

Quantum microcanonical ensemble

1 Macrostate vs. microstates

To make things easier, let us use a generic example here as well. It will turn out that an ideal gas is too difficult to treat in the microcanonical ensemble formalism (I will show why a bit later on) and we will have to postpone that until we learn the grand-canonical formalism – there, the ideal gas can be studied quite easily. For the time being, we will choose an even simpler model: a lattice of two-level systems (TLS). Each TLS has only two eigenstates, namely a ground-state of energy $\epsilon_{gs} = -\epsilon_0$ and an excited state with energy $\epsilon_{exc} = +\epsilon_0$ (we can shift these values around if we want to, but it will not make any real difference). One possible realization of such a TLS is a spin- $\frac{1}{2}$ placed in a magnetic field. As you know (see short primer at the end, if the next few equations look totally unfamiliar), a spin $1/2$ has two eigenstates, $|\frac{1}{2}, \frac{1}{2}\rangle$ and $|\frac{1}{2}, -\frac{1}{2}\rangle$ – I’m using the usual $|S, m_z\rangle$, $m_z = -S, -S + 1, \dots, S - 1, S$ notation. In this basis

$$\vec{S}^2|S, m_z\rangle = \hbar^2 S(S + 1)|S, m_z\rangle; \hat{S}_z|S, m_z\rangle = \hbar m_z|S, m_z\rangle$$

i.e. when in this state, the total spin has magnitude $\hbar\sqrt{S(S + 1)}$ and its projection on the z-axis has magnitude $\hbar m_z$.

If a spin is placed in an external magnetic field \vec{B} , they interact as described by the Zeeman Hamiltonian:

$$\hat{h} = -\frac{g\mu_B}{\hbar}\vec{S} \cdot \vec{B} = -\frac{g\mu_B}{\hbar}\hat{S}_z B$$

if we choose $Oz \parallel \vec{B}$. g is the Landé factor, equal to about 2 for an electron in vacuum, and μ_B is the Bohr magneton. The eigenstates of this Hamiltonian are the eigenstates of \hat{S}_z , and the eigenvalues will be $\epsilon_{gs} = -\epsilon_0 = -g\mu_B B/2$ for $|\frac{1}{2}, \frac{1}{2}\rangle$ and $\epsilon_{exc} = \epsilon_0 = g\mu_B B/2$ for $|\frac{1}{2}, -\frac{1}{2}\rangle$. By changing the value of B , we can “tune” the value of the splitting $2\epsilon_0 = g\mu_B B$.

Our system will be a lattice of N such TLS, which do not interact with one another. Therefore, its macrostate is characterized by its energy which is in the interval $E, E + \delta E$ and by the number N of TLS. (For other problems we may need additional parameters, for example for a gas we would need to specify the volume V . The volume of a crystal is fixed, however, we cannot change it, so energy and number of microsystems are the only variables we need to define the macrostate).

Step 2 is to characterize the microstates of the system, i.e. specify what the individual constituents are doing.

For our problem, this is schematically shown in Fig. 1, where the black dot indicates the state of each TLS (excited or not). Each of these possible arrangements is a different microstate.



Fig 1. One possible microstate of a system of N independent TLS: some are in the ground state and some are in the excited state.

Therefore, the first big difference between classical and quantum systems is how we define the microstate. As discussed, in classical systems we find the number of degrees of freedom and what are the generalized coordinates and momenta for each constituent microsystem, and all of those together define the microstate. In contrast, for a quantum system we simply need to specify the quantum numbers for each of microsystem. The microstate shown in the Fig would be labeled as $(-, +, +, -, +, -, \dots)$ since the first TLS has spin $-1/2$ (it’s in the excited state), the next two have spin $+1/2$ (they are in the ground-state) etc.

