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

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

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.
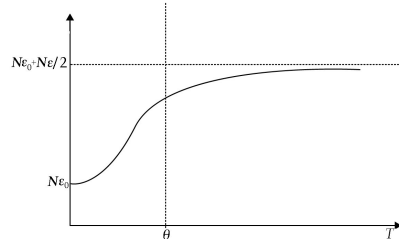
Exercise. Compute the internal energy by using the formula $E = -N \frac{\partial \ln Z}{\partial \beta}$

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

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

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 quit 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).
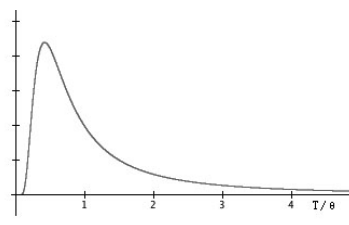
We can understand the heat capacity curve by qualitative reasoning. At low temperatures the distance between the energy levels is so large that it is very difficult to excite thermally the particles from the ground state, this implies a small heat capacity. As the temperature then approaches the scale 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
$$dE = TdS + SdT - SdT - pdV + \mu dN =$$
$$d(TS) - SdT - pdV + \mu dN$$

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

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

Inserting the expression for Z we get

$$F = N\varepsilon_0 + Nk_B T \ln\left(1 + e^{-\theta/T}\right)$$

that after derivation with respect to temperature gives

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

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.
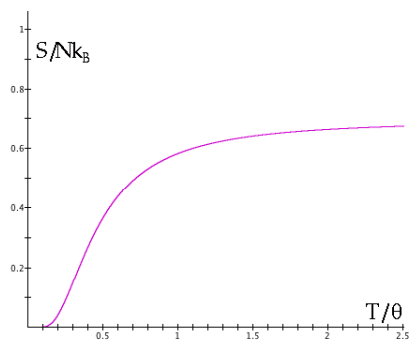
Exercise. Why is this limit correct?

*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:

$$dF = -SdT - pdV + \mu dN =$$
$$- SdT - pdV - Vdp + Vdp + \mu dN =$$
$$- SdT - d(pV) + Vdp + \mu dN$$

This gives

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

with a new function of state

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

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

$$dE = TdS - pdV + \mu dN = TdS - pdV - Vdp + Vdp + \mu dN =$$
$$TdS - d(pV) + Vdp + \mu dN$$

This implies

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

with

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

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 influence 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 $B \approx 1$ 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 wit 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.
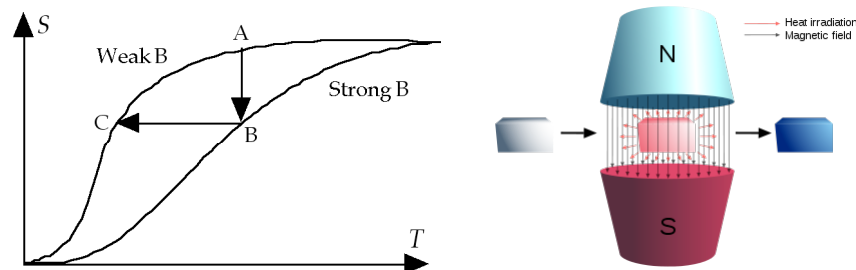
The two curves describe precisely the same mathematical function but have different scale temperatures, as they are proportional to the strength of the magnetic field. The path from A to B corresponds to an increase in the strength of the magnetic field while keeping the temperature constant. The path 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

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

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 µK.

4.5. The magnetisation

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

$$M=n_0\cdot\mu+n_1\cdot\left(-\mu\right)=\mu N\frac{e^{-\varepsilon_0/k_BT}-e^{-\varepsilon_1/k_BT}}{e^{-\varepsilon_0/k_BT}+e^{-\varepsilon_1/k_BT}}=$$

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

For large values of $\frac{\mu B}{k_BT}$, (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 $\frac{\mu B}{k_BT}$ we can use a Taylor expansion of the hyperbolic function and get

$$M\approx N\mu\frac{\mu B}{k_BT}$$

In this approximation the magnetisation is inversely proportional temperature. This is *Curie's law* that agrees very well with experiment, see the diagram.
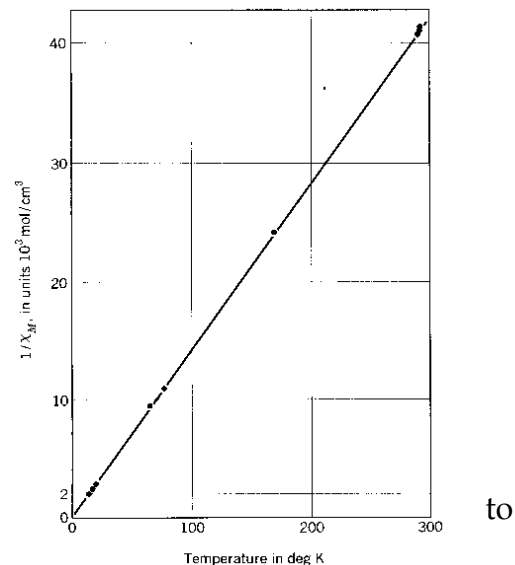
We can use measurements of the magnetisation as a thermometer! For electronic systems we can then measure temperatures down to about 10 mK when the magnetic field from internal interactions interfere and also the Taylor expansion requires more terms. Instead we can then use a nuclear-spin system and 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

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

We can now easily write down the partition function

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

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.

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

$$e^{-\theta/2T}\left(1 + e^{-\theta/T} + e^{-2\theta/T} + \ldots\right) = \frac{e^{-\theta/2T}}{1 - e^{-\theta/T}} = \frac{1}{e^{\theta/T} - 1}$$

The internal energy is

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

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

$$E = Nk_B T$$

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 $C = \dfrac{dE}{dT} = Nk_B \dfrac{(\theta/T)^2 e^{\theta/T}}{\left(e^{\theta/T} - 1\right)^2}$.

It starts from zero at $T = 0$ and saturates as expected for high temperatures at Nk_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 $S = -\dfrac{\partial F}{\partial T}$ where $F = -Nk_B T \ln Z$.
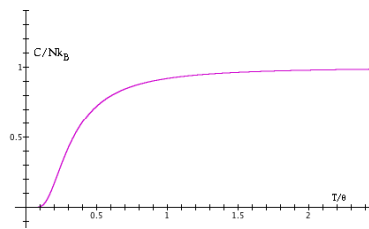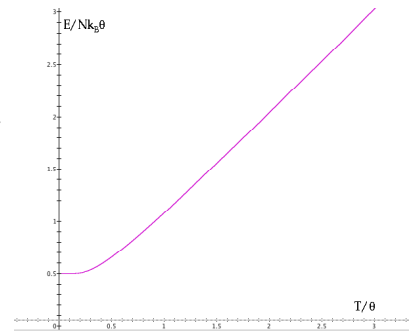
Exercise. Show that $S = Nk_B \left[\ln \dfrac{e^{\theta/T}}{e^{\theta/T}-1} + \dfrac{\theta/T}{e^{\theta/T}-1} \right]$
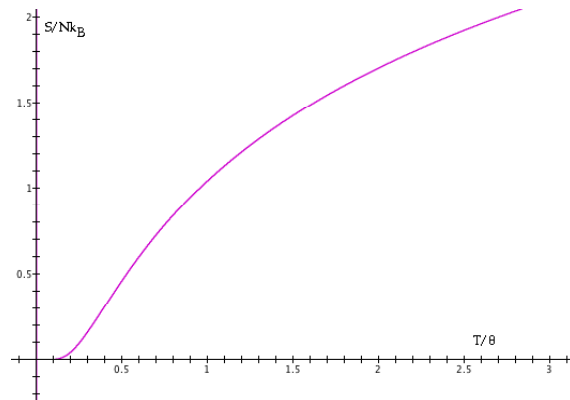

Exercise. Show that $S \to 0$ when $T \to 0$ and $S \to Nk_B \ln \dfrac{T}{\theta} = Nk_B \ln \dfrac{k_B T}{\hbar \omega}$ when $T \to \infty$.

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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 is 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
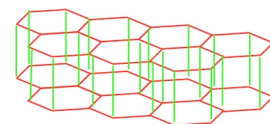
one for vibrations in the layer and a low one for vibrations between the layers. Actually only the vibrations between the layers are activated at room temperature. When we count quadratic terms in the total energy we should only count these latter vibrations. This implies that the number of quadratic 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 I has to be counted several times, as many times as the degeneracy or the *multiplicity* of the degeneration. Mathematically we write this

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

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 $E = -N \dfrac{\partial \ln Z}{\partial \beta}$ 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 energi 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 detects the split in the energy levels. What is in this case the NMR frequency?

