

Chapter 4

Distinguishable particles

Let us now consider atoms that are *fixed* in a crystal. This means that they are *distinguishable*, even if otherwise identical (which we assume they are).

We make some assumptions:

- There are quantised energy levels with energy \mathcal{E}_i for each atom. This is a reasonable assumption.
- There is no degeneracy, so each state has a distinct energy \mathcal{E} . This is actually not such a reasonable assumption, but is a useful simplification for a starting analysis like this one. This assumption will be relaxed later.
- The system is isolated from its environment, which is achievable.
- There are small atom-atom interactions to allow the flow of energy through the system, but the interactions are small on the scale of the energies of individual atoms. This is a reasonable assumption.

Suppose that there are N particles, and that the total system has energy U . This total energy U is distributed among the particles by having a certain number of particles with energy \mathcal{E}_1 , another number with energy \mathcal{E}_2 and so on. We denote these *occupation numbers* by n_1, n_2 , etc. We need to relate the macroscopic U and N to the microscopic \mathcal{E}_i and n_i :

$$N = \sum_i n_i \tag{4.1}$$

$$U = \sum_i \mathcal{E}_i n_i \tag{4.2}$$

Note that the two sums above are over all the *energy levels*. In Guénault's discussion (chapter 2, section 1), he takes the sum over the *states*. In our case, we are assuming that each state has a distinct energy, so we are *also* effectively taking the sum over all the states. [Later (when we relax the condition that each state has a distinct energy), we will take steps to account for the fact that more than one state may have the same energy, so we will still be effectively taking the sum over all the states.]

A convenient definition of the *macrostate* of this system is the distribution $\{n_i\}$. By analogy with and/or extension of (3.2), we can write down the expression for the occupation of each macrostate:

$$\Omega = \frac{N!}{n_1! n_2! n_3! \dots n_i!} = \frac{N!}{\prod_i n_i!} \quad (4.3)$$

4.1 The most probable macrostate for distinguishable particles

Now that we have an expression for Ω in terms of n_i , we want to find the most probable distribution n_i , i.e., we want to find the n_i that maximises Ω . We will use the “standard tactic” (well, we have already used it once...) of working with $\ln \Omega$ so that we can use Stirling’s formula. Taking logs of (4.3) we get:

$$\begin{aligned} \ln \Omega &= \ln N! - \sum_i \ln n_i! \\ &\approx (N \ln N - N) - \sum_i (n_i \ln n_i - n_i) \end{aligned} \quad (4.4)$$

Equation 4.4 may look reasonably innocuous, but is in fact much harder to maximise than our earlier coin-game example as now Ω is a function of many variables. What we have to do now is perform the maximisation, subject to the two *constraints*:

$$N = \text{const} : \quad \sum_i dn_i = 0 \quad (4.5)$$

as the total number of particles remains constant, and

$$U = \text{const} : \quad \sum_i \mathcal{E}_i dn_i = 0 \quad (4.6)$$

since the total internal energy is constant (which was one of the assumptions we made when setting up the system). Luckily for us, the necessary mathematics to handle a problem like this was worked out by Joseph-Louis Lagrange (1736–1813), and is called *Lagrange’s Method of undetermined multipliers*.

$$d(\ln \Omega) = -d\left(\sum_i n_i \ln n_i - n_i\right) = -\sum_i dn_i \left(\ln n_i + \frac{n_i}{n_i} - 1\right) = 0 \quad (4.7)$$

so

$$\sum_i \ln n_i dn_i = 0 \quad (4.8)$$

We have three things that must be zero simultaneously, so we are perfectly at liberty to multiply two of them by arbitrary constants α and β :

$$\sum_i \ln n_i dn_i = 0 \quad \alpha \sum_i dn_i = 0 \quad \beta \sum_i \mathcal{E}_i dn_i = 0 \quad (4.9)$$

We can combine these three expressions to write our overall constrained maximisation problem as

$$\sum_i (\ln n_i + \alpha + \beta \mathcal{E}_i) dn_i = 0 \quad \forall \alpha, \beta \quad (4.10)$$

The only way that this can be solved is for every term in the sum to be zero, i.e.

$$\ln n_i + \alpha + \beta \mathcal{E}_i = 0 \quad \forall i, \text{ but specific } \alpha, \beta \quad (4.11)$$