Step 3 is to find the energy of each given microstate, which then allows us to identify the allowed microstates as being those whose energy $\in [E, E + \delta E]$. Because the spectrum of each quantum microsystem is discrete, so is the spectrum of the entire system – for non-interacting microsystems, the total energy is the sum of individual energies. For our example, the energy of the microstate is:

$$E_{-,+,+,-,+,-,\dots} = -\frac{g\mu_B B}{2} (-1 + 1 + 1 - 1 + 1 - 1\dots)$$

i.e. it's obtained by adding together the numbers that characterize the microstate and then multiplying by the appropriate “quantum” of energy. Clearly if we calculate all the energies of all possible microstates, we find that only certain discrete values are possible. For instance, it's not possible to get a half-integer multiple of $\frac{g\mu_B B}{2}$ as a total energy of a microstate.

This (a discrete spectrum) will be true for all the quantum systems that we will consider. The multiplicity, then, is just the number of microstates that happen to have their energy in the specified range. For quantum systems we will *always* assume that δE is so small that precisely a single allowed value E falls inside it. If there is a single microstate with that energy E , i.e. that eigenstate of the total system is non-degenerate, then the multiplicity of this macrostate is $\Omega = 1$. In general, however, the eigenstate will be degenerate, i.e. there will be several microstates that all have the same total energy E . In this case, the multiplicity is simply be $\Omega = g(E)$, where $g(E)$ is the degeneracy. Calculating Ω , then, reduces to counting how many microstates have the energy E of the macrostate (this replaces calculating ω and dealing with the hyperspheres and all that for classical systems).

Boltzmann's formula then gives us the entropy $S(E, N, \dots) = k_B \ln \Omega(E, N, \dots)$ from where we can proceed in the usual way to find the temperature, etc.

Let us calculate $\Omega(E, N)$ for our system of TLS. Clearly, the allowed eigenvalues are:

$$E = N_1(-\epsilon_0) + N_2\epsilon_0 = (N_2 - N_1)\epsilon_0$$

where $0 \leq N_1, N_2 \leq N$ are the numbers of TLS in the ground-state and excited state, respectively. Since we must have $N_1 + N_2 = N$, it follows that:

$$N_2 = \frac{1}{2} \left(N + \frac{E}{\epsilon_0} \right); N_1 = \frac{1}{2} \left(N - \frac{E}{\epsilon_0} \right)$$

The degeneracy of this level is

$$\Omega(E, N) = \frac{N!}{N_1!N_2!}$$

since this is the distinct number of ways to pick which N_2 TLS are excited (the TLS are separated spatially, so they are “distinguishable” because of their different locations in space).

According to Boltzmann's formula, the entropy is:

$$S(E, N) = k_B \ln \frac{N!}{N_1!N_2!} = k_B [N \ln N - N_1 \ln N_1 - N_2 \ln N_2] = k_B \left[N_1 \ln \frac{N}{N_1} + N_2 \ln \frac{N}{N_2} \right]$$

since $N = N_1 + N_2$. After substituting the expressions of N_1, N_2 , we finally find that:

$$S(E, N) = \frac{k_B}{2\epsilon_0} \left[N\epsilon_0 \ln \frac{4\epsilon_0^2 N^2}{N^2\epsilon_0^2 - E^2} + E \ln \frac{N\epsilon_0 - E}{N\epsilon_0 + E} \right]$$

Correct units? Check! Extensive? $S(2E, 2N) = 2S(E, N)$ so check! So we can continue.