6. Experimental results from measurements of the specific heat capacity of gadolinium are shown in the figure. At low temperatures you see a bump in the curve caused by a few low lying energy levels. Explain this and estimate the distance between these levels. Give your answer in electron volts. You have to motivate your answer but you don't have to make detailed computations.
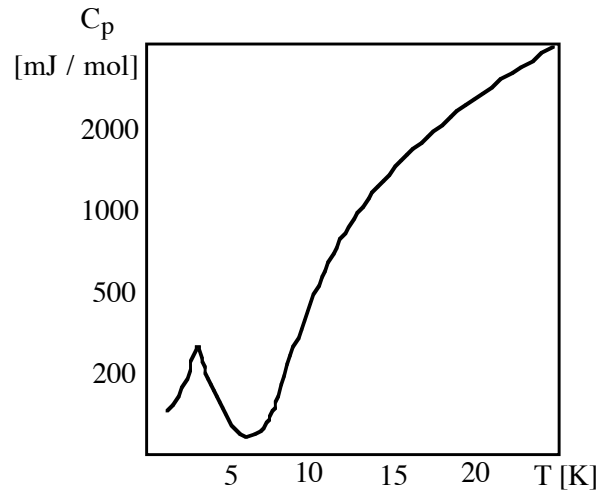
5. The ideal gas

5.1 Density of states

To begin with we will consider gases with non-relativistic massive particles. We will need the *density of state* in energy.

We now study bas particles in a "box" with dimensions *LxLxL*.
If we solve the Schödinger equation for such a particle we get wave functions of the type

$$\varphi(x,y,z) = Ae^{ik_x x}e^{ik_y y}e^{ik_z z}$$

We now use so-called periodic boundary conditions where we demand that

$$\varphi(x + n_x L, y + n_y L, z + n_y L) = \varphi(x,y,z)$$

This implies

$$k_x = n_x \frac{2\pi}{L}, \quad k_y = n_y \frac{2\pi}{L}, \quad k_z = n_z \frac{2\pi}{L}$$

In *k*-space, these *k*-values form a cubic lattice with a distance $\frac{2\pi}{L}$ between the lattice points. Each lattice point corresponds to a state of the gas particle. In an elementary cube we then have exactly one state. The volume of an elementary cube is evidently $\left(\frac{2\pi}{L}\right)^3 = \frac{(2\pi)^3}{V}$. The density of states in *k*-space is then

$$1 / \frac{(2\pi)^3}{V} = \frac{V}{(2\pi)^3}$$

You always start with the number of states in an infinitesimal cube in *k*-space and the transform step by step to ε-space:

$$\frac{V}{(2\pi)^3}d^3k = \frac{V}{(2\pi)^3}\frac{1}{\hbar^3}d^3p \overset{\substack{spherical\\symmetry}}{=}$$

$$\frac{V}{(2\pi)^3}\frac{4\pi}{\hbar^3}p^2dp \overset{p^2=2m\varepsilon}{=} \frac{V}{(2\pi)^3}\frac{4\pi m(2m)^{1/2}}{\hbar^3}\cdot\varepsilon^{1/2}d\varepsilon = g(\varepsilon)d\varepsilon$$

where *V* is the normalisation volume. The factor 4π comes from that we integrate over the uninteresting space angles. We have also exploited that the momentum $p = \hbar k$ and the relation (in this case) between energy and momentum $\varepsilon = \frac{p^2}{2m}$.

The relation between energy and momentum/wave vector is called a *dispersion relation*.

This gives the density of states in energy $g(\varepsilon) = \frac{V}{(2\pi)^2}\frac{(2m)^{3/2}}{\hbar^3}\varepsilon^{1/2}$

This expression must be corrected with a spin factor, 2 for spin 1/2 particles and 3 for (massive) spin 1 particles. The density of states is such that $g(\varepsilon)d\varepsilon$ is the number of states in the energy interval $[\varepsilon, \varepsilon + d\varepsilon]$.

Note 1. It is easy to realise that our box doesn't have to be cubic. Actually out derivation works for a volume of arbitrary form, thermodynamical properties do not depend on the form of the container.

Note 2. We could have used the usual condition when you solve the Schödinger equation in a box, namely that we have standing waves between the walls. This gives a final result that is identical to that we got here but the method with periodic boundary conditions often is simpler to use.

5.2 Group distributions

First we observe that the number of states in a gas in a macroscopic volume is enormous and that the energy levels are very close to each other. To handle this situation we introduce something called *group distributions*. See the figure!
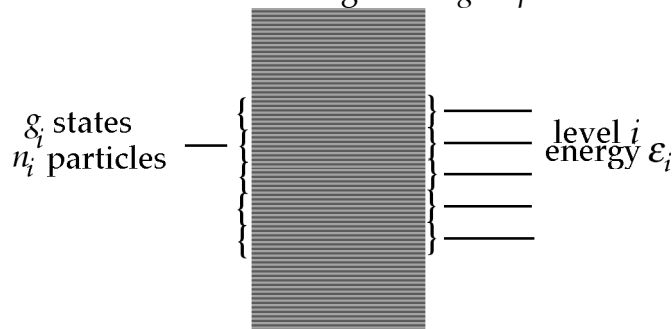
We group such that the number of levels within a group i, g_i, is very large, and such that the number of particles within the group, n_i, also is large, but such that the average distances $\Delta\varepsilon_i$ between the levels in the different groups still is very small. In practice it turns out that you can g_i of order 10^{10} and still have $\Delta\varepsilon_i \approx 10^{-9} \cdot k_B T$. It also turns out that it is not critical for the final result how we do the grouping.

5.3 Identical particles

We now want to count the number of microstates in a certain distribution. We then have to take into account an important fact: particles in a gas are fundamentally *identical,* that is it is *impossible* to tell them apart. We cannot decide *which* particle occupies a certain state; we can only decide the *number* of particles in a certain state. The other important fact is that we have two kinds of particles in nature, *fermions* and *bosons*. Fermions follow the *Pauli principle* that says that two fermions cannot be in the same state. Fermions always have *half integer spin*; examples are electrons, protons, and neutrons. Bosons do *not* follow the Pauli principle; an arbitrary number of bosons can be in the same state. Bosons have *integer spin*; examples of bosons are photons, helium-4 atoms, and deuterons. This means that we have to count microstates

differently for fermions and bosons. For fermions we will get Fermi-Dirac (FD) statistics for bosons we will get Bose-Einstein (BE)-statistics.

5.4. Counting microstates for fermions

Consider the level group i where we have g_i possible states and n_i particles to occupy these states. As we deal with fermions we can have at most one particle in each state. Consequently we have $g_i - n_i$ empty states. We then can arrange filled and empty states in

$$\frac{g_i!}{n_i!(g_i - n_i)!}$$

ways. The total number of microstates for all levels then is

$$\Omega_{FD} = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!}$$

5.5. Counting microstates for bosons

Again consider level group i. We have g_i possible states and n_i particles to distribute in these states. We can now have several particles in each state something that complicates the counting. However, we can get around this problem using a trick. Consider the states as slots with walls in between. If there are g_i states there are $g_i - 1$ walls between them. Together with the n_i particles we now have $g_i + n_i - 1$ objects to handle, $g_i - 1$ of one kind (the walls) and n_i of the other kind (the particles) and we can arrange them in

$$\frac{(g_i + n_i - 1)!}{n_i!(g_i - 1)!} \approx \frac{(g_i + n_i)!}{n_i! g_i!}$$

ways. The total number of microstates for all level is then $\Omega_{BE} = \prod_i \frac{(g_i + n_i)!}{n_i! g_i!}$

5.6. Dilute gases

Now suppose that we have a dilute gas. By this we mean that $n_i \ll g_i$ (but still $n_i \gg 1$). This is a very common situation if we for instance consider air at normal temperature and pressure. In the fermion case we then can make the approximation

$$\frac{g_i!}{n_i!(g_i - n_i)!} = \frac{g_i(g_i - 1)\dots(g_i - n_i + 1)}{n_i!} \approx \frac{g_i^{n_i}}{n_i!}$$

In the boson case we have

$$\frac{(g_i + n_i)!}{n_i! g_i!} = \frac{(g_i + n_i)(g_i + n_i - 1)\dots(g_i + 1)}{n_i!} \approx \frac{g_i^{n_i}}{n_i!}$$

that is we get the same result. This "classical limit" gives us the so-called Maxwell-Boltzmann (MB) statistics where we have

$$\Omega_{MB} = \prod_i \frac{g_i^{n_i}}{n_i!}$$

5.6. Distributions in thermodynamical equilibrium

5.6.1. Fermions

We now copy the procedure that we used for distinguishable particles in chapter 3. We define the entropy

$$S = k_B \ln \Omega$$

and try to maximise the entropy given the constraints

$$N = \sum_i n_i \text{ and } E = \sum_i \varepsilon_i n_i$$

that is the number of particles and the internal energy are conserved.

We maximise the function

$$f = \sum_i \left(g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln(g_i - n_i) \right) - \alpha \left(\sum_i n_i - N \right) - \beta \left(\sum_i \varepsilon_i n_i - E \right)$$

where we have used Stirling's approximation and introduced Lagrangian multipliers. We compute all partial derivatives with respect to n_i and put them to zero and get after some manipulation

$$n_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i} + 1}$$

It is here useful to define the *filling factor*, the ratio between the number of particles and the number of accessible states in this level

$$f_i = \frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta \varepsilon_i} + 1}$$

As the levels are very close we can id we want write this as a continuous distribution

$$f_{FD}(\varepsilon) = \frac{1}{e^{\alpha + \beta \varepsilon} + 1}$$

5.6.2 Bosons

We repeat the procedure for the boson case and get with a similar computation

$$f_{BE}(\varepsilon) = \frac{1}{e^{\alpha + \beta \varepsilon} - 1}$$

Exercise. Show this by doing the detailed calculations.