(where ' $\forall i$ ' just means "for all i "). This rearranges to $\ln n_i = -\alpha - \beta \mathcal{E}_i$ which gives an exponential form for n_i :

$$\begin{aligned} n_i &= e^{-\alpha - \beta \mathcal{E}_i} \\ &= A e^{-\beta \mathcal{E}_i} \end{aligned} \quad (4.12)$$

where we have introduced $A \equiv e^{-\alpha}$. Equation 4.1 becomes

$$N = A \sum_i e^{-\beta \mathcal{E}_i} \quad (4.13)$$

A is derived from α and α was introduced as the multiplier for the term that stipulates that the particle number is fixed. So, A is a constant to normalise the distribution so that it describes the right number (i.e. N) of particles in the system.

4.2 The Lagrange multiplier β and temperature

Our main aim now is to find β . We know that its dimensions are J^{-1} but that's it so far. To go further, we will refer back to the laws of thermodynamics.

Let's now consider *two* assemblies of particles, each like that described earlier. For example, we could imagine having two crystals which we clamp tightly together so that they can exchange energy *but not particles*. They will thus be in thermal equilibrium, so by definition will be at the same temperature T .

Let's define some notation: in our first crystal we have energy levels \mathcal{E}_i and occupation numbers n_i . In our second crystal we have energy levels \mathcal{E}'_i and occupation numbers m_i . The energy levels are allowed to be the same between the two systems, and so are the occupation numbers, but they are not forced to be so. We'll refer to the total crystal energies as U_1 and U_2 . Energy may flow freely between the two crystals, so we don't know that U_1 and U_2 are individually constant, but their *sum*, $U_1 + U_2$ is constant.

Obviously we need to calculate the probability that the joint system is in some given state. Recall that to calculate the probability of, for example, two sixes in a game of dice, we need to use the product of the individual results, i.e. $p_{66} = 1/6 \times 1/6 = 1/36$. We clearly need to take products so if we want to calculate the number of microstates in a macrostate of the joint system, we must again take a product:

$$\Omega = \frac{N_1!}{\prod_i n_i!} \times \frac{N_2!}{\prod_i m_i!} \quad (4.14)$$

where N_1 and N_2 are the total particle numbers in crystals 1 and 2 respectively.

We now need to go through the maximisation process again for (4.14). As before, we work with $\ln \Omega$.

$$\begin{aligned}\ln \Omega &= (N_1 \ln N_1 - N_1) - \sum_i (n_i \ln n_i - n_i) + (N_2 \ln N_2 - N_2) - \sum_i (m_i \ln m_i - m_i) \\ d(\ln \Omega) &= -d\left(\sum_i n_i \ln n_i - n_i\right) - d\left(\sum_i m_i \ln m_i - m_i\right)\end{aligned}$$

Following the same procedure as for the initial case where we just considered a single crystal, and again making use of the fact that N_1 and N_2 are each constant, we have:

$$\sum_i \ln n_i dn_i + \sum_i \ln m_i dm_i = 0 \quad (4.15)$$

The above equation is therefore our equivalent for the two-crystal system to equation 4.8 for the single crystal system. We need to solve the above equation subject to modified constraints that take into account the two number conservations and the total energy conservation. We introduce a new set of Lagrange multipliers and get

$$\alpha_1 \sum_i dn_i = 0 \quad \alpha_2 \sum_i dm_i = 0 \quad \beta \left(\sum_i \mathcal{E}_i dn_i + \sum_i \mathcal{E}'_i dm_i \right) = 0 \quad (4.16)$$

This step gives us the clue about the point of what we are doing: because there is one conserved total energy we have a common β between the two systems. We also know that the condition given by equation 4.15, subject to the constraints given by equation 4.16 is that for equilibrium. Our new equivalent to equation 4.10 is

$$\sum_i (\ln n_i + \alpha_1 + \beta \mathcal{E}_i) dn_i + \sum_i (\ln m_i + \alpha_2 + \beta \mathcal{E}'_i) dm_i = 0 \quad (4.17)$$

The particles in the two crystals are independent, so the two sums above must also be independent. Thus we can, in a similar way to what we did for the single crystal case, deduce that

$$n_i = A_1 e^{-\beta \mathcal{E}_i} \quad \text{and} \quad m_i = A_2 e^{-\beta \mathcal{E}'_i} \quad (4.18)$$

We know from the *zeroth* law of thermodynamics that two systems in equilibrium have a common temperature. Thus, even at this stage, we can infer that β is some function of temperature because β is the only parameter appearing in equation 4.18 that is *independent of the details of one system or the other*. The two distributions have their own values of α (as the two sub-systems have their own particle numbers) but share the same β .

