Lecture 3

I. THE PARTITION FUNCTION OF A SYSTEM

Thus far we have considered the so-called single particle partition function, defined as $Z_{sp} = \sum\limits_i g_i e^{-\frac{\epsilon_i}{k_B T}}$, and then got $F = -Nk_B T \ln Z_{sp}$. However, it is also possible to define a partition function for the whole system. For distinguishable particles we can define

$$Z_N = (\sum_i g_i e^{-\frac{\epsilon_i}{k_B T}})^N = Z_{sp}^N \tag{1}$$

and we now get $F = -k_B T \ln Z_N$. Similarly U, and S are the same as before, apart from the factor of N. The reason this works can be seen by writing

$$Z_N = \sum_i g_i e^{-\frac{\epsilon_i}{k_B T}} \times \sum_j g_j e^{-\frac{\epsilon_j}{k_B T}} \times \sum_k g_k e^{-\frac{\epsilon_k}{k_B T}} \times \ldots\ldots.. \tag{2}$$

where each sum is for a different particle. Note that the $\epsilon_i, \epsilon_j, \epsilon_k$..... are independent of each other (because the particles are separate and distinguishable) and so this is equivalent to

$$Z_N = \sum_l g_l e^{-\frac{E_l}{k_B T}} \tag{3}$$

where E_l is one of the energy levels of the entire system of particles. Thus for distinguishable particles

$$Z_N = Z_{sp}^N \tag{4}$$

$$U = \frac{\partial \ln Z_N}{\partial(\frac{-1}{k_B T})} = k_B T^2 \frac{\partial \ln Z_N}{\partial T} \tag{5}$$

$$S = k_B \ln Z_N + k_B T \frac{\partial \ln Z_N}{\partial T} \tag{6}$$

$$F = -k_B T \ln Z_N \tag{7}$$

You are probably asking yourself why we bothered to do this. What was wrong with our formulae before? Well, nothing really. It's just that when we go on to deal with indistinguishable (rather than distinguishable) particles that obey Boltzmann statistics we will find that they also obey equations (5) to (7). However, for indistinguishable particles there is a different relationship between the single particle partition function, and that for the whole system. We will deal with this in the next lecture.

II. EXAMPLE 1 - A PARAMAGNET

Up until now everything has been quite general, and no doubt you are starting to wonder what is the relevance of all these pages of formulae to the price of sugar. So, before you get lost in the abstractness of it all, lets start to apply these formulae to some relatively simple physical systems. I have picked two - a paramagnetic solid, and an array of simple harmonic oscillators. You will also encounter these again later in your course - when you cover solid state physics.

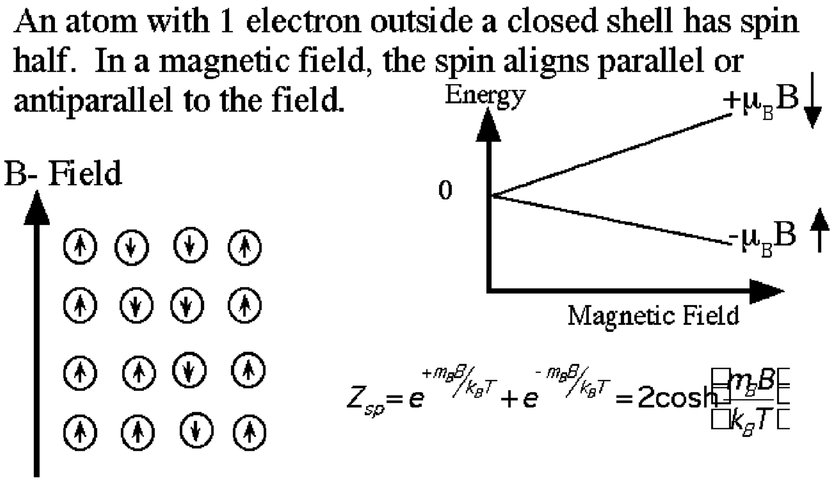

Figure 1: The paramagnet is an array of particles with net angular momentum. In this simple case $J = S = 1/2$, and in the presence of a magnetic field the spins align parallel or antiparallel with the field, with energies $\pm\mu_B B$

The paramagnet consists of a set of atoms in a crystal lattice. Because the atoms are situated at particular positions we can tell which is which - that is to say they are distinguishable because they are localised. Now, suppose each atom has angular momentum J. You will recall from your study of quantum mechanics that this means that the z component of the angular momentum can take on all the values from $-m_J$ to $+m_J$, and the state is $(2J+1)$ degenerate. For simplicity, let's assume $J = S = 1/2$, so the state is only doubly degenerate. When we apply a magnetic field, B, the degeneracy is lifted, and the two states shift in energy by $\pm g\mu_B m_J B = \pm\mu_B B$ (here g is the g-factor, and μ_B the Bohr magneton). The energy levels are shown in Fig. 1.