5.6.3 Dilute gases

Finally, for dilute gases we have

$$f_{MB}(\varepsilon) = \frac{1}{e^{\alpha + \beta \varepsilon}}$$

Exercise. Show this.

5.7. Summary

As before $\beta = 1/k_B T$. α can in principle be determined from the condition $\sum_i n_i = N$ but it turns out that you can explicitly solve the resulting equation only in the MB case, we will return to this in the next chapter. If we for the moment introduce $e^\alpha = B$, we can summarize our results in the following way

$$
f(\varepsilon) = \begin{cases} \dfrac{1}{Be^{\varepsilon/k_B T} + 1} & \text{(FD)} \\[2ex] \dfrac{1}{Be^{\varepsilon/k_B T} + 0} & \text{(MB)} \\[2ex] \dfrac{1}{Be^{\varepsilon/k_B T} - 1} & \text{(BE)} \end{cases}
$$

As we will see the different kinds of particle system will have very different physical properties.

6. Maxwell-Boltzmann gases

6.1. The partition function

We start by rewriting the filling factor

$$f_i = \frac{1}{Be^{\varepsilon_i/k_BT}} = Ae^{-\varepsilon_i/k_BT}$$

In this case we can easily compute A (i.e. implicitly the value of α). We have

$$N = \sum_i n_i = \sum_i g_i f_i = A\sum_i g_i e^{-\varepsilon/k_BT}$$

or

$$f_i = \frac{N}{Z}e^{-\varepsilon_i/k_BT}$$

with

$$Z = \sum_i g_i e^{-\varepsilon_i/k_BT}$$

the *partition function*. This is very similar to what we had before in chapter 3.

We now consider a monoatomic gas where the gas atoms have spin zero as for instance in helium-4. The partition function can be written as an integral as the energy levels are close

$$Z = \sum_i g_i e^{-\varepsilon_i/k_BT} \rightarrow \int_0^\infty g(\varepsilon)d\varepsilon \cdot e^{-\varepsilon/k_BT} = \frac{V}{(2\pi)^2}\frac{(2m)^{3/2}}{\hbar^3}\int_0^\infty \varepsilon^{1/2}d\varepsilon \cdot e^{-\varepsilon/k_BT}$$

We put $x^2 = \varepsilon/k_BT$ and get

$$Z = \frac{V}{2\pi^2}\frac{(2m)^{3/2}}{\hbar^3}(k_BT)^{3/2}\int_0^\infty x^2 e^{-x^2}dx$$

where we have "extracted the physics" from the integral that is now just a number. The integral has the numerical value $\pi^{1/2}/4$ and we have finally

$$Z = \frac{V}{2\pi^2}\frac{(2m)^{3/2}}{\hbar^3}(k_BT)^{3/2}\frac{\pi^{1/2}}{4}$$

We can now check if our gas can be considered as dilute when for instance the temperature is 5 K. If we insert physical values (at normal pressure we have that N/V is one mol of particles per 20 litres) we find $f \approx N/Z \approx 0.1$, still quite small. The quantity N/Z is sometimes called the *degeneracy parameter*. At room temperature this parameter is extremely small which shows that we then safely can describe normal gases using MB statistics. For further use we can also note that $Z \propto V$.

6.2. Velocity distributions

In many cases in kinetic gas theory we are interested in the velocity distribution of the molecules of the gas. We then need the density of states in speed that we easily derive

$$\frac{V}{(2\pi)^3}d^3k = \frac{V}{(2\pi)^3}\frac{1}{\hbar^3}d^3p =$$

$$\frac{V}{(2\pi)^3}\frac{1}{\hbar^3}p^2dp\cdot 4\pi \overset{p=mv}{=} \frac{V}{2\pi^2}\frac{1}{\hbar^3}(mv)^2 m\, dv$$

that gives

$$g(v) = \frac{V}{2\pi^2}\frac{1}{\hbar^3}(mv)^2 m$$

we then have

$$n(v)dv = g(v)dv\cdot f(v) = g(v)dv\frac{N}{Z}e^{-\varepsilon(v)/k_B T}$$

If we insert our expression for the density of states and the earlier derived expression for the partition function we get

$$n(v)dv = 4\pi N\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_B T}\, dv,$$

the number of particles with speed in the interval $[v, v+dv]$.

Maxwell derived this relation was by long before quantum mechanics was known. We also see that the result does not contain Planck's constant that means that the result is "classical" and consequently be derived without using quantum mechanics. We also know that the result cannot be expected to be valid for very dense or cold gases when quantum phenomena start to appear. The distribution $n(v)$ as a function of v, starts from zero, increases as the speed increases, has a maximum and then decreases exponentially. You can compute some interesting representative speed for the distribution:

1. The speed for which $n(v)$ has a maximum. Maximum occurs when

$$v_{max} = \sqrt{2}\left(\frac{k_B T}{m}\right)^{1/2} \approx 1.4\left(\frac{k_B T}{m}\right)^{1/2}$$

Exercise. Show this!

2. The average speed is

$$\langle v\rangle = \frac{\displaystyle\int_0^\infty v\, n(v)dv}{\displaystyle\int_0^\infty n(v)dv} = \sqrt{\frac{8}{\pi}}\left(\frac{k_B T}{m}\right)^{1/2} \approx 1.6\left(\frac{k_B T}{m}\right)^{1/2}$$

Exercise. Show this!

3. The RMS (root mean square) speed is

$$\sqrt{\langle v^2 \rangle} = \left(\dfrac{\int\limits_0^\infty v^2\, n(v)dv}{\int\limits_0^\infty n(v)dv} \right)^{1/2} = \sqrt{3}\left(\dfrac{k_B T}{m} \right)^{1/2} \approx 1.7\left(\dfrac{k_B T}{m} \right)^{1/2}$$

From the last result we find that

$$\langle \varepsilon \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T \,,$$

a result that we got in chapter 3 using the equipartition theorem: a free particle has three quadratic terms in the total energy, each one corresponding to an (average) energy of $\frac{1}{2} k_B T$.

6.3. Internal energy and heat capacity

We use $E = -N \dfrac{\partial \ln Z}{\partial \beta} = \frac{3}{2} N k_B T$

From which follows $C_V = \dfrac{dE}{dT} = \frac{3}{2} N k_B$

Here, we could have used the result from the last section where we computed the average energy of *one* molecule.

6.4. Entropy and free energy and more

We use

$$S = k_B \ln \Omega = k_B \ln \prod_i \frac{g_i^{n_i}}{n_i!} =$$

$$k_B \sum_i \left(n_i \ln g_i - n_i \ln n_i + n_i \right) = k_B \sum_i n_i \left(\ln \left(g_i / n_i \right)_i + 1 \right) =$$

$$k_B \sum_i n_i \left(\ln Z - \ln N + \varepsilon_i / k_B T + 1 \right) =$$

$$N k_B \ln Z - N k_B \ln N + N k_B + E / T = N k_B \ln Z - k_B \ln N! + E / T$$

We note that this expression is similar to what we had before for distinguishable particles only we also have the term $k_B \ln N!$. The extra term compensates for that we count to many permutations if we have distinguishable particles.

For the free energy we now have

$$F = E - TS = -N k_B T \left(\ln Z - \ln N + 1 \right)$$

Pressure is defined by

$$p = -\frac{\partial F}{\partial V} = N k_B T \frac{\partial}{\partial V} \ln Z = N k_B T \frac{\partial}{\partial V} \ln(const \cdot V) = N k_B T / V$$

or

$$pV = N k_B T$$

We have derived the equation of state for an ideal gas!

Exercise problems. Chapter 6

1. What is the RMS speed for air molecules at room temperature? Why doesn't the moon have an atmosphere?

2. Consider a model of a HCl molecule (chloric acid). You may assume that the molecule consists of two pointlike atoms at a fixed distance a from each other. The molecule can rotate around an axis perpendicular to the line connecting the atoms.
a) Write down the partition function for the rotational states of this moelcule.
b) Then estimate the contribution from the rotations to the heat capacity at *low* temperatures.
c) Estimate what is meant by low temperatures if $a = 0.12$ nm.
Hint: Do a suitable approximation in the partition function.

3. Assume that the partition function is such that $Z \propto V^x T^y$ with certain numbers x and y. What is the pressure and heat capacity?