Our task is now to determine what function of T that β is. We move back to considering a single system, and use Boltzmann's postulate of equation 3.6, repeated here:

$$S = k_B \ln \Omega \quad (4.19)$$

So how does this key relation help us? Well, for reversible changes, the differential form of the first law of thermodynamics tells us

$$dU = dQ + dW \quad (4.20)$$

and by using the second law to substitute for dQ we get

$$dU = TdS + dW \quad (4.21)$$

We know that $U = \sum_i \mathcal{E}_i n_i$, so we can write another expression for dU based on this:

$$dU = d\left(\sum_i \mathcal{E}_i n_i\right) = \sum_i \mathcal{E}_i dn_i + \sum_i n_i d\mathcal{E}_i \quad (4.22)$$

The first term in equation 4.22 gives us the change in internal energy due to the rearrangement of particles in existing energy levels: considering equation 4.19, this must correspond to the entropic change term in equation 4.21 (the first term in the RHS of that equation).

Given that we are identifying equation 4.22 with equation 4.21, then we need to consider whether it makes sense that the second term in (4.22) could correspond to work being done on the system. Think about the form: $\sum_i n_i d\mathcal{E}_i$. Microscopically it corresponds to the results of a process which leaves the degree of order, i.e. the arrangement of particles in energy levels the same (as only n_i features in the term, and not dn_i). What is changing is the spectrum of characteristics energies available to those particles (as $d\mathcal{E}_i$ features in the term, which accounts for changes in the energy levels \mathcal{E}_i).

Imagine a well-known form of work like $dW = -PdV$, in which we apply pressure to a crystal and compress it. The chemical bond lengths would change and the details of the individual atomic potentials would therefore change as well. This would naturally change the individual energy levels \mathcal{E}_i , just as in $\sum_i n_i d\mathcal{E}_i$.

Being able to account for the two terms in equation 4.22 is actually quite something as what it gives us is a microscopic understanding of the difference between heat and work: *heat alters the internal energy by disordering the system while work alters the microscopic energy levels in an ordered way*.

We are quite capable of making a small change (for example, putting in some heat without doing work) and in this circumstance we have the simple relationship

$$dU = TdS = \sum_i \mathcal{E}_i dn_i \quad (4.23)$$

Inserting the expression for S (equation 4.19) into this, then we get

$$T d(k_B \ln \Omega) = \sum_i \mathcal{E}_i dn_i \quad (4.24)$$

But we already have an expression for $d(\ln \Omega)$ (equation 4.7): $d(\ln \Omega) = -\sum_i \ln n_i dn_i$ so $d(k_B \ln \Omega) = -k_B \sum_i \ln n_i dn_i$ which means that we can write equation 4.24 as

$$-k_B T \sum_i \ln n_i dn_i = \sum_i \mathcal{E}_i dn_i \quad (4.25)$$

Substitute for $(\ln n_i)$ using equation 4.11, and we get

$$-k_B T \sum_i (-\alpha - \beta \mathcal{E}_i) dn_i = \sum_i \mathcal{E}_i dn_i \quad (4.26)$$

If we look at the LHS of the above equation and imagine expanding the sum: the particle number is constant, so $-\alpha \sum_i dn_i$ will be zero, and so

$$k_B T \cdot \beta \sum_i \mathcal{E}_i dn_i = \sum_i \mathcal{E}_i dn_i \quad (4.27)$$

and hence

$$\beta = \frac{1}{k_B T} . \quad (4.28)$$

4.3 The Boltzmann distribution and the partition function

Now that we know β , we can use equation 4.1 to write a microscopic expression for the occupation number:

$$n_i = A e^{-\mathcal{E}_i/k_B T} \quad (4.29)$$

The occupation of the i -th energy level falls off exponentially as the energy of the level becomes large on the scale of $k_B T$. This is the core characteristic of the *Boltzmann distribution*.