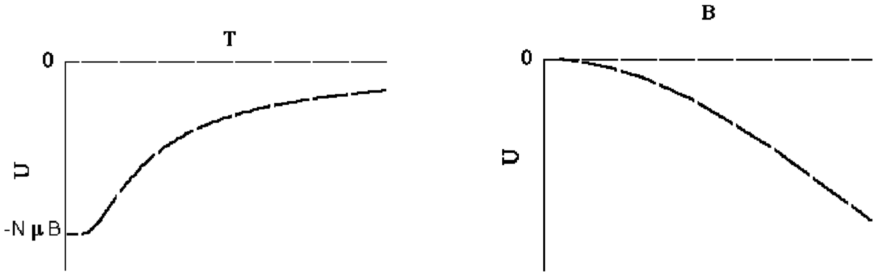

Figure 2: (a) The internal energy as a function of temperature. At low T it is $-N\mu_B$, with 0 energy taken to be the high temperature limit. (b) Internal energy as a function of magnetic field, at a temperature of $T = \mu_B/k_B$

Now, what's the single particle partition function? Well, in this particular case it's easy, as there are only two states (this is a bit like our first example of tossing coins, but now one of the states - the head or the tail, whichever we chose, has more energy than the other). So

$$Z_{sp} = e^{\frac{-\mu_B B}{k_B T}} + e^{\frac{+\mu_B B}{k_B T}} = 2\cosh\left(\frac{\mu_B B}{k_B T}\right) \tag{8}$$

I have claimed that we can get all the thermodynamic functions from this partition function. As examples, we will derive the internal energy, the specific heat, the entropy and the magnetisation. First the internal energy. Using equation (5)

$$U = N k_B T^2 \frac{\partial \ln Z_{sp}}{\partial T} = N k_B T^2 \frac{\partial}{\partial T}\left(\ln 2 + \ln\cosh\frac{\mu_B B}{k_B T}\right) = -N\mu_B B \tanh\left(\frac{\mu_B B}{k_B T}\right) \tag{9}$$

The internal energy as a function of T and B is shown in Fig.2.

The heat capacity can be found by differentiating the internal energy with respect to temperature. I leave it as an exercise (it is on the problem sheets) for you to demonstrate that:

$$C = \frac{\partial U}{\partial T} = N k_B \left(\frac{\theta}{T}\right)^2 \frac{e^{\frac{\theta}{T}}}{(e^{\frac{\theta}{T}}+1)^2} \qquad \text{where} \qquad \theta = \frac{2\mu_B B}{k_B} \tag{10}$$

Notice the limiting forms of the heat capacity, i.e.

$$C \to\propto \frac{1}{T^2} \qquad \text{as} \qquad \mathrm{T} \to \infty \tag{11}$$

$$C \to\propto \frac{1}{T^2} e^{\frac{-\theta}{T}} \qquad \text{as} \qquad \mathrm{T} \to 0 \tag{12}$$

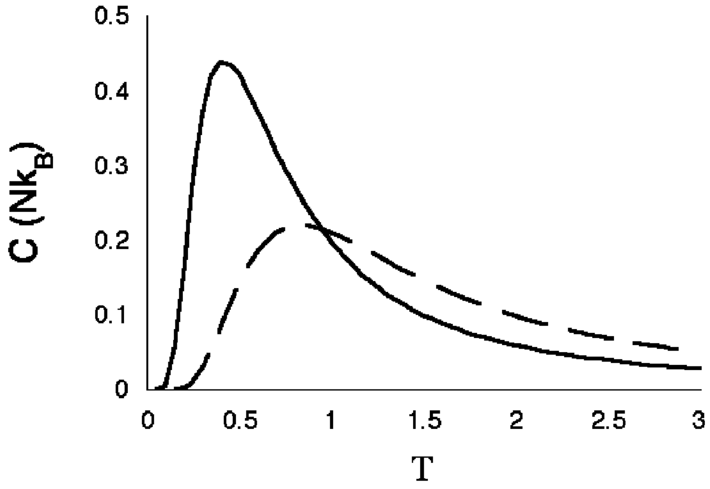

Figure 3: Heat capacity of the paramagnet for two different magnetic fields - the full line is for 1 Tesla, the dotted line is 2 Tesla. Temperature in units of μ_B/k_B