7. Diatomic gases

In a diatomic gas you can have several kinds of energy levels. In general the energy of a molecule is a sum of four energy contributions:

$$\varepsilon = \varepsilon_{trans} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{elektron}$$

The first term is the translational energy of the molecule that we have already treated in the previous chapter. The second term is the rotational energy; the molecule can rotate around the mass centre between the atoms. The third term is the vibrational energy; the two atoms can vibrate along the line connecting them. The last term is due to electronic excitations in the molecule. We expect, and assume in our description that there is very little interaction between the different energy modes. We write down the partition function

$$Z = \sum_{\substack{all \\ states}} e^{-\beta(\varepsilon_{trans} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{elec})} = \sum_{trans} e^{-\beta\varepsilon_{trans}} \sum_{rot} e^{-\beta\varepsilon_{rot}} \sum_{vib} e^{-\beta\varepsilon_{vib}} \sum_{elec} e^{-\beta\varepsilon_{elec}}$$

$$= Z_{trans} Z_{rot} Z_{vib} Z_{elec}$$

As the partition function appears everywhere in thermodynamical quantities in the form of $\ln Z$, the different energy modes will be additive and we can handle then one by one.

7.1 Heat capacity

7.1.1 Contribution from the translational energy

We have already shown that this gives a contribution

$$C_{V,trans} = \tfrac{3}{2} N k_B$$

7.1.2 Contribution from the electronic excitations

Typical excitation energies in a molecule are of order eV that corresponds to a scale temperature of some 10 000 K. This means that we can normally neglect these contributions to the heat capacity at room temperature. The only exception is NO where we have a Schottky anomaly around 75 K caused by two close energy levels. We will neglect electronic contribution in what follows.

7.1.3 Contribution from the vibrational energy

We have already treated this. The atoms in a diatomic molecule can vibrate along the line connecting the atoms; this is a one-dimensional harmonic oscillator. This gives a contribution to the heat capacity the increases from zero at low temperatures and starts to be important at the scale temperature and becomes $N k_B$ at high temperatures. The scale temperature is of order some thousands of Kelvins for ordinary gases. This means that we can in most cases ignore the vibrational contribution to the heat capacity.

7.1.3 Contribution from the rotational energy

Our molecule can rotate around an axis through the mass centre, perpendicular to the line connecting the atoms. From quantum mechanics you can show that the quantum mechanical rotator has energy eigenvalues given by

$$\varepsilon_\ell = \frac{\hbar^2}{2I}\ell(\ell+1) = k_B\ell(\ell+1)\theta$$

where $\theta = \hbar^2/2Ik_B$ is the scale temperature. I is the moment of inertia with respect to the rotation axis. For O_2 the scale temperature is 2 K, far below the boiling point, for oxygen in gas form, lots of rotational modes are excited and give contribution the heat capacity. For H_2 the scale temperature is 85 K, which means that the rotational contributions for H_2 give a contribution at a temperature substantially above the boiling point 20 K.

The eigenfunctions of the rotator are the spherical harmonics Y_ℓ^m that have a degeneracy of $2\ell+1$ given ℓ. We can now write down the partition function for the rotator

$$Z_{rot} = \sum_{\ell=0}^{\infty}(2\ell+1)e^{-\ell(\ell+1)\theta/T}$$

If we exclude hydrogen, room temperature is much larger than the scale temperature. This means that there are many excited states and we can replace the sum by an integral. Set $y = \ell(\ell+1)\theta/T$. Then $dy = (2\ell+1)\theta/T \cdot dl = (2\ell+1)\theta/T \cdot 1$. Note that $\theta \ll T$ we can consider dy as infinitesimal and get

$$Z_{rot} = \sum_{\ell=0}^{\infty}(2\ell+1)e^{-\ell(\ell+1)\theta/T} = \frac{T}{\theta}\int_0^{\infty} dy \cdot e^{-y} = \frac{T}{\theta}$$

Thus

$$E_{rot} = -N\frac{\partial \ln Z_{rot}}{\partial \beta} = Nk_BT$$

and

$$C_{V,rot} = Nk_B$$

The total heat capacity at room temperature then is

$$C_V = C_{V,trans} + C_{V,rot} = \tfrac{3}{2}Nk_B + Nk_B = \tfrac{5}{2}Nk_B$$

in complete agreement with experiment. Before quantum mechanics people couldn't understand why the vibrational contributions shouldn't be included.

Exercise. Why do we neglect rotations along the connection line between the atoms?

Exercise. Compute the contribution to internal energy and heat capacity at a temperature that it much *below* the scale temperature. *Hint*: Only consider the first terms in the partition function. (Why?)

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8. Fermi-Dirac gases, metals, white dwarves, neutron stars and black holes

If we look at a FD gas at low temperature, the particles are stacked on top of each other, one in each state (actually two because we have spin 1/2 particles) from the lowest energy and upwards due to the Pauli principle. This implies that we have a rather high zero-point energy, typically of order some eV. Then what do we mean by low temperature? Looking at a MB gas the degeneracy parameter

$$A = N / Z$$

In which situations is this parameter large enough that we cannot treat the FD gas as a MB gas? In nature we have essentially three such situations, one every day situation and two more exotic:

1. The conduction electrons in a metal have to be treated as a FD gas at all reasonable temperatures. Also for some semiconductors we need to use FD statistics.

2. Liquid -3 at low temperatures (some Kelvins).

3. Electrons in white dwarf stars and neutrons in neutron stars.

8.1 The Fermi-Dirac distribution

We can write

$$f_{FD}(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/k_B T} + 1}$$

where we have defined the parameter $B = e^{-\mu / k_B T}$.

In principle we could determine μ, the *chemical potential*, by the normalisation $N = \sum n_i$ but do that we have to solve an implicit equation for μ that is quite complicated. Without solving the equation we can see that μ has to depend on the temperature (why?) but μ is a very slowly varying function of temperature. We can make a graph of the distribution
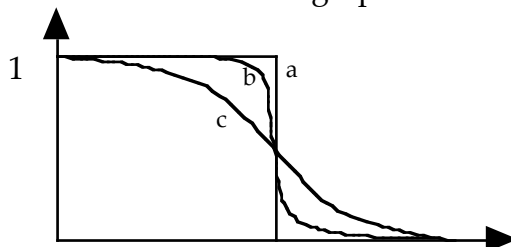
Curve a) shows the distribution when $T = 0$. It is a step function with all levels below $\mu(0)$ occupied and all levels above empty.
Curve b) shows the distribution at a higher temperature and c) at *very* high temperature. It is easy to see that μ is the energy value for which the filling

factor is exactly $1/2$. The value of μ moves very slowly towards lower energies as the temperature increases.

We will now compute μ for low temperatures (in reality for $T = 0$). We assume that we have spin $1/2$ fermions. There are two ways of doing this computation:

1) We first determine the density of states in energy. We have already done this earlier; the only modification will be to multiply with the spin factor 2 due to the two possible spin states. We get

$$g(\varepsilon) = 2 \cdot \frac{V}{(2\pi)^2} \frac{(2m)^{3/2}}{\hbar^3} \varepsilon^{1/2} = \frac{V}{2\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \varepsilon^{1/2}$$

The number of particles is given by

$$N = \sum g_i n_i \to \int_0^\infty g(\varepsilon) d\varepsilon \frac{1}{e^{(\varepsilon-\mu)/k_B T} + 1}$$

If $T = 0$, the distribution is a step function and we get

$$N = \int_0^{\mu(0)} g(\varepsilon) d\varepsilon \cdot 1 = \frac{V}{\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \int_0^{\mu(0)} \varepsilon^{1/2} d\varepsilon = \frac{V}{2\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \frac{2}{3} \mu^{3/2}(0)$$

After some manipulation we get

$$\mu(0) = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} \equiv \varepsilon_F \quad \text{the } \textit{Fermi energy}.$$

2) If we instead think of k-space at absolute zero temperature, the particles will be packed as a sphere around the origin with a certain radius k_F. We know the density of states in k-space and can then easily compute the number of particles in the sphere

$$N = 2 \cdot \frac{V}{(2\pi)^3} \cdot \frac{4\pi k_F^3}{3} = \frac{V}{\pi^2} \frac{k_F^3}{3}$$

We use

$$\varepsilon_F = \frac{p_F^2}{2m} = \frac{k_F^2 \hbar^2}{2m}$$

and immediately get

$$\mu(0) \equiv \varepsilon_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

We now can define the *Fermi temperature* as

$$T_F = \varepsilon_F / k_B$$

If we insert typical values, for instance for metallic sodium where we have one conduction electron per atom, we find that the Fermi temperature is about 70 000 K. Room temperature is VERY much less than this and in most situations we then can pretend that room temperature correspond to zero temperature. The electron gas in a metal is extremely quantum mechanical, *we cannot understand or describe a metal without quantum mechanics.*

Exercise. Compute the Fermi temperature of sodium.