Since $dS = \frac{1}{T}dE - \frac{\mu}{T}dN$ (there is no volume dependence here, volume is fixed because the equilibrium positions are not allowed to change – so $dV = 0$ forever), we have $\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_N$ from

which one finds after a bit of work (see solutions to first assignments from previous years, if details are needed):

$$E = -N\epsilon_0 \tanh \frac{\epsilon_0}{k_B T}$$

and the specific heat is:

$$C = \left(\frac{\partial E}{\partial T} \right)_N = Nk_B \left[\frac{\beta\epsilon_0}{\cosh(\beta\epsilon_0)} \right]^2$$

where $\beta = 1/(k_B T)$ is a notation that we will use extensively. Let us analyze these results: first, if $T \rightarrow 0 \rightarrow \beta\epsilon_0 \rightarrow \infty \rightarrow E \rightarrow -N\epsilon_0$. This makes sense, since at very low temperatures we expect the system to go into its ground state, which consists of each TLS being in the ground-state. You can verify that in this limit $S \rightarrow 0$, as required by the 3rd law of thermodynamics (this is easiest seen from degeneracy, since in this limit $N_1 = N, N_2 = 0 \rightarrow \Omega = 1 \rightarrow S = 0$).

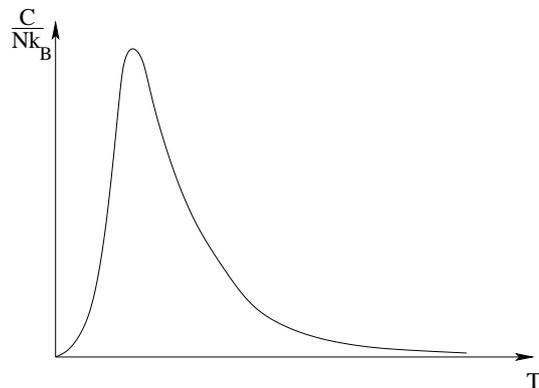


Fig 2. Specific heat of Schottky type.

(We haven't done this check for the classical calculations, since the entropy expressions we get there usually violate this law. But then, we know that classical models are only valid at high energies and high temperatures, so it is no too surprising that they fail to behave correctly as $T \rightarrow 0$.) A specific heat of this type is said to be of Schottky type. I sketched its shape in Fig. 2 (use Maple to generate a realistic curve, if you want to see the exact shape). As you can see, this is very different from what we usually obtain in classical systems, where specific heats are generally constants independent of T .

While this solution was quite simple, you can convince yourself that we cannot generalize the solution easily. For example, if we had spins $S = 1$ in a magnetic field, then there would be three levels per microsystem – this problem we can no longer solve using the microcanonical ensemble, although it (as well as any value of S whatsoever) will become trivial to solve using canonical ensembles – this is what we will learn next.

We can also generate a “classical” version of this model, by assuming each spin to be a classical vector that can point in any direction. It turns out that this problem is also too hard to solve using the classical microcanonical ensemble, because we cannot do the integrals entering in the multiplicity formula (the integrals do not reduce to a hypersphere, but something much more complicated). Again, use of canonical ensembles will allow us to solve this problem really easily. So after we learn the canonical formalism (in a few lectures) we will be able to study both the full quantum (for any spin value) and the classical versions of this problem, and we will be able to compare the similarities and the differences between the two version.

Luckily, there is one problem where we can solve the quantum as well as the classical version using microcanonical ensembles – the chain of harmonic oscillators (This is discussed in your textbooks starting on the bottom of page 213). We already have the classical solution, so let us derive the quantum one as well. For simplicity, I'll assume again only 1D motion, and I'll comment at the end on the generalization to 3D motion.

Remember that the classical Hamiltonian for this problem was $\mathcal{H} = \sum_{i=1}^N h_i$, where $h_i = \frac{p_{x,i}^2}{2m} + \frac{m\omega^2(x_i - X_i)^2}{2}$ is the contribution (the hamiltonian) of the i th atom, X_i being its the equilibrium position.

The quantum Hamiltonian will look the same, except that the momenta and positions now become

operators. Let us look at a single atom first. Its quantum Hamiltonian is:

$$\hat{h} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{m\omega^2}{2} (x - X)^2$$

I am sure you remember from quantum mechanics that the eigenenergies of this hamiltonian are $e_n = \hbar\omega \left(n + \frac{1}{2}\right)$, where $n = 0, 1, 2, \dots$ is an integer. This is all the knowledge we need.

