the others such that it is not influenced by the magnetic moment of its neighbours. We have this situation in *paramagnetic* solids.

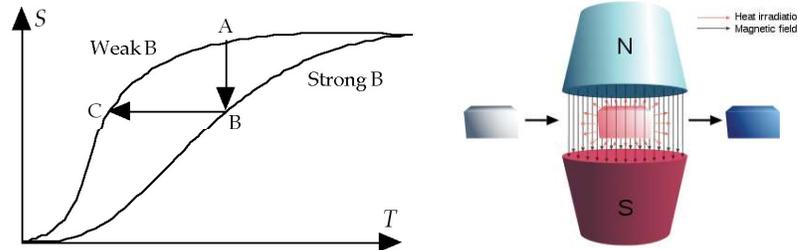
The scale temperature is $\theta = 2\mu B / k_B$. We observe the following:

1. The thermal properties only depend on the quantity θ/T , or for a given magnetic field on the ratio B/T .
2. If we insert numerical values and assume that $B \approx 1 \text{ T}$, the scale temperature will be of order a few Kelvins for an electron-spin system and a few milliKelvin for nuclear-spin system. At these low temperatures the thermal properties of the system is almost entirely determined by the two-level system.

4.4 Cooling by adiabatic demagnetisation

An interesting application that exploits the properties of a paramagnetic solid is cooling by adiabatic demagnetisation. We will now describe this process.

The paramagnetic solid is put in good thermal contact with a cooling medium, most often liquid helium. A strong magnetic field is applied. This increases the gap between the energy levels and forces the spins to line up in the direction of the magnetic field that means that the electrons occupy the ground state. This in turn means that the paramagnetic solid rids itself of energy that is taken up by the cooling medium. We now isolate thermally the paramagnetic solid and then let the magnetic field go to zero. We will then have a situation where the major part of the electrons occupy the lower energy level, the ground state. As we have now removed the magnetic field, the higher energy level is very close to the ground level but contains very few electrons. This corresponds to a very low temperature. We can also interpret what is happening by studying how the entropy depends on temperature.



The two curves describe precisely the same mathematical function but have different scale temperatures, as they are proportional to the strength of the magnetic field. The path from A to B corresponds to an increase in the strength of the magnetic field while keeping the temperature constant. The path B to C corresponds to an adiabatic decrease (no change in entropy $dQ =$

0) of the magnetic field but now with the system isolated from the outside world. This means that we change the scale temperature back to what it was before but move along a line parallel to the T axis. The entropy curves are universal functions meaning that

$$S_C(\theta_C/T_C) = S_B(\theta_B/T_B) \Rightarrow \theta_C/T_C = \theta_B/T_B \Rightarrow B_C/T_C = B_B/T_B$$

or

$$T_C = T_B \frac{B_C}{B_B}$$

The final temperature depends on how small the magnetic interaction B_C is from neighbouring atoms. For electron-spin systems you can, using this method, reach temperatures as low as 1 mK, for nuclear-spin system the final temperature can reach 0.1 μ K.

4.5. The magnetisation

The magnetisation M is the net sum of all magnetic moment. We have

$$M = n_0 \cdot \mu + n_1 \cdot (-\mu) = \mu N \frac{e^{-\epsilon_0/k_B T} - e^{-\epsilon_1/k_B T}}{e^{-\epsilon_0/k_B T} + e^{-\epsilon_1/k_B T}} =$$

$$\mu N \frac{e^{\mu B/k_B T} - e^{-\mu B/k_B T}}{e^{\mu B/k_B T} + e^{-\mu B/k_B T}} = N \mu \tanh \frac{\mu B}{k_B T}$$

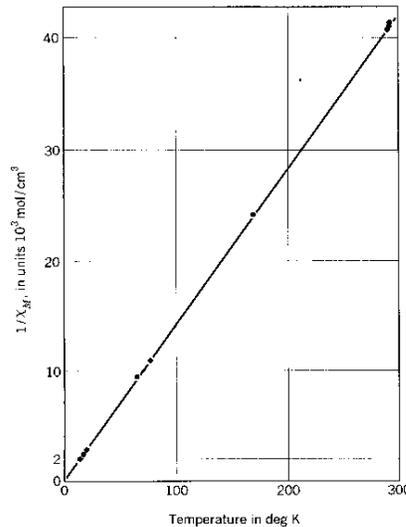
For large values of $\frac{\mu B}{k_B T}$, (B large or T small) the magnetisation saturates to $M = N\mu$ when all magnetic moments have lined up along the external

magnetic field. For small values of $\frac{\mu B}{k_B T}$

we can use a Taylor expansion of the hyperbolic function and get

$$M \approx N \mu \frac{\mu B}{k_B T}$$

In this approximation the magnetisation is inversely proportional temperature. This is *Curie's law* that agrees very well with experiment, see the diagram.