Using $N = \sum_i n_i$ and $U = \sum_i \mathcal{E}_i n_i$, it's easy to extend the expression for the occupation number to the total particle number:

$$N = A \sum_i e^{-\mathcal{E}_i/k_B T} \quad (4.30)$$

It's trivial to re-express this as $N = A Z_{\text{sp}}$, where we simply *define* the partition function Z_{sp} as

$$Z_{\text{sp}} = \sum_i e^{-\mathcal{E}_i/k_B T} \quad (4.31)$$

Putting everything together, we arrive at the *Boltzmann distribution for distinguishable particles*:

$$n_i = \frac{N}{Z_{\text{sp}}} e^{-\mathcal{E}_i/k_B T} \quad (4.32)$$

This means that

$$\frac{n_i}{N} = \frac{e^{-\mathcal{E}_i/k_B T}}{Z_{\text{sp}}} \quad (4.33)$$

will tell us how what proportion of our particles have a particular energy (and because each state has a unique energy, this means that we know what proportion of particles are in a particular *state*.)

The *partition function*, Z , is arguably *the most important class of function in statistical physics*. If we know the partition function for the system that we are studying, then we *can calculate all the thermodynamic properties of that system*. Read that sentence again, for it is a remarkable statement: if you can construct the partition function for a system, then you know all the thermodynamic properties for that system.

We have done things in terms of energies, rather than states, and because we're considering a system where the states have *unique* energies, we have come to the same definition of the partition function as if we'd considered states.

It's important to recognise, however, than the partition function is **defined as a sum over states**¹. If we use \mathcal{E}_j (note: the subscript is j , rather than i) to denote the energy of a state, then we can say

$$Z_{\text{sp}} = \sum_j e^{-\mathcal{E}_j/k_B T} \quad (4.34)$$

(This seems like a big song and dance to make since equation 4.34 looks the same as equation 4.31 except for the (seemingly arbitrary!) change of index. However, if there was more than one level with the same energy, then equation 4.31 would need to be modified to ensure that we are counting *all* the states, whereas equation 4.34 would not require modification as it is already over the states. We'll keep taking the sum over energies, rather than states, and when we consider systems where the states energies are *not* unique, then we'll modify our expression for Z_{sp} accordingly to keep everything in order.)

The relationship between n_j , N and Z_{sp} means that the probability p_j of a particle being in a state \mathcal{E}_j is given by

$$p_j = \frac{e^{-\mathcal{E}_j/k_B T}}{Z_{\text{sp}}} \quad (4.35)$$

(For a system in which each state has a unique energy, then we could say that the probability, p_i of a particle having energy \mathcal{E}_i is $(e^{-\mathcal{E}_i/k_B T})/Z_{\text{sp}}$, which will do us for now.)

4.4 Internal energy

Let's illustrate the importance of the partition function by calculating the internal energy U .

Combining equation 4.32 for the Boltzmann distribution n_i and $U = \sum_i \mathcal{E}_i n_i$ yields

$$U = \frac{N}{Z_{\text{sp}}} \sum_i \mathcal{E}_i e^{-\mathcal{E}_i/k_B T} \quad (4.36)$$

Now, from our definition of the single-particle partition function, $Z_{\text{sp}} = \sum_i e^{-\mathcal{E}_i/k_B T}$, therefore from

$$\frac{\partial Z_{\text{sp}}}{\partial T} = \sum_i \frac{\mathcal{E}_i}{k_B T^2} e^{-\mathcal{E}_i/k_B T} \quad \text{and} \quad \frac{1}{Z_{\text{sp}}} \frac{\partial Z_{\text{sp}}}{\partial T} = \frac{\partial \ln Z_{\text{sp}}}{\partial T} \quad (4.37)$$

we obtain an expression for the internal energy U in terms of the single particle partition function:

$$U = N k_B T^2 \frac{\partial \ln Z_{\text{sp}}}{\partial T} \quad (4.38)$$

¹The reason the partition function is denoted by Z is that the German word for 'sum over states' is 'Zustandssumme'.

4.5 Entropy

Now let's have a stab at entropy. Recalling equations 3.6 and 4.4 and using 4.32 for the Boltzmann distribution, we can write

$$\begin{aligned} S &= k_B \ln \Omega = k_B \left(N \ln N - \sum_i n_i \ln n_i \right) \\ &= k_B \left(N \ln N - \sum_i n_i \left[\ln N - \ln Z_{\text{sp}} - \frac{\mathcal{E}_i}{k_B T} \right] \right) \end{aligned} \quad (4.39)$$

For the next step, remember that $\sum_i n_i = N$ and that $\sum_i \mathcal{E}_i n_i = U$.