For N non-interacting oscillators, we will need N integers $n_i, i = 1, N$ to specify in what eigenstate is each harmonic oscillator – if we know all these numbers, we have fully specified the corresponding microstate $= (n_1, \dots, n_N)$. Since $\hat{H} = \sum_{i=1}^N \hat{h}_i$, the total energy of the system in a given microstate is simply the sum of energies of the individual oscillators:

$$E_{(n_1, \dots, n_N)} = \sum_{i=1}^N \hbar\omega \left(n_i + \frac{1}{2}\right) = \frac{N\hbar\omega}{2} + M\hbar\omega$$

where

$$M = \sum_{i=1}^N n_i$$

We need to find the multiplicity Ω of the macrostate with a given energy E and given N . This is just the degeneracy of the eigenstate of energy E . In this particular case, we have to count in how many different ways can we choose the N integers n_i so that their total sum is always $\sum_{i=1}^N n_i = M$, where the desired $E = M\hbar\omega + \frac{N\hbar\omega}{2} \rightarrow M = \frac{E}{\hbar\omega} - \frac{N}{2}$ is known.

This might look like a complicated calculation, but there is a very nice and simple solution. It goes like this: imagine we have M white balls and $N - 1$ black balls. Consider some possible ordering of these balls, and let n_1 be the number of white balls before the first black ball, n_2 be the number of white balls between the 1st and 2nd black ball, and so on (see Fig 3). Clearly, each n_i is such that $0 \leq n_i \leq M$, and they are always such that $\sum_{i=1}^N n_i = M$. So the question of the degeneracy is now in how many distinct ways we can distribute the balls (each different sequence gives us a different possible choice of the n_i values), and the answer is:

$$\Omega = \frac{(M + N - 1)!}{M!(N - 1)!}$$

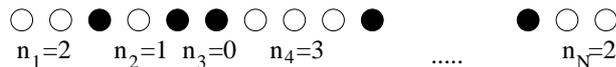


Fig 3. Strategy to generate all the possible sequences satisfying $\sum_{i=1}^N n_i = M$: we have $N - 1$ black balls, M white balls, and for each possible sequence we define n_1 as no. of white balls before the first black ball, n_2 as number of white balls between 1st and 2nd black balls, etc. In the example shown, $n_1 = 2, n_2 = 1, n_3 = 0, \dots$

Then,

$$S = k_B \ln \Omega = \dots = M k_B \ln \frac{M + N}{N} + N k_B \ln \frac{M + N}{N}$$

where I used Stirling's formula, and approximated $M + N - 1 \approx M + N$ and $N - 1 \approx N$ (N is the number of oscillators and it is of order 10^{23} , as usual). Now we can write $S(E, N)$, since we know how M depends on E, N :

$$S(E, N) = k_B \left[\frac{E}{\hbar\omega} - \frac{N}{2} \right] \ln \frac{\frac{E}{\hbar\omega} + \frac{N}{2}}{\frac{E}{\hbar\omega} - \frac{N}{2}} + N k_B \ln \frac{\frac{E}{\hbar\omega} + \frac{N}{2}}{N}$$

Now, using $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N$ and inverting, we find:

$$E = N\frac{1}{2}\hbar\omega + \frac{N\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

and the corresponding specific heat is:

$$C = \frac{\partial E}{\partial T} = Nk_B \frac{(\beta\hbar\omega)^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

Let us analyze these results. First, at large temperatures $k_B T \gg \hbar\omega \leftrightarrow \beta\hbar\omega \ll 1$ (i.e., temperatures much larger than the interval between consecutive eigenstates) we can approximate:

$$e^{\beta\hbar\omega} \approx 1 + \beta\hbar\omega$$

and therefore:

$$E \approx N\frac{1}{2}\hbar\omega + \frac{N\hbar\omega}{\beta\hbar\omega} \approx Nk_B T$$

while

$$C \approx Nk_B \frac{(\beta\hbar\omega)^2}{(\beta\hbar\omega)^2} = Nk_B$$

i.e. indeed we recover the results predicted by the classical calculation (see appropriate writeup, or Ex. 6.3. page 157 of textbook).