The heat capacity for two different magnetic fields is plotted in Fig. 3. Note that we predict a peak in the specific heat due to the magnetic spins which depends on the applied field. This is called the Schottky Anomaly, and can actually be observed in real systems. Having predicted the behaviour of U and C from the partition function, let us turn our attention to the entropy, using equation (6):

$$S = Nk_B \ln Z_{sp} + Nk_B T \frac{\partial \ln Z_{sp}}{\partial T} = Nk_B \ln \left[2\cosh\left(\frac{\mu_B B}{k_B T}\right)\right] - \frac{N\mu_B B}{T} \tanh\left(\frac{\mu_B B}{k_B T}\right) \tag{13}$$

And the limiting values of the entropy are:

$$\text{When} \qquad \mathrm{k_B T} \gg \mu_\mathrm{B}\mathrm{B}, \qquad \mathrm{S} \rightarrow \mathrm{Nk_B} \ln 2 \qquad \text{and} \qquad \mathrm{k_B T} \ll \mu_\mathrm{B}\mathrm{B}, \qquad \mathrm{S} \rightarrow 0 \tag{14}$$

This is exactly what we would expect. At very low temperatures, all of the electrons must be in the lower state. There is only one way for all of them to be there (just like there is only one way of getting 10 heads when we flip a coin 10 times). So, $W = 1$, and $S = k_B \ln 1 = 0$. This is an example of the third law of thermodynamics, which states that the entropy of a system in thermodynamic equilibrium tends to zero as the temperature tends to zero. On the other hand, at extremely high temperatures $k_B T$ is very large compared to the magnetic splitting between the levels, and in the limit of the temperature tending to infinity, the magnetic splitting might as well not be there. In this case we are back to our normal coin tossing again - each state is equally likely - we expect half to be in the upper level, and half in the lower level. We also know the number of ways this can happen, because we worked it out for the coins (see the notes from Lecture 1). Convince yourself that this leads to an entropy of $Nk_B \ln 2$.

Thus far we have derived U, C, S from the partition function. The last parameter I promised to derive was the magnetisation. There is rather an elegant way of doing this, which will, I hope, make you realise the importance of the free energy, F, which we haven't yet used. From our knowledge of thermodynamics we know that for a magnetic system

$$dF = -MdB - SdT \tag{15}$$

$$M = -\left(\frac{\partial F}{\partial B}\right)_T = +Nk_B\left(\frac{\partial \ln Z_{sp}}{\partial B}\right)_T \tag{16}$$

Convince yourself that this leads to

$$M = N\mu_B \tanh\left(\frac{\mu_B B}{k_B T}\right) \tag{17}$$

In the limit of weak fields (i.e. $B \to 0$) this yields Curie's law of paramagnetism:

$$M = \frac{N\mu_B^2 B}{k_B T} \tag{18}$$

Although you may not have thought of it in this way before, Curie's law is actually the equation of state of the magnetic system - it links the three variables (M, B, T) just like the EOS of a gas in its usual form links (P, V, T). This is an important characteristic of the free energy F - it leads easily to the normal form of the equation of state of a system. Of course, we will see later on how the partition function and F lead to the ideal gas EOS - we have not covered that so far because the form of the partition function for the gas is slightly more involved - but don't worry, we will get there soon!

III. EXAMPLE 2 - THE SIMPLE HARMONIC OSCILLATOR

The paramagnet was a very simple system, insomuch that it only had two levels. We now turn our attention to a localised array (i.e. distinguishable) of 1-dimensional SHOs. This time there are an infinite number of energy levels:

$$E_n = (n + \frac{1}{2})h\nu \tag{19}$$

It is trivial to show that the single particle partition function is now a geometric progression

$$Z_{sp} = e^{-\frac{h\nu}{2k_B T}} \sum_{n=0}^{\infty} e^{\frac{-nh\nu}{k_B T}} = \frac{e^{-\frac{h\nu}{2k_B T}}}{1 - e^{-\frac{h\nu}{k_B T}}} \tag{20}$$

This time, I will just state the internal energy and then leave the derivation of the heat capacity (see the problem sheet) as an exercise for both your enjoyment and edification. Given the partition function above we find

$$U = Nk_BT^2 \frac{\partial \ln Z_{sp}}{\partial T} = \frac{Nh\nu}{2} + \frac{Nh\nu}{e^{\frac{h\nu}{k_BT}} - 1} \tag{21}$$