So finally we have an expression for the entropy S :

$$S = N k_B \ln Z_{\text{sp}} + \frac{U}{T} \quad (4.40)$$

4.6 The Helmholtz free energy

Another method of extracting thermodynamic information is to go via the Helmholtz function (section 1.2). As mentioned in the introduction to the course, this is defined as

$$F = U - TS \quad (1.8)$$

If we start with our expression for the entropy in terms of the partition function and the internal energy:

$$S = N k_B \ln Z_{\text{sp}} + \frac{U}{T} \quad (4.40)$$

so

$$TS = TN k_B \ln Z_{\text{sp}} + U \quad (4.41)$$

and thus

$$F = -N k_B T \ln Z_{\text{sp}} \quad (4.42)$$

4.7 The story so far...

Starting with the minimum number of sensible assumptions about distinguishable quantum particles, we have deduced that:

1. The occupation of state i with energy \mathcal{E}_i falls off exponentially, with the exponent depending on the ratio of \mathcal{E}_i to the thermal energy $k_B T$, the main feature of the **Boltzmann distribution**:

$$n_i = \frac{N}{Z_{\text{sp}}} e^{-\mathcal{E}_i/k_B T}.$$

2. One can derive a remarkable function, the **single-particle partition function**:

$$Z_{\text{sp}} = \sum_i e^{-\mathcal{E}_i/k_B T}$$

which, if we know it for a set of distinguishable particles, allows us to calculate all the thermodynamic properties. This is an extremely powerful statement: knowing the partition function is more useful than knowing a thermodynamic equation of state!

3. The internal energy U , the entropy S and the Helmholtz free energy F can be expressed in terms of the single particle partition function:

$$U = Nk_B T^2 \frac{\partial \ln Z_{\text{sp}}}{\partial T}$$

$$S = Nk_B \ln Z_{\text{sp}} + \frac{U}{T}$$

$$F = -Nk_B T \ln Z_{\text{sp}}$$

We will go on to relax our assumptions about our system (in section 5.4) and shall see that the form of Z will alter, but the power of Z will not. In some respects, one can view the whole point of statistical mechanics as constructing partitions functions for systems of interest and then extracting system behaviour from the partition function.

Chapter 5

An application of Boltzmann statistics: Paramagnets

5.1 Hyperbolic functions

In the subsequent discussion we'll make good use of *hyperbolic functions*. Since it may have been a while since you have come across these, it's worth a quick reminder of their definitions and how they relate to each other.

$$\cosh x = \frac{e^x + e^{-x}}{2} \quad (5.1)$$

$$\sinh x = \frac{e^x - e^{-x}}{2} \quad (5.2)$$

$$\tanh x = \frac{\sinh x}{\cosh x} = \frac{e^x - e^{-x}}{e^x + e^{-x}} \quad (5.3)$$

If you know the definitions of sinh and cosh, then tanh and the derivatives of sinh and cosh follow easily:

$$(\cosh x)' = \sinh x \quad (\sinh x)' = \cosh x \quad (\tanh x)' = \frac{1}{\cosh^2 x} \quad (5.4)$$

5.2 Paramagnets

After a load of maths, and many promises about how useful all this was going to be, we'll use what we have accumulated so far to calculate the magnetic field and temperature dependence of the magnetic properties of some simple classes of material.

In Quantum Mechanics you have encountered the notion that atoms can have tiny magnetic moments, and that these are *quantised* in a special way. In particular, the moment takes a set of discrete values along the direction of an externally applied magnetic field. We'll begin with the simplest case, which

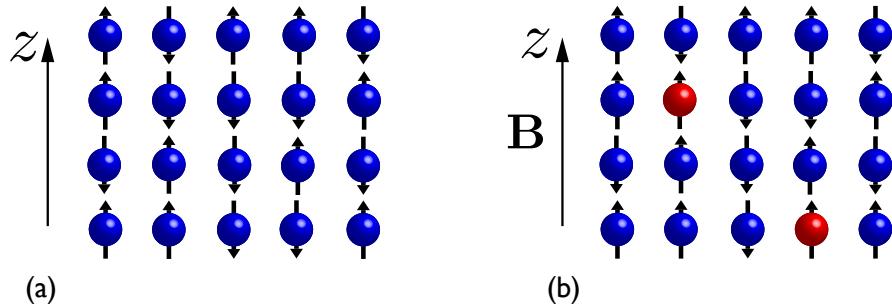


Figure 5.1: (a) With no external field applied, the magnetic moments due to spin are as likely to point up as to point down.