However, at low temperatures $k_B T \ll \hbar\omega \rightarrow \beta\hbar\omega \gg 1$ (i.e., where we cannot ignore the discrete nature of the spectrum), we have $e^{\beta\hbar\omega} \gg 1$ and therefore:

$$E \approx N\frac{1}{2}\hbar\omega + N\hbar\omega e^{-\beta\hbar\omega}$$

showing that as $T \rightarrow 0$, the system approaches its ground-state (or zero-point) energy $N\hbar\omega/2$; and

$$C \approx Nk_B(\beta\hbar\omega)^2 e^{-\beta\hbar\omega} \rightarrow 0$$

The T -dependence of the specific heat is sketched in Fig. 3. The high- T , classical limit value, is known as the ‘‘Dulong -Petit law’’. In fact, the Dulong-Petit law is that $C = 3Nk_B$ at high temperatures – the reason is that in real materials, the atoms can vibrate in all 3 directions, not only x-axis as assumed here. You should be able to show that the only effect of that is to change $N \rightarrow 3N$ in all the above formulae, whether classical or quantum.

But the point is that we have derived how much energy is stored in this vibrational motion of the atoms and what is its contribution to the specific heat. At high temperatures it is $3Nk_B$, as had been experimentally observed to be the case by Dulong and Petit – and both the classical and the quantum models predict that. However, at low temperatures the specific heat becomes dependent on temperature and we need the quantum calculation to find out the correct result.

Before concluding, let us quickly analyze why we cannot successfully investigate quantum ideal gases in this formalism. Assume a cubic box of volume $V = L^3$. As we have already discussed, the

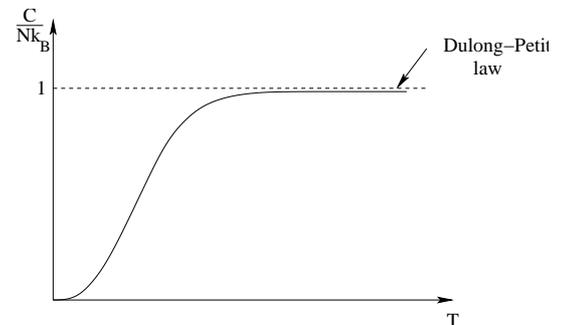


Fig 4. Specific heat for a system of non-interacting harmonic oscillators.

spectrum of a single atom placed in this box is:

$$E_{n_1, n_2, n_3} = \frac{h^2}{8mL^2}(n_1^2 + n_2^2 + n_3^2)$$

Now try to imagine repeating the same calculation as before, i.e. summing N such spectra and trying to figure out what is the degeneracy corresponding to a given total energy E ! It is basically impossible (well, one can make some horrendous approximations to obtain the high E behavior and see that it agrees with the classical predictions – this is done somewhere in your textbook. However, we already know the classical predictions, what we'd like to find are the quantum predictions). In fact, even much simpler problems, such as N three-level systems (see homework for previous year) become prohibitively difficult in this approach. Since the main goal of our course is to study quantum ideal gases, it follows that we have to find a smarter and simpler way to do these calculations. This is why we will now learn how to deal with canonical and grandcanonical ensembles.

2 Spins - brief review

Let me review the specific bits and pieces of information we'll need to know about quantum spins, for our course. I won't give any proofs (look at your quantum mechanics notes, or come talk to me if you don't remember where these equations came from).