Notice the high temperature limit:-

$$U \to Nk_BT \qquad \text{as} \qquad T \to \infty \tag{22}$$

as we would expect by equipartition of energy. The specific heat of the system can be shown to be:

$$C = \frac{dU}{dT} = Nk_B \left(\frac{\theta}{T}\right)^2 \frac{e^{\frac{\theta}{T}}}{(e^{\frac{\theta}{T}} - 1)^2} \qquad \text{where} \qquad \theta = \frac{h\nu}{k_B} \tag{23}$$

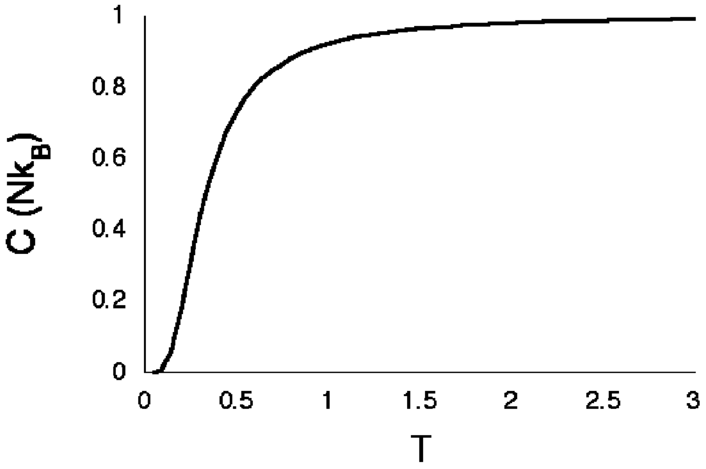

Figure 4: Heat capacity of an array of simple harmonic oscillators. Temperature in units of θ - see text for definition.

Note the similarity with the form of the specific heat for the paramagnet (a - instead of a +). It is plotted as a function of temperature below. Einstein used this model (extending it to 3 dimensions) to show that the specific heat of a solid should tend to zero at low temperatures. As you can see, his model predicts an exponentially decreasing heat capacity as the temperature drops. Next year you will find out that Einstein's model doesn't work(!)

for a solid - the heat capacity actually falls off as T^3: Einstein's assumption that all the oscillators are independent is not correct - they are coupled together, and this makes the difference to the low-temperature form of the heat capacity. On the other hand, the model is a good description of the vibrational component of the specific heat of a diatomic molecule, more of which later.

IV. SUMMARY OF LECTURE 3

1) For distinguishable particles, we can define a partition function for the system, Z_N, which is related to the single particle partition function by $Z_N = Z_{sp}^N$.

2) In terms of the partition function of the system, the thermodynamic variables become:

$$U = k_B T^2 \frac{\partial \ln Z_N}{\partial T} \tag{24}$$

$$S = k_B \ln Z_N + k_B T \frac{\partial \ln Z_N}{\partial T} \tag{25}$$

$$F = -k_B T \ln Z_N \tag{26}$$

The above arrangement is convenient, as we will show later on that it holds for indistinguishable particles as well (but in that case Z_N is related to the single particle partition function in a different way).

3) The single particle partition function for a spin -1/2 paramagnet is:

$$Z_{sp} = 2\cosh\left(\frac{\mu_B B}{k_B T}\right) \tag{27}$$

Using this we can work out the internal energy, specific heat, entropy, magnetisation etc. For example, we found:

$$C = N k_B \left(\frac{\theta}{T}\right)^2 \frac{e^{\frac{\theta}{T}}}{(e^{\frac{\theta}{T}}+1)^2} \qquad \text{where} \qquad \theta = \frac{2\mu_B B}{k_B} \tag{28}$$

and

$$M = N\mu_B \tanh\left(\frac{\mu_B B}{k_B T}\right) \qquad \text{and} \quad \text{when} \qquad B \to 0 \qquad M = \frac{N\mu_B^2 B}{k_B T} \tag{29}$$

4) For a localised array of SHOs,

$$Z_{sp} = \frac{e^{-\frac{h\nu}{2k_B T}}}{1 - e^{-\frac{h\nu}{k_B T}}} \tag{30}$$

Again we can use this to work out all of the thermodynamics - for example the heat capacity is:

$$C = Nk_B \left(\frac{\theta}{T}\right)^2 \frac{e^{\frac{\theta}{T}}}{(e^{\frac{\theta}{T}} - 1)^2} \qquad \text{where} \qquad \theta = \frac{h\nu}{k_B} \tag{31}$$

5) The most important point is that for any system, all we need to do is write down the partition function then we know <u>all</u> of the thermodynamics.