(b) With a magnetic field applied, there will be more moments aligned with the field than against. Here, the atoms in red have switched their alignment.

are atoms whose total angular momentum L (which gives their magnetic moment) is due entirely to the intrinsic “spin” s of one of their electrons.

For an electron, $s = 1/2$, which means that an isolated electron has intrinsic angular momentum of $\hbar/2$, which is therefore that of our simple atom. The laws of quantum physics say that no quantity is absolutely certain, and in the case of spin-1/2 particles this uncertainty is manifest by the fact that the projected component of the spin along a single axis will take one of two values, namely $\pm\hbar/2$. In the absence of any external perturbation or any internal spin-spin interaction, the probability of either of the quantised values is the same, and we have a random arrangement of spins on our distinguishable atoms, as illustrated in figure 5.1 (a). If, however, we apply a magnetic field to the system, we change that perfect balance, because we make it energetically more favourable for an atom’s moment to align along the field. This alignment energy gain will tend to flip some individual spins, as shown in figure 5.1 (b), and we can study this using statistical mechanics.

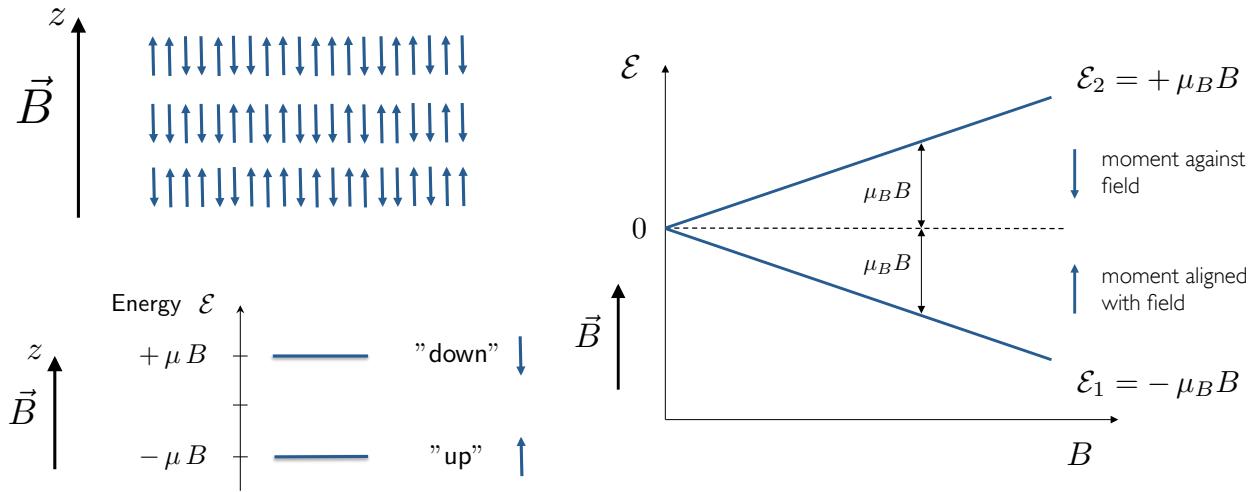


Figure 5.2: Energy levels of a paramagnet in an applied magnetic field. The magnetic moments aligned *with* the magnetic field (looking “up” in our case) have energy $\mathcal{E}_1 = -\mu_B B$ and the magnetic moments aligned *against* the field (looking “down”) have energy $\mathcal{E}_2 = +\mu_B B$. Alignment with the field is energetically more favourable.

This is a nice and easy case to deal with, because each atom can only have two energy levels (see figure 5.2):

$$Z_{\text{sp}} = \sum_i e^{-\mathcal{E}_i/k_B T} = e^{-\mu_B B/k_B T} + e^{+\mu_B B/k_B T} = 2 \cosh(\mu_B B/k_B T) \quad (5.5)$$

