Lecture_11

October 18, 2022

1 Paramagnetism

In this lecture, we're going to discuss how some of the tools we have developed can be used for studying different physical effects. In particular, we're going to look at the relationship between thermodynamics and magnetic dipoles.

Recall from lecture 2 that the magnetic dipole moment is given by $-\mu \cdot \mathbf{B}$. Now, imagine we have a lattice of dipoles, and that the dipoles do not interact with each other. If we then apply a magnetic field to this lattice, the dipoles will line up and either contribute $-\mu B$ or μB to the energy of the system. This effect, where a magnetic field applied to the a system causes the magnetic moments to line up, is called **paramagnetism**.

First, let's figure out what classical thermodynamic quantities we need to address this problem. Recall that the first law of thermodynamics is

$$U = Q + W$$

The work on dipole to line it up is given by $-\mathbf{m} \cdot \mathrm{d}\mathbf{B}$. This is analogous to the work done compressing a gas. As such, we can write an equivalent of the first law of thermodynamics as

$$\mathrm{d}U = T\mathrm{d}S - m\mathrm{d}B$$

The magnetic moment is $m = MV$, where M is the magnetization and V is the volume. We are now going to define the magnetic susceptibility to be

$$\chi = \lim_{H \to 0} \frac{M}{H}$$

whe H is the magnetic field strength (and is related to the magnetic flux density, B, through $B = \mu_0(H + M)$. For paramagnets, $\chi << 1$ which implies that $M << H$, meaning we can approximate it as

$$\chi \approx \frac{\mu_0 M}{B}$$

Our new definition of the first law also implies that we can write an equivalent of the Helmholtz function
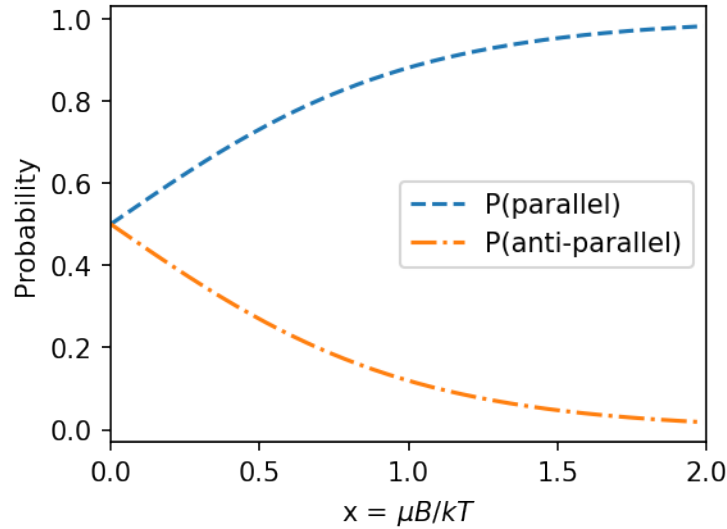
$$F = U - TS$$

such that

$$\mathrm{d}F = -S\mathrm{d}T - m\mathrm{d}B$$

Now, let's consider a single dipole in our system, and write down the partition function:

$$Z_1 = \sum_i \mathrm{e}^{-\beta E_i} = \mathrm{e}^{-\beta\mu B} + \mathrm{e}^{\beta\mu B} = 2\cosh(\beta\mu B)$$

This means the probability of having a dipole contribute an interaction energy of $\mp\mu B$ looks like

So what does this graph tell us? Over on the left $x << 1$. This means that the magnetic field is weak, and the temperature is high. Under such conditions, each dipole has a 50/50 chance of being parallel or anti-parallel. Over on the far right, we have $x >> 1$, which means the magnetic field is strong and the temperature is small. Under these conditions, the dipoles all end up parallel.

Looking at this picture, and thinking about it for a while, should convince you that in this situation we are balancing internal energy versus entropy - when we hav a low temperature and high magnetic field, then we are maximising the internal energy. When we have a low magnetic field and a high temperature, we are maximising the entropy of the system. As such, we can use Helmoholtz's function for this problem.