8.2 Zero-point energy and heat capacity

We have

$$E = \int_0^\infty \varepsilon g(\varepsilon) d\varepsilon \cdot f_{FD}(\varepsilon)$$

For the zero-point energy, the distribution function is a step function and we have

$$E(0) = \int_0^{\mu(0)} \varepsilon g(\varepsilon) d\varepsilon$$

This gives after simple integration

$$E(0) = \tfrac{3}{5} N \mu(0)$$

In order to compute the heat capacity we need to know the temperature dependence of the internal energy. This is hard to compute. Instead we will use a more hand-waving argument. At "low" temperatures the energy interval where the distribution function changes from1 to 0 is of order $k_B T$. Only electrons in this region can be excited, electrons in lower levels are locked by those electrons that occupy in the levels above them. Thus, only a number of electrons of order $g(\mu \approx \varepsilon_F) k_B T$ can absorb thermal energy and contribute to the heat capacity. They then absorb typical energies of order $k_B T$. We then have

$$E_{thermal} \approx g(\varepsilon_F)(k_B T)^2 = \frac{3}{2} N k_B T \frac{k_B T}{\varepsilon_F}$$

where we have used

$$N = g(\varepsilon_F) \frac{2}{3} \varepsilon_F .$$

´With these approximations we get

$$C_{electron} = \frac{dE_{thermal}}{dT} = 3 N k_B \frac{T}{T_F}$$

(The correct result is $C_{electron} = \frac{\pi^2}{2} N k_B \frac{T}{T_F}$, see below in section 8.3)

We can note several interesting facts on the expression. Firstly, we have the factor T/T_F that at room temperature is of order 0.5%. The electronic heat capacity is *very* small at room temperature. This explains why metals and non-metals have essentially the same heat capacity at room temperature. Secondly, we see that the electronic heat capacity is a linear function of temperature. We can check that experimentally. At low temperatures the heat capacity for the vibrating mother atoms in the lattice is proportional to T^3 which we will show at the end of next chapter. The total heat capacity of a metal at low temperature will then be

$$C(T) = C_{lattice} + C_{electron} = A T^3 + B T$$

with known constants A and B.

If we rewrite this

$$\frac{C(T)}{T} = AT^2 + B$$

we see that if we plot experimental values of the quantity $\frac{C(T)}{T}$ against T^2 ,
we expect the measured values to lie on a straight line and we can
experimentally check the theoretically known values of the constants A and B.
The graph below shows such a plot and is a nice confirmation of the theory.
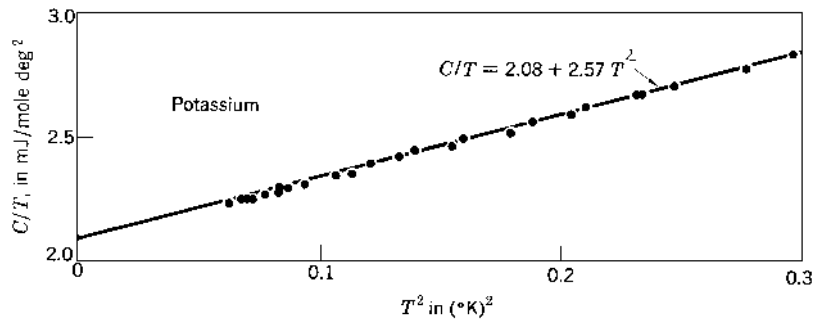
*8.3 Detailed computation of the heat capacity

We use

$$C_{el} = \frac{dE}{dT} = \int_0^\infty d\varepsilon \cdot \varepsilon g(\varepsilon) \frac{\partial f}{\partial T}$$

and

$$0 = \varepsilon_F \frac{dN}{dT} = \int_0^\infty d\varepsilon \cdot \varepsilon_F g(\varepsilon) \frac{\partial f}{\partial T}$$

Subtract the equations

$$C_{el} = \int_0^\infty d\varepsilon \cdot (\varepsilon - \varepsilon_F) g(\varepsilon) \frac{\partial f}{\partial T} \approx g(\varepsilon_F) \int_0^\infty d\varepsilon \cdot (\varepsilon - \varepsilon_F) \frac{\partial f}{\partial T}$$

where we have used that at temperatures that are small compared to the
Fermi temperature, the derivative of f is large only in a surrounding of $\varepsilon = \varepsilon_F$.
In f we exchange to first order the chemical potential to the Fermi energy,
$\mu(T) \approx \mu(0) = \varepsilon_F$. We get

$$\frac{\partial f}{\partial T} = \frac{\varepsilon - \varepsilon_F}{k_B T^2} \frac{e^{\frac{\varepsilon - \varepsilon_F}{k_B T}}}{\left(e^{\frac{\varepsilon - \varepsilon_F}{k_B T}} + 1\right)^2}$$

Let

$$x = \frac{\varepsilon - \varepsilon_F}{k_B T}$$

that gives

$$C_{el} = g(\varepsilon_F)(k_B^2 T) \int_{-\varepsilon_F / k_B T}^\infty dx \cdot \frac{x^2 e^x}{(e^x + 1)^2} \approx g(\varepsilon_F)(k_B^2 T) \int_{-\infty}^\infty dx \cdot \frac{x^2 e^x}{(e^x + 1)^2} = g(\varepsilon_F)(k_B^2 T) \frac{\pi^2}{3}$$

55

and finally we use $g(\varepsilon_F) = \dfrac{3N}{2\varepsilon_F}$ and get the result

$$C_{el} = \frac{\pi^2}{2} N k_B \frac{k_B T}{\varepsilon_F} = \frac{\pi^2}{2} N k_B \frac{T}{T_F}$$

*8.2. Dwarf stars, neutron stars and black holes

When a star has used up its nuclear fuel, it will collapse under influence of the gravitation and shrink. The star contains mainly protons and electrons. As the star shrinks, its density and thereby also the electron density and Fermi temperature increases. It becomes that high, that in spite of the star having a temperature of order 10^7 K, we can describe it as if it was at absolute zero in comparison with the Fermi temperature. There are now two kinds of energy in the star: the potential energy of the gravitation and the zero-point energy of the electrons. For the gravitational energy we have

$$E_g \propto -\frac{M^2}{R}$$

where M is the mass of the star and R its radius.

The electronic zero-point energy is, as we have seen,

$$E_e \approx N \cdot \mu(0) \propto N\left(\frac{N}{V}\right)^{2/3} \propto \frac{N^{5/3}}{R^2} \propto \frac{M^{5/3}}{R^2}$$

Where we have used that $V \propto R^3$ and $N \propto M$. The total energy then is

$$E = E_g + E_e = -A\frac{M^2}{R} + B\frac{M^{5/3}}{R^2}$$

with certain known constants A and B. If we sketch the total energy as a function of the radius of the star (do it!) we find that the energy has a minimum; we have a stable equilibrium radius. We can easily determine the equilibrium radius by putting the derivative of the total energy to zero. We then get

$$R_{equilib} \propto M^{-1/3}$$

The larger the mass of the star is, the smaller is the equilibrium radius. If we insert numerical values of the constants A and B, a dwarf star with the mass of the Sun will have an equilibrium radius of about the radius of the Earth.

However, if the mass of the star is large, larger than about 1.4 solar masses, the so-called *Chandrasekhar mass*, the zero-point energy of the electrons will get very high and some of the electrons become extreme-relativistic. For extreme-relativistic electrons the Fermi energy is not proportional to $V^{-2/3}$ but to $V^{-1/3}$ that implies that the zero-point energy will be proportional to $1/R$. We now do *not* any more have an equilibrium radius but an instable situation; the star collapses and the electrons react with the protons, forming neutrons via the process

$$e^- + p \rightarrow n + \nu_e$$
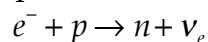
The neutral neutrinos (ν_e) that are created disappear from the star, the process is irreversible and we have now a very compact star object, a *neutron star*.
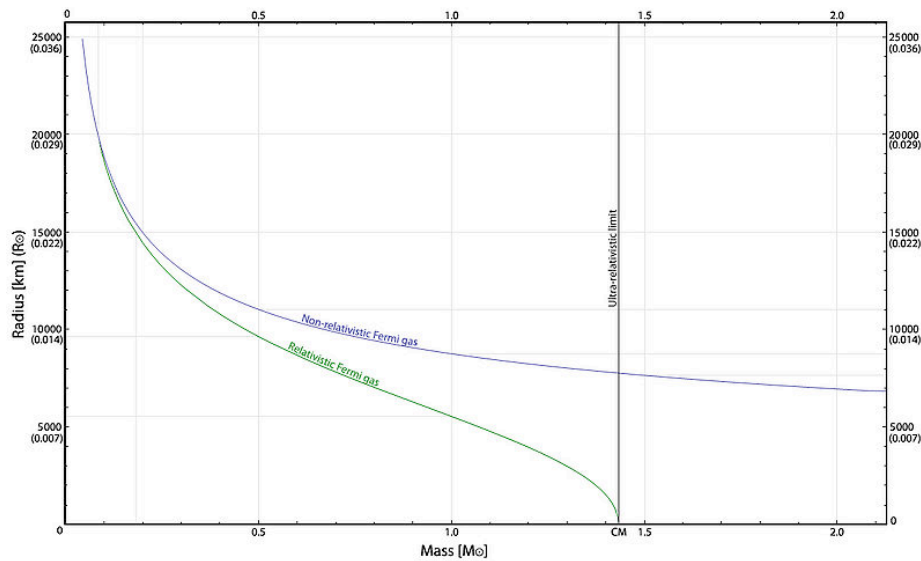
The neutrons, like the electrons are fermions and we can treat the neutron star as a FD gas. The only difference is that the neutron mass in the expression for the Fermi energy is about 2000 times heavier than the electron mass. We will again have a balance between negative gravitational energy and positive neutron zero-point energy. Again we get an equilibrium radius $R_{equilib} \propto M^{-1/3}$ but now much smaller due to the larger neutron mass. For a neutron star with a solar mass, the equilibrium radius will be about 10 km. Neutron star have been observed. They often rotate rapidly, typically with a rotation period of order a millisecond and often emit a rotating beam of electromagnetic radiation that we can observe on Earth as a "blip" when it happens to be directed towards us. Such neutron starts are called *pulsars*.