So, we now have the single particle partition function, equation 5.5:

$$Z_{\text{sp}} = 2 \cosh(\mu_B B/k_B T)$$

This is the equation that we need in order to know everything about the thermodynamics of the magnetic properties of a crystal of these atoms in an applied field! Recall that we derived an expression for the internal energy in terms of the partition function, equation 4.38:

$$U = N k_B T^2 \frac{\partial(\ln Z_{\text{sp}})}{\partial T} \quad (4.38)$$

We can use this expression along with our Z_{sp} for our system:

$$\begin{aligned} U &= N k_B T^2 \frac{\partial}{\partial T} \left[\ln 2 + \ln \left(\cosh \frac{\mu_B B}{k_B T} \right) \right] \\ U &= -N \mu_B B \tanh \left(\frac{\mu_B B}{k_B T} \right) \end{aligned} \quad (5.6)$$

(All the intermediate maths has been omitted here, so make sure that you *do this as an exercise*, and if you can't make it work out, ask for help.)

Note: It is perhaps better to denote this purely magnetic internal energy as U_{mag} , as the full internal energy includes not just the magnetic term but also, for example, the energy of vibration of the atoms.

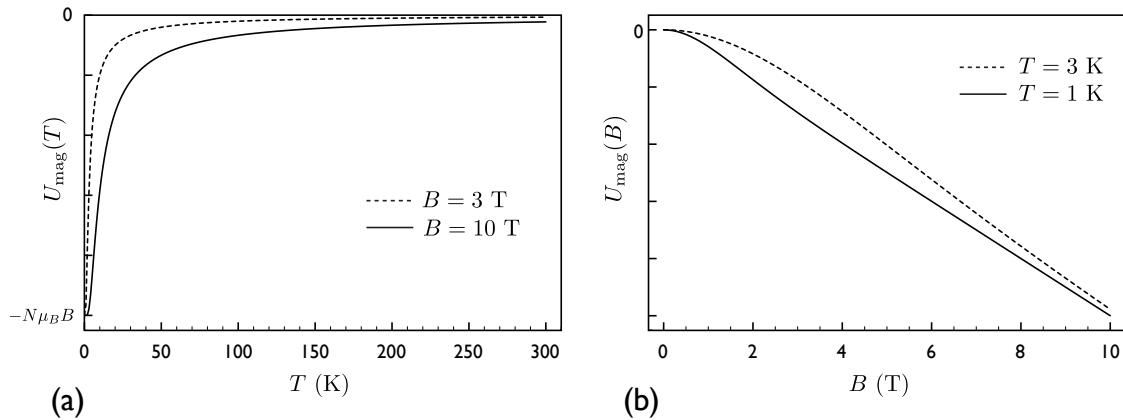


Figure 5.3: Magnetic contribution to internal energy for a spin-1/2 paramagnet as (a) function of temperature for two different constant fields and (b) function of magnetic field for two different constant temperatures.

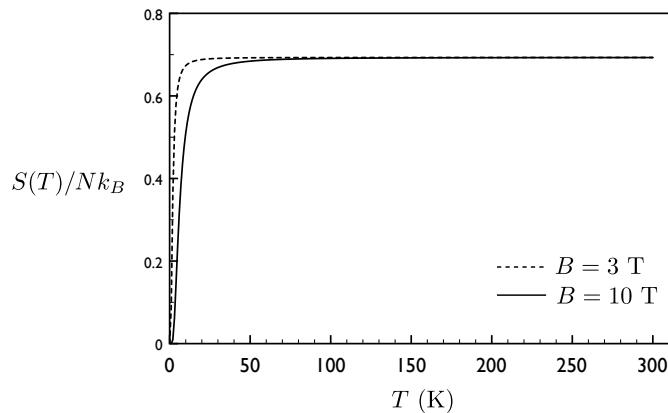


Figure 5.4: The entropy of our spin-1/2 paramagnet at two different constant applied fields as a function of temperature

Figure 5.3 (a) shows the dependence of U_{mag} on temperature at a couple of realistic laboratory magnetic fields, 3 Tesla and 10 Tesla, and reveals some intuitive physics: the field is trying to order all the spins along itself, whilst the temperature is trying to populate the higher energy level, which increases U_{mag} towards zero. The *isothermal* field dependence of U_{mag} , shown in figure 5.3 (b) can also be intuitively understood: at low fields, the temperature dominates and the counter-aligned spin state is populated. At very low fields, $U_{\text{mag}} \sim B^2$ (for small x , $\tanh x \approx x$), so the simple linear dependence of U on B is 'spoiled'.