to

We can use measurements of the magnetisation as a thermometer! For electronic systems we can then measure temperatures down to about 10 mK when the magnetic field from internal interactions interfere and also the Taylor expansion requires more terms. Instead we can then use a nuclear-spin system and measure somewhat lower temperatures. For really low temperatures we can measure the energy split between the energy levels using the method of nuclear magnetic resonance (NMR). We then apply a radio frequency to the system with frequency f and use the resonance condition $hf = 2\mu B$ to select the relevant energy levels. The strength of the

NMR signal will be proportional to the difference in occupation number of the levels, which in turn is proportional $1/T$.

4.6 Localised one-dimensional harmonic oscillators

From quantum mechanics we have that the energy levels of a harmonic oscillator are given by

$$\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \dots$$

We can now easily write down the partition function

$$Z = \sum_n e^{-\varepsilon_n/k_B T} = \sum_n e^{-(n+\frac{1}{2})\hbar\omega/k_B T} = \sum_n e^{-(n+\frac{1}{2})\theta/T} = e^{-\frac{1}{2}\theta/T} \sum_n e^{-(n+\frac{1}{2})\theta/T} = Z_0 \cdot Z_{term}$$

where we have introduced the scale temperature $\theta = \hbar\omega/k_B$.

In this case we can explicitly sum the partition function, it is a geometrical series.

$$Z = \sum_n e^{-(n+\frac{1}{2})\theta/T} = e^{-\theta/2T} \sum_n e^{-n\theta/T} = e^{-\theta/2T} \left(1 + e^{-\theta/T} + e^{-2\theta/T} + \dots\right) = \frac{e^{-\theta/2T}}{1 - e^{-\theta/T}} = \frac{1}{e^{\theta/2T} - 1}$$

The internal energy is

$$E = -N \frac{\partial \ln Z}{\partial \beta} = \frac{1}{2} N \hbar \omega + \frac{N \hbar \omega}{e^{\hbar\omega/k_B T} - 1} = \frac{1}{2} N k_B \theta + \frac{N k_B \theta}{e^{\theta/T} - 1}$$

The first term is the zero-point energy. At high temperatures the internal energy is

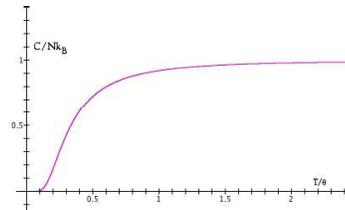
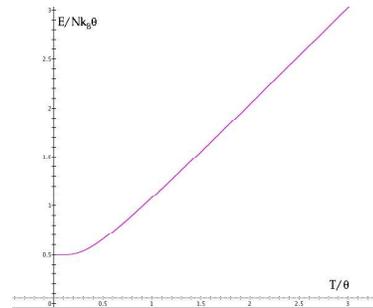
$$E = N k_B T$$

a result that we derived in an earlier chapter by counting the number of quadratic terms in the expression for the total energy. However, the quantum mechanical model also gives the behaviour at low temperature.

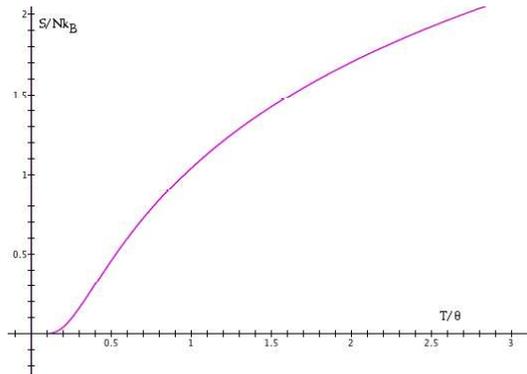
The heat capacity is $C = \frac{dE}{dT} = N k_B \frac{(\theta/T)^2 e^{\theta/T}}{(e^{\theta/T} - 1)^2}$.

It starts from zero at $T = 0$ and saturates as expected for high temperatures at $N k_B$. Again quantum mechanics describes correctly the behaviour at low temperatures. We can see the need for a quantum mechanical description as for low temperatures both the internal energy and the heat capacity contain Planck's constant.

We can finally compute the entropy from $S = -\frac{\partial F}{\partial T}$ where $F = -N k_B T \ln Z$.