Exercise. Show that the equatorial speed of a typical pulsar is of order the speed of light!

In spite of the rapid rotation the pulsar is, due to its large mass and enormous density, almost perfectly spherical.

If a neutron star is very heavy, also the neutrons become relativistic and the star collapses, this time to a *black hole*. Normally, black holes are not created in this relatively non-dramatic way but are created in supernovas where the violent explosion compresses the central parts of the star into a black hole. The radius of a black hole is uniquely determined by its mass

$$R = 2G \frac{M}{c^2}$$

where G is the gravitational constant. The radius of a black hole with the mass of the Sun is about 1 km.

Exercise problems. Chapter 8

1. Compute numerically the Fermi energy and Fermi temperature of copper. Assume one conduction electron per atom.

9. Bose-Einstein gases

The Bose-Einstein distribution is

$$f_{BE}(\varepsilon) = \frac{1}{Be^{\varepsilon/k_B T} - 1}$$

where $B = e^{\alpha}$.

We will start with the simplest case and assume that our bosons are photons. This will lead us to a derivation of the important *Planck's law*.

9.1. Photons and Planck's law

Photons are massless bosons with spin 1. The fact that they are massless means that we must treat them relativistically but also that we get a very simple relation between momentum and energy (the dispersion relation)

$$p = \varepsilon/c$$

We begin by deriving the density of state in energy and start as usual with the density of states in k-space:

$$\frac{V}{(2\pi)^3} d^3k = \frac{V}{(2\pi)^3} \frac{1}{\hbar^3} d^3p \overset{\substack{spherical \\ symmetry}}{=} \frac{V}{(2\pi)^3} \frac{1}{\hbar^3} p^2 dp \cdot 4\pi \overset{p=\varepsilon/c}{=}$$

$$\frac{V}{2\pi^2} \frac{1}{\hbar^3} \frac{1}{c^3} \varepsilon^2 d\varepsilon$$

Thus

$$g(\varepsilon) = 2 \cdot \frac{V}{2\pi^2} \frac{1}{\hbar^3} \frac{1}{c^3} \varepsilon^2 = \frac{V}{\pi^2} \frac{1}{\hbar^3} \frac{1}{c^3} \varepsilon^2$$

where the factor of 2 is due to that the photon can have two independent polarisation directions.

The second simplification with photons is that they are massless: the number of photons in a photon gas is not conserved. We take this into account by skipping that constraint in the computation of the entropy, most simply by making $\alpha = 0$ that implies $B = 1$. For photons the BE distribution then is

$$f(\varepsilon) = \frac{1}{e^{\varepsilon/k_B T} - 1}$$

The number of photons in an infinitesimal energy interval $d\varepsilon$ then is

$$n(\varepsilon)d\varepsilon = g(\varepsilon)d\varepsilon \cdot f(\varepsilon)$$

and the distribution in energy is

$$u(\varepsilon)d\varepsilon = \varepsilon \cdot g(\varepsilon)d\varepsilon \cdot f(\varepsilon) = \frac{V}{\pi^2} \frac{1}{\hbar^3 c^3} \frac{\varepsilon^3}{e^{\varepsilon/k_B T} - 1} d\varepsilon$$

This is the famous *Planck's law*

Exercise. Show that the number density N/V of photons is proportional to T^3.
Hint: Integrate one of the expressions above.

Normally what we mean by Planck's law or the blackbody radiation law is the energy that every second leaves a small hole with area A from an oven with T. We will now derive this formula. We consider a box that contains a photon gas at temperature T.

There is a small hole with area A in the box. During one second all photons within a half-sphere with radius c will have a possibility to exit through the hole. We look at the photons in an infinitesimal volume dV at distance r from the hole and investigate the probability that they pass through the hole. The hole, as seen from this volume occupies a solid angle of
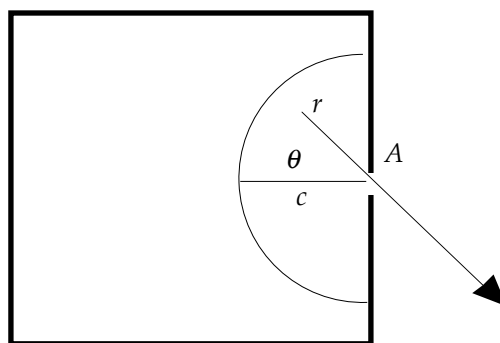
$$\Omega_A = \frac{A\cos\theta}{r^2}$$

were the cosine factor takes into account that the hole is seen from an oblique angle. The solid angle for all directions is 4π, that is the probability of exiting through the hole is

$$\frac{\Omega_A}{4\pi} = \frac{A\cos\theta}{4\pi r^2}$$

The number of particles in the energy interval $[\varepsilon, \varepsilon + d\varepsilon]$ that exit the hole during one second from the infinitesimal volume dV is then

$$\frac{n(\varepsilon)d\varepsilon}{V} dV \cdot \frac{A\cos\theta}{4\pi r^2} = \frac{n(\varepsilon)d\varepsilon}{V}\frac{A\cos\theta}{4\pi r^2}r^2 dr \cdot \sin\theta d\theta d\varphi$$

and the energy in the interval $[\varepsilon, \varepsilon + d\varepsilon]$ leaving the hole per second is

$$\varepsilon d\varepsilon\frac{n(\varepsilon)}{V}\frac{A\cos\theta}{4\pi r^2}r^2 dr \cdot \sin\theta d\theta d\varphi = \frac{u(\varepsilon)d\varepsilon}{V}\frac{A\cos\theta}{4\pi r^2}r^2 dr \cdot \sin\theta d\theta d\varphi$$

We integrate this over the entire half-sphere

$$\frac{u(\varepsilon)d\varepsilon}{V}\frac{A}{4\pi}\int_0^c dr \int_0^{\pi/2} d\theta \sin\theta\cos\theta\int_0^{2\pi} d\varphi = \frac{u(\varepsilon)d\varepsilon}{V}\frac{Ac}{4}$$

If we insert the Planck distribution that we derived earlier, we get the power (energy / time) that is emitted from the hole in the energy interval $d\varepsilon$

$$P(\varepsilon)d\varepsilon = A\frac{1}{4\pi^2\hbar^3 c^2}\frac{\varepsilon^3}{e^{\varepsilon/k_BT}-1}d\varepsilon$$

The formula us usually rewritten in frequency units using

$$\varepsilon = \hbar\omega = 2\pi\hbar f = hf$$

Thus

$$P(f)df = A\frac{2\pi h}{c^2}\frac{f^3}{e^{hf/k_BT}-1}df$$

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We get the totally emitted power by integrating over all frequencies

$$P = \int_0^\infty P(f)df = A\frac{2\pi h}{c^2}\int_0^\infty \frac{f^3}{e^{hf/k_BT}-1}df \overset{x=hf/k_BT}{=}$$

$$A\frac{2\pi h}{c^2}\left(\frac{k_BT}{h}\right)^4 \int_0^\infty \frac{x^3}{e^x-1}dx$$

It can be shown that the integral has the numerical value $\pi^4/15$ and we finally have

$$P = A\frac{2\pi^5 k_B^4}{15c^2 h^3}T^4 = A\sigma_{SB}T^4$$

This is *Stefan-Boltzmann's law*. If we insert numerical values of the constants we can compute the value of Stefan-Boltzmann's constant

$$\sigma_{SB} = \frac{2\pi^5 k_B^4}{15c^2 h^3} \approx 5.67\cdot 10^{-8}\,\text{Wm}^{-2}\text{K}^{-4}$$

in perfect agreement with the experimental value.

It is also interesting to compute the maximum of the Planck distribution, the most probable frequency. We then search for the maximum of the function

$$F(f) = \frac{f^3}{e^{hf/k_BT}-1}$$

We set the derivative to zero

$$0 = 3f^2\left(e^{hf/k_BT}-1\right) - f^3 e^{hf/k_BT}\cdot h/k_BT$$

or after having divided out the uninteresting solution $f=0$ and defined $x = hf/k_BT$ we get

$$(3-x)e^x = 3$$

This is a transcendental equation that we can solve easily numerically for instance on a calculator using the updating scheme $x \leftarrow 3(1-e^{-x})$ and starting the iteration with a preliminary $x = 1$. The iterations converge very quickly and give

$$x_{max} \approx 2.82144\ldots$$

Thus

$$f_{max} = \frac{x_{max}k_B}{h}T \approx 5.88\cdot 10^{10}[Hz/K]\cdot T$$

that is the frequency of the maximum increases linearly with temperature. This is *Wien's law*. It expresses the everyday experience that if you heat a piece of iron it first becomes dark red (low frequencies), then red, then orange, white, and finally bluish white (high frequencies). Actually it is possible to determine the temperature of a piece of iron by looking at its colour. Astronomers determine the temperature of distant stars by observing their colour.