5.3 The entropy of a spin-1/2 paramagnet

Remember that with equation 4.40 we obtained an expression for the entropy in terms of the single-particle partition function:

$$S = Nk_B \ln Z_{\text{sp}} + \frac{U}{T} \quad (4.40)$$

We can use this together with Z_{sp} for our spin-1/2 system to obtain the entropy of our system:

$$S = Nk_B \ln \left[2 \cosh \frac{\mu_B B}{k_B T} \right] - \frac{N\mu_B B}{T} \tanh \frac{\mu_B B}{k_B T} \quad (5.7)$$

noting that for the U in equation 4.40 we have used U_{mag} . The entropy as a function of temperature at two constant fields is shown in figure 5.4. We can see that as $T \rightarrow 0$, $S \rightarrow 0$, corresponding to the system being completely ordered, since all the spins are in the lower energy level as their magnetic moments are aligned with the field \mathbf{B} . This is consistent with the third law of thermodynamics. As the temperature increases, the upper level gets populated, so the system is becoming a bit ‘disordered’, and entropy rises. For high T , the thermal energy $k_B T$ is so large that the difference in energy between the two spin states has become irrelevant. The probability of being in either state is now the same, i.e. particles are randomised between the two states. ‘Total disorder’ is ensuing which corresponds to a maximum entropy:

$$S = Nk_B \ln 2 \quad \text{with} \quad \Omega = 2^N .$$

Note that the maximum value of entropy would be different for particles with different spins: $s = \frac{3}{2}, \frac{5}{2}$, etc.

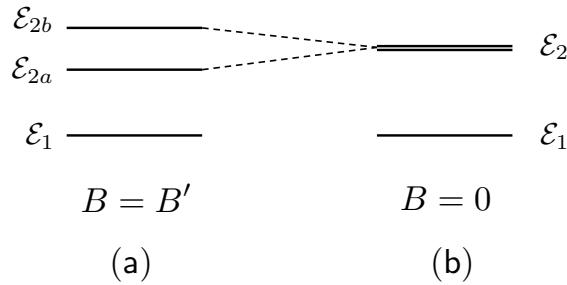


Figure 5.5: Energy levels in a system with one field-independent energy level and two energy levels that are field dependent. (a) In a magnetic field, the energy of the field-dependent levels are different, but when there is no applied field, as in (b), they are the same.

5.4 Accounting for degeneracy in our treatment of statistical physics

Note that in our spin-1/2 paramagnet, when $B = 0$, the two spin states (\uparrow and \downarrow) have the same energy, i.e. they are *degenerate*. Degeneracies like this are the norm rather than the exception in the quantum physics of *real* systems, so we should introduce a formalism that takes them into account.

Imagine for illustration that we had a system with three energy levels, two of which are dependent on field (like our spin \uparrow and spin \downarrow), and a third level that is independent of field. This situation is shown in figure 5.5. For the case shown in part (a) of the figure, the single particle partition function is given by

$$Z_{\text{sp}} = e^{-\mathcal{E}_1/k_B T} + e^{-\mathcal{E}_{2a}/k_B T} + e^{-\mathcal{E}_{2b}/k_B T} \quad (5.8)$$

and for the case shown in part (b), when the field is turned off, the partition function is

$$Z_{\text{sp}} = e^{-\mathcal{E}_1/k_B T} + 2e^{-\mathcal{E}_2/k_B T} \quad (5.9)$$

Note the factor of 2 in the second term of equation 5.9: we require this because we now have *two* levels with energy \mathcal{E}_2 . By extension we can hence define g_i as the *degeneracy factor* of the level with energy \mathcal{E}_i , and thus give appropriate and more general expressions for Z_{sp} and, for example, n_i :

$$Z_{\text{sp}} = \sum_i g_i e^{-\mathcal{E}_i/k_B T} \quad (5.10)$$

$$n_i = \frac{N}{Z_{\text{sp}}} g_i e^{-\mathcal{E}_i/k_B T} \quad (5.11)$$

This corresponds to a modification of equation 4.3 from $\Omega = N! / \prod_i n_i!$ to

$$\Omega = N! \prod_i \frac{g_i^{n_i}}{n_i!} \quad (5.12)$$

This means that although we are still technically taking our sum over energy levels, we are effectively summing over all the *states*, even if the energy levels are not unique to a single state. The partition function is always a sum over all the *states*, so when it is done in terms of energies (i.e., what we've done), we need to ensure we account for degeneracy.