Spin is a purely quantum mechanical property (it has no classical analogue, which makes it a bit more difficult to understand what is it) associated with elementary particles. The operators describing “the spin” are angular momentum operators. If you wish, there is an intrinsic “rotation” or “spin” associated with each elementary particle, and what we call spin is just the operator measuring how much of this rotation there is. In fact, there are three of them, $\hat{S}_x, \hat{S}_y, \hat{S}_z$ characterizing rotation about the 3 axes. We can also define a total spin operator $\vec{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$ – precisely what you'd expect. It should not be surprising that the operators are angular momentum operators, since angular momentum is what characterizes rates of rotation.

We are interested in the eigenstates of these operators, since those are the values we expect to see when we measure the spin. Because of their commutation relations $[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z$ etc, we cannot simultaneously know the eigenstates of all these 3 operators (just like p, x case). However, we can find simultaneous eigenstates of \vec{S}^2 and one of the projections, which is usually chosen to be \hat{S}_z .

The eigenvalues are those listed at the beginning of the notes. The total angular momentum is quantized, i.e. it can only have values of $\hbar\sqrt{S(S+1)}$, where S can only be an integer or a half-integer. For example, electrons, neutrons and protons are all particles with $S = 1/2$. The \hbar is simply the units: the “quantum” of angular momentum is \hbar .

For any specified value of S (i.e., for a total angular momentum $\hbar\sqrt{S(S+1)}$), the z -axis projection measured by \hat{S}_z is also quantized: it can only take values of $m_z\hbar$, where again \hbar is just the units, and m_z is restricted to the values $-S, -S+1, \dots, S-1, S$, i.e. it can only increase in steps of 1. It's not surprising that it cannot go above S or below $-S$, because that would mean that the z -axis projection would become larger than the total angular momentum. So, if $S = 1/2$, then $m_z = -1/2, 1/2$. If $S = 1$ then $m_z = -1, 0, 1$; if $S = 3/2$, then $m_z = -3/2, -1/2, 1/2, 3/2$ and so on and so forth. Basically this is all you have to remember.

It turns out that because of this spin, when particles are put in a magnetic field they act like magnetic dipoles: it is energetically favorable to align this axis of rotation (spin) with the external magnetic field direction. Remember that if we have a classical magnetic dipole $\vec{\mu}$ in a magnetic field,

its energy is $-\vec{\mu} \cdot \vec{B}$, showing a minimum value when $\vec{\mu} \parallel \vec{B}$, and a maximum to the most unstable situation when they are antiparallel.

Well, a quantum spin has a magnetic dipole $\vec{\mu} = \frac{g\mu_B}{\hbar} \vec{S}$ – it is proportional to its spin, and the constants in front basically just fix the units. Its Hamiltonian is obtained from the classical one by replacing the classical vector $\vec{\mu}$ by its quantum operator written just above, therefore the Hamiltonian for a single spin is:

$$\hat{h} = -\vec{\mu} \cdot \vec{B} = -\frac{g\mu_B}{\hbar} \vec{S} \cdot \vec{B} = -\frac{g\mu_B}{\hbar} B_z \hat{S}_z$$

if we take B to point along the z -axis. So the allowed eigenenergies are proportional to the allowed eigenvalues of \hat{S}_z , which we know to be $m_z \hbar$ and thus:

$$e_{m_z} = -g\mu_B B m_z, m_z = -S, -S + 1, \dots, S - 1, S$$

Examples: a spin $S = 1/2$ has energy $-g\mu_B B/2$ if $m_z = 1/2$ (spin-up state has the lowest energy) or energy $+g\mu_B B/2$ if $m_z = -1/2$ (spin-down state has a higher energy). If $S = 1$, there are three possible energies $-g\mu_B B, 0, g\mu_B B$, for the three possible spin projections $m_z = -1, 0, 1$ and so on and so forth.

All we will need in this course are these eigenenergies (the same way that all we need for a quantum harmonic oscillators is its spectrum, $\hbar\omega(n + 1/2), n = 0, 1, \dots$).