Due to the exponent 4 in Stefan-Boltzmann's law a blue super-giant star, with a surface temperature of maybe 60 000 K and a radius that is about 4 times the radius of the Sun, will emit a much larger power that the Sun that has a surface temperature of about 6 000 K. The mass of the blue giant is about 100 times that of the Sun. As the emitted power comes from a transformation of

the mass of the star to energy, a simple calculation shows that the blue giant will have a lifetime of order 1/1 000 of that of the Sun or about 5 million years that is a very short time in the cosmic time scale.

If we look out in the universe in any direction we will see the photons that once were created in the Big Bang. It is an almost perfect Planck radiation with a temperature of 2.726 K.

COSMIC MICROWAVE BACKGROUND SPECTRUM FROM COBE
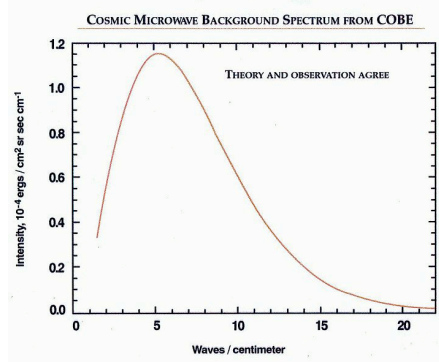
9.2. Phonons and the Debye model

We will now study lattice vibrations in a solid (crystal). We know that we can represent the harmonic oscillator with energy quanta with energy $\hbar\omega$. We can interpret these quantas as massless particles or *phonons* or sound waves in the crystal. We can now by analogy with the photons exploit the theory we have developed for photons with some minor changes:

1) Sound waves in a solid can be transversal waves with two possible polarisation directions or longitudinal waves. The two types of waves can have different propagation speeds c_T and c_L.

2) The dispersion relation is different. For small values of the wave number $k = \dfrac{2\pi}{\lambda}$ (long wavelengths) we have $\varepsilon = \hbar\omega = \hbar c_{(T,L)}k$
This is however *not* correct for larger wave numbers (short wavelengths).

We will anyhow use the linear approximation for the dispersion relation and then have a density of state in energy

$$g(\varepsilon) = \frac{V}{2\pi^2}\frac{1}{\hbar^3}\left(\frac{2}{c_T^3} + \frac{1}{c_L^3}\right)\varepsilon^2$$

We introduce an average speed of sound and three polarisations (two transversal and one longitudinal) by

$$\frac{3}{c_S^3} \equiv \left(\frac{2}{c_T^3} + \frac{1}{c_L^3}\right)$$

We then can write the density of states on a form that is very similar to the one we had for photons except that the spin factor 2 now is 3 and the speed of light is now the average speed of sound c_S.

$$g(\varepsilon) = \frac{V}{2\pi^2}\frac{1}{\hbar^3}\frac{3}{c_S^3}\varepsilon^2$$

3) There are only a finite number of phonon modes in a solid. The solid consists of N atoms that can each vibrate in 3 directions. If we had used the correct dispersion relation this would have been taken into account automatically. In the Debye model, we simulate this by saying that we only integrate up to a suitable "cut-off" frequency ω_D, the *Debye frequency* defined by

$$3N = \int_0^{\hbar\omega_D} g(\varepsilon)d\varepsilon = \frac{V}{2\pi^2}\frac{1}{\hbar^3}\frac{3}{c_S^3}\int_0^{\hbar\omega_D}\varepsilon^2 d\varepsilon = \frac{V}{2\pi^2}\frac{\omega_D^3}{c_S^3}$$

that gives the correct number of phonon modes.

For the total internal energy we have

$$E = \int_0^{\hbar\omega_D} g(\varepsilon)\frac{\varepsilon^3}{e^{\varepsilon/k_B T}-1}d\varepsilon = \frac{V}{2\pi^2}\frac{1}{\hbar^3}\frac{3}{c_S^3}(k_B T)^4\int_0^{\hbar\omega_D/k_B T}\frac{x^3 dx}{e^x-1} = 9N\frac{(k_B T)^4}{(\hbar\omega_D)^3}\int_0^{\hbar\omega_D/k_B T}\frac{x^3 dx}{e^x-1}$$

In the last step we have used the definition of the Debye frequency. There are two interesting special cases where we can compute the integral explicitly:

1) *Low temperatures*. We then replace the upper limit in the integral by infinity and the integral then has a definite numerical value ($\pi^4/15$). We see that

$$E \propto T^4 \quad \Rightarrow \quad C_V \propto T^3$$

The heat capacity is proportional to the third power of the temperature something that we have used earlier and that agrees extremely well with experiment.

2) *High temperatures*. The upper integration limit the approaches zero. We can Taylor expand the denominator in the integrand:

$$e^x - 1 = 1 + x + \ldots - 1 \approx x.$$

The total integrand then becomes simply x^2 and we can perform the integration that gives

$$E = 9N\frac{(k_B T)^4}{(\hbar\omega_D)^3}\int_0^{\hbar\omega_D/k_B T} x^2 dx = 9N\frac{(k_B T)^4}{(\hbar\omega_D)^3}\frac{1}{3}\left(\frac{\hbar\omega_D}{k_B T}\right)^3$$

Cancelling common factors gives us the well-known high temperature result

$$E = 3Nk_B T \quad \Rightarrow \quad C_V = 3Nk_B$$

or Dulong-Petit's law.

It is worth noting that the scale temperature in the model is the *Debye temperature* $T_D = \dfrac{\hbar\omega_D}{k_B}$

*9.3 The Bose-Einstein condensation

We close by studying a gas of massive, non-relativistic bosons at such low temperature that it has to be described by the BE distribution. To simplify we study bosons with spin 0, in the real world we could use helium-4.

The density of states in this case is

$$g(\varepsilon) = \frac{V}{(2\pi)^2} \frac{(2m)^{3/2}}{\hbar^3} \varepsilon^{1/2}$$

As the particles are massive we have to use the full BE distribution

$$f_{BE}(\varepsilon) = \frac{1}{Be^{\varepsilon/k_B T} - 1}$$

The number of particles in the gas is

$$N = \sum_i n_i = \sum_i g_i f_i \rightarrow \int_0^\infty d\varepsilon\, g(\varepsilon) f(\varepsilon) =$$

$$\frac{V}{(2\pi)^2} \frac{(2m)^{3/2}}{\hbar^3} \int_0^\infty d\varepsilon \frac{\varepsilon^{1/2}}{Be^{\varepsilon/k_B T} - 1}$$

As usual we extract the physics from the integral by the variable substitution $y^2 = \varepsilon/k_B T$ or $\varepsilon = y^2 \cdot k_B T$. We then get

$$N = \frac{V}{2\pi^2} \frac{(2m)^{3/2}}{\hbar^3} (k_B T)^{3/2} \frac{\pi^{1/2}}{4} \cdot \frac{4}{\pi^{1/2}} \int_0^\infty dy \frac{y^2}{Be^{y^2} - 1} \qquad (**)$$

If we look back on page 42, we see that the factor in the beginning of the expression is precisely the classical partition function and we can write
$$N = ZF(B)$$
with
$$F(B) = \frac{4}{\pi^{1/2}} \int_0^\infty dy \frac{y^2}{Be^{y^2} - 1}$$

Given N, T, and V, this determines the value of B. At high temperature or low density (N/V) that value of B is large, we then can neglect the term –1 in the denominator of the integral and get back the MB result.

However, at low temperatures (or high particle densities) we get a paradox. The smallest possible value of B is 1 and the function F has a finite value for B = 1. Explicitly $F(1) = 2.612\ldots$ This means that for fixed N and V there is a smallest value of the temperature, T_B, for which we can have the relation (**)

$$N = \frac{V}{2\pi^2} \frac{(2m)^{3/2}}{\hbar^3} (k_B T_B)^{3/2} \frac{\pi^{1/2}}{4} \cdot 2.612$$

or

$$T_B = \left(\frac{N}{V} \frac{1}{2.612} \right)^{2/3} \frac{2\pi\hbar^2}{k_B m}$$

It seems as if we cannot have a lower temperature than T_B that is evidently nonsense.