In the last lecture, we found that the partition function for N particles which are not intereacting and which are distinguishable, the partition function is then given by

$$Z = Z_1^N.$$

The internal energy of the system is given by

$$U = -\frac{\mathrm{d}\ln Z}{\mathrm{d}\beta} = -N\mu B\tanh\left(\mu\beta B\right)$$

The Helmholtz function is then given by

$$F = -k_{\mathrm{B}}T\ln(Z_N) = -Nk_{\mathrm{B}}T\ln[2\cosh(\beta\mu B)]$$

Also, given that the Helmholtz function

$$\mathrm{d}F = -S\mathrm{d}T - m\mathrm{d}B$$

leads to

$$m = -\left(\frac{\partial F}{\partial B}\right)_T = N\mu\tanh(\beta\mu B)$$
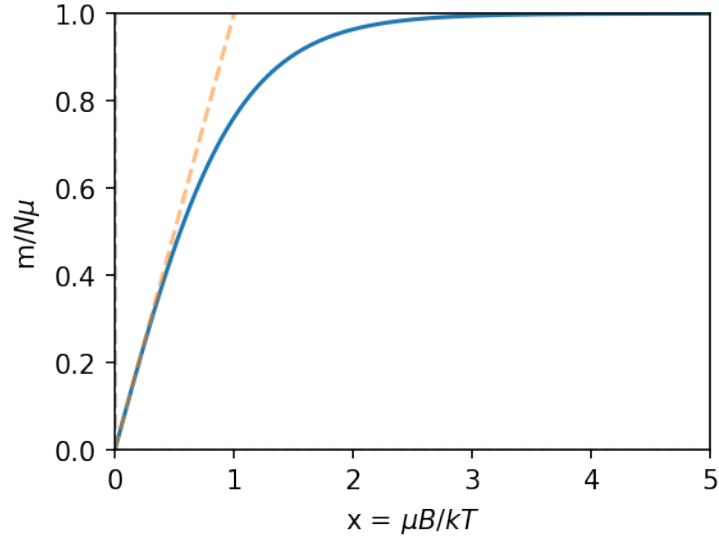
Returning to the magnetisation, we wrote this quantity down earlier as

$$M = \frac{m}{V} = \frac{N\mu}{V} \tanh(\beta\mu B)$$

If we focus on the weak field regime (where the dependance between m and tanh is basically linear, orange line above), then we have that

$$M = \frac{N\mu^2 B}{V k_{\mathrm{B}} T}$$

This combined with the expression above for susceptability gives us that

$$\chi = \frac{N\mu^2 \mu_0}{V k_{\mathrm{B}} T}$$

This shows that the magnetic susceptability of a paramagnet is inversely proportional to its temperature. This is known as Curie's law, and also means that since

$$\chi \propto \frac{1}{T}$$

then this means that

$$\left(\frac{\partial \chi}{\partial T}\right)_B < 0$$

We'll need this in a second.

So, what does this let us accomplish? Well, let's consider the Helmholtz Free Energy again. It leads to the equiavelent Maxwell relation of

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial m}{\partial T}\right)_B \approx \frac{VB}{\mu_0}\left(\frac{\partial \chi}{\partial T}\right)_B$$

Thus, the change in heat during an isothermal change in the B field is

$$\Delta Q = T\left(\frac{\partial S}{\partial B}\right)_T \Delta B = \frac{TVB}{\mu_0}\left(\frac{\partial \chi}{\partial T}\right)_B \Delta B < 0$$

This means that heat is emitted from the matieral during this process.

We can use our usual trick of dealing with differentials

$$\left(\frac{\partial T}{\partial B}\right)_S \left(\frac{\partial B}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_B = -1$$

to obtain an expression for change in temprature due to an adiabatic change in the B field

$$\left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial S}{\partial B}\right)_T \left(\frac{\partial T}{\partial S}\right)_B.$$

If we define the heat capacity at constant magnetic field to be $C_B = T\left(\frac{\partial S}{\partial T}\right)_B$ then we get

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{TVB}{\mu_0 C_B}\left(\frac{\partial \chi}{\partial T}\right)_B$$

where has to be > 0. This means that we can cool down the paramagnet by adiabatically reducing the magnetic field on the sample. This is an incredibly useful result, as experimentally it allows for cooling of systems to millikelin (for electronic systems) and microkelvin (nuclear systems).

Such a cooling proceeds in the following manner.

1. A paramagnetic system is coupled to a heat bath, which is typically liquid helium at 4.2 K.
2. Isothermal magnetisation of the sample proceeds. Since in this process $\Delta Q < 0$ for positive increases in the B field, the para