Exercise. Show that $S = Nk_B \left[\ln \frac{e^{\theta/T}}{e^{\theta/T} - 1} + \frac{\theta/T}{e^{\theta/T} - 1} \right]$

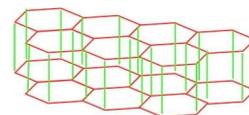


Exercise. Show that $S \rightarrow 0$ when $T \rightarrow 0$ and $S \rightarrow Nk_B \ln \frac{T}{\theta} = Nk_B \ln \frac{k_B T}{\hbar \omega}$ when $T \rightarrow \infty$.

Note that also in the high temperature limit the entropy contains Planck's constant. Entropy is fundamentally a quantum mechanical quantity. On the other hand the energy and heat capacity can be described classically at high temperatures.

Albert Einstein used the above model with one-dimensional harmonic oscillators in the so-called *Einstein model* to explain the properties of solids at low temperatures. The model is qualitatively correct but with closer comparison with experiment it has the wrong temperature dependence. Experiments show that the heat capacity at low temperatures must be proportional to T^3 . We will in a later chapter present the *Debye model* that has a correct T dependence. However, we can already now explain that small heat capacities of graphite and diamond. As we have seen, the scale temperature determines the transition between the quantum mechanical and classical regions in temperature, in this case $\theta = \hbar \omega / k_B$. For a harmonic oscillator we have that the frequency $\omega = \sqrt{k/m}$ where k is the spring constant of the force between the atoms in the solid. Diamond is a *very* hard solid, thus we can expect that the spring constants in diamond are very large. This implies that the scale temperature is high, about 500 K for diamond. This means that the heat capacity is quite far away from its asymptotic value at room temperature and that the heat capacity is much below the classical Dulong-Petit value.

Even more interesting is the situation with graphite. The molecular structure of graphite is such that it consists of layers of carbon atoms with each layer being a very rigid hexagonal lattice. These layers are stacked on top of each other and quite loosely connected. This is one of the reasons for graphite being used in pencils; the layers are easily ripped off and get attached to the paper. This is also the reason for graphite being used as a lubricant, the different layers in the graphite can slide relative one another with little friction. This structure means that the chemical bindings (the spring constants) are strong in two dimensions, in the hexagonal layer, and weak between these layers. We then have two different scale temperatures, a high



one for vibrations in the layer and a low one for vibrations between the layers. Actually only the vibrations between the layers are activated at room temperature. When we count quadratic terms in the total energy we should only count these latter vibrations. This implies that the number of quadratic vibration terms only is 1/3 of the number in a solid where the vibrations can happen in three dimensions and the heat capacity thus only becomes 1/3 of the normal, something that agrees perfectly with experiment.

4.7. A note about the partition function for systems with degenerate energy levels

We have earlier noted that we should sum over all possible states in the partition function. This means that if an energy level is degenerate it has to be counted several times, as many times as the degeneracy or the *multiplicity* of the degeneration. Mathematically we write this

$$Z = \sum_i g_i e^{-\epsilon_i / k_B T}$$

where g_i is the multiplicity of energy level i . We will use this way of writing very often when we in the next chapter will treat the statistical description of gases where we will use so-called group distributions.

Exercise problems. Chapter 4

1. Compute the internal energy of a two-level system using $E = -N \frac{\partial \ln Z}{\partial \beta}$ and check that you get the same result as we got in the lecture.
2. Assume that we could have a stable equilibrium for a two-level system where we had more particles in the upper level than in the lower one. What can you say about the temperature of such a system? In reality such systems are not stable but can be realised quasi-stably in for instance a laser by pumping particles to the upper level using external energy. Such systems are said to have an inverted population.
3. Compute the internal energy and heat capacity for a system with one non-degenerate level with energy 0, two degenerate levels with energy ϵ and one nondegenerate level with energy 2ϵ . *Hint:* Chose a suitable zero-point energy.
4. Below what temperature do you have deviations that are larger than 5% from Curie's law in an ideal electronic spin 1/2 system?
5. Magnetisation of Pt nuclei is often used as a thermometer for low temperatures. The external magnetic field is 10 mT and the magnetic moment of a Pt nucleus is 0.60 nuclear magnetons. Estimate the usable temperature interval of the thermometer if we assume a) that a magnetisation less than 1/10 000 of the maximal one cannot be measured with precision and b) that deviations from Curie's law that are larger than 5% are unacceptable. Assume that we use NMR technique to detect the split in the energy levels. What is in this case the NMR frequency?