The reason for our problem is that in our approximation, the density of states goes to zero as the energy goes to zero. We have no particles in the ground

stat! On the other hand we see that the filling factor is very large when the temperature $T \to 0$ and $B \to 1$. We can resolve the problem by separating out $\varepsilon = 0$, the ground state, and treat all the other levels as before with the density of states. Assume that the number of particles in the ground state is N_0. We then have for temperatures less than T_B

$$N = N_0 + \frac{V}{2\pi^2} \frac{(2m)^{3/2}}{\hbar^3} (k_B T)^{3/2} \frac{\pi^{1/2}}{4} \cdot F(1)$$

$$= N_0 + \left(\frac{T}{T_B}\right)^{3/2} \frac{V}{2\pi^2} \frac{(2m)^{3/2}}{\hbar^3} (k_B T_B)^{3/2} \frac{\pi^{1/2}}{4} \cdot F(1) =$$

$$N_0 + N\left(\frac{T}{T_B}\right)^{3/2}$$

or

$$N_0 = N\left(1 - \left(\frac{T}{T_B}\right)^{3/2}\right)$$

At $T = 0$ all the particles are in the ground state. But also at a slightly higher temperature a large fraction of the particles are in the ground state. This is called a *Bose-Einstein condensation*. These particles do not contribute to the internal energy and heat capacity. For temperatures above T_B, the *Bose-Einstein temperature*, there are a negligible number of particles in the ground state. Earlier the BE condensation was considered as a quantum mechanical curiosity but in later years people have succeeded in creating and study quite large Bose-Einstein condensates and there are some expectations that such system could be used in the quantum computer of the future.
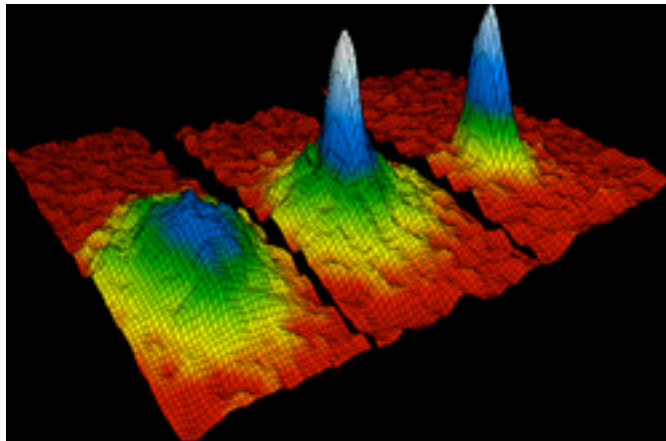
Velocity-distribution data of a gas of rubidium atoms, confirming the discovery of a new phase of matter, the Bose–Einstein condensate.

Exercise problems. Chapter 9

1. Compute numerically the Fermi energy and Fermi temperature of copper. Assume one conduction electron per atom.

2. If you use the computation on page 52 with particles with speed v, you can show that the number of particles that per second passes a hole with area A is $\dfrac{nvA}{4}$ where n is the particle density. Assume you have a bicycle tyre with an excess pressure of two times normal atmospheric pressure. Assume that you have a small circular hole on the tyre with diameter 10 µm. How long do you have to wait until the pressure in the tyre has been halved?

3. A keratin thread in wool can be described as a chain of oblong molecules as shown in the figure.
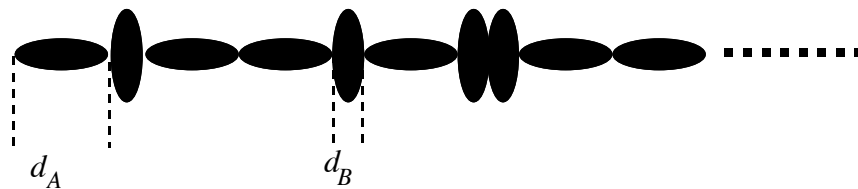

Each molecule can have one of two possible orientations: along the chain or perpendicular to it. A molecule that is oriented along the chain has energy E_A and length d_A. A molecule that is oriented perpendicular to the chain has energy E_B and width d_B. Determine the average length of a keratin thread that consists of N molecules at temperature T.
Describe what happens with the length at high and low temperatures.
Assume that $E_A < E_B$.

4. A very simplified model of the way the double helix in a DNA molecule opens up at different temperatures is the following. A "zipper" consists of N pairs of links (see figure). N is a large number. A closed link represents an energy of 0, an open link the energy $\varepsilon > 0$. The zipper can only be opened from the left, that is to open the link # i, all link pairs 1, 2 .. $i-1$ must be open. Each open

länkpar

link pair can be in G different positions/states (due to that the free links can rotate), this means that the degeneracy when i link pairs are open is G^i. We assume that the last link pair cannot be opened (the chain then falls apart).
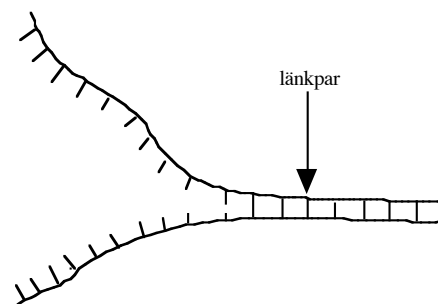
a) Write down the partition function of the system and compute the sum.

Hint: Introduce the variable $x = Ge^{-\varepsilon/kT}$.

b) Compute the average number of open link pairs as a function of temperature and as a function x.

c) Make a rough sketch showing how the average number of open links varies as a function of x or better the temperature.

Hint: Computations are simpler if you let $N \to \infty$.

Answers:

1.2. Temperature of order 500°C, pressure about 25 times normal pressure. In the second process the pressure is about 10 normal pressure.

2.1. 156

2.2. $11/36 \approx 0.3$

2.4. a) $1 - p \cdot dx$ b) $(1 - p \cdot dx)^N p \cdot dx$ c) $e^{-px} p \cdot dx$ d) $\langle x \rangle = 1/p$

3.2. 6.1 kJ/K, 1.3 kJ/K

3.3. 0.18 kJ/K

4.4. 2.6 $\dfrac{\mu B}{k_B}$

4.5. 5.7 µK to 22 mK; 91 kHz

4.6. ≈ 0.3 meV

6.1. ≈ 500 m/s

6.2. c) $<<100$ K

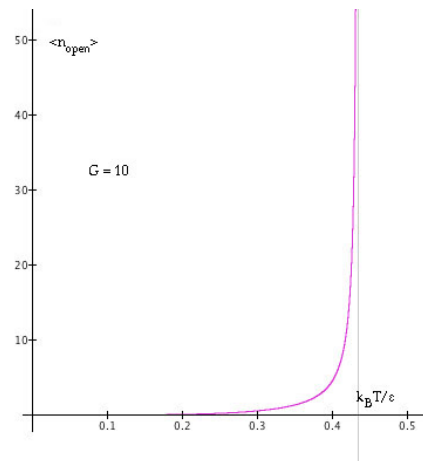6.3. $p = \dfrac{x N k_B T}{V}$ $c = y N k_B$

8.1. 7 eV; 80 000 K

9.1. Some days.

9.2. $\langle L \rangle = N \dfrac{d_A e^{-E_A/kT} + d_B e^{-E_B/kT}}{e^{-E_A/kT} + e^{-E_B/kT}}$

9.3.
$$\langle n_{open} \rangle = \dfrac{x}{1-x} \ ; x << 1 \ (T \text{ small}) \Rightarrow \langle n_{open} \rangle \propto x; x \rightarrow 1 \quad (T \text{ large}) \Rightarrow \langle n_{open} \rangle \rightarrow N$$

STATISTICAL MECHANICS REPETITION QUESTIONS Autumn 2009

1. Explain what is meant by thermodynamical equilibrium?
2. Formulate the first law. What is the meaning of the different terms ?
3. Give examples of intensive and extensive parameters.
4. Define macrostate och microstate.
5. Define entropy. Give some reasons for defining entropy in this way.
6. Formulate the second law (any of the formulations). Motivate why the entropy is maximum at thermodynamical equilibrium.
7. Define temperature using the entropy. Motivate the definition by showing that it implies that energy flows spontaneously from a warm to a cold object.
8. Derive the historic-classical definition of entropy.
9. Why do we need a quantum mechanical description of the world in order to get a correct theory of statistical mechanics.
10. Study a system of N distinguishable particles and total energy E with non-degenerate energy levels. Determine the occupation numbers at thermodynamical equilibrium. Define the Boltzmann factor and the partition function. What is the entropy?
11. Express the energy E using the partition function Z.
12. What is the implication of the equipartition theorem? Give some simple applications.
13. Compute energy, heat capacity and entropy for a two-level system.
14. Define Helmholtz' free energy and indicate how the entropy can be computed using it.
15. Describe qualitatively cooling by adiabatic demagnetisation.
16. Compute energy, heat capacity, and entropy for a system of N one-dimensional harmonic oscillators.
17. Explain the small heat capacity of diamond och graphite.
18. Derive the density of states in energy for an ideal gas of spinless, massive and non-relativistic atoms.
19. Give the filling factor of respectively FD, MB, and BE gases.
20. Start with Helmholtz' free energy for an ideal MB gas and derive the gas law.
21. What extra contributions to the heat capacity do you get for an ideal diatomic gas? What contributions can be negleced and why?
22. Give the properties of a FD gas. Why is the electronic heat capacity of such a gas very small?
23. Sketch a derivation of Planck's law.

24. Plancks law can be formulated $P(f)df = A\dfrac{2\pi h}{c^2}\dfrac{f^3}{e^{hf/k_BT}-1}df$. Indicate how you derive Stefan-Boltzmann's T^4 law and Wien's law from this expression.

25. Give a qualitative description of the Debeye modell and its results.