Paramagnetism

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1. Paramagnetic solid in a heat bath

Earlier, we discussed paramagnetic solid, which is a material in which each atom has a magnetic dipole moment; when placed in an external magnetic field the magnetic moment is aligned either parallel or anti-parallel to the magnetic field. The energy associated with each state is $E = -\vec{\mu}\cdot\vec{B}$, hence when considering N dipoles, there are many ways to obtain a given (total) energy: if n are aligned parallel to the magnetic field, the other $N-n$ are aligned anti-parallel, and the total energy is $E_{tot} = E_{tot}(n) = -\mu B n + \mu B(N-n) = (N-2n)\mu B$. This example served us to demonstrate the difference between macrostates and microstates.

1.1. A single dipole

Let us now take this simple example and extend the discussion to a paramagnet that is in contact with a heat bath. Let us begin the discussion by looking at only one (single) dipole. Recall the definition of the partition function,

$$Z_1 = \sum_r e^{-\beta E_r} = e^{\mu B/k_B T} + e^{-\mu B/k_B T} = 2\cosh\left(\frac{\mu B}{k_B T}\right). \tag{1}$$

The probabilities P_+ and P_- that the (single) dipole be in the states with μ parallel and anti-parallel to B, respectively are

$$P(r) = \frac{1}{Z}e^{-\beta E_r} \rightarrow P_+ = \frac{1}{Z_1}e^{\mu B/k_B T}\ ;\quad P_- = \frac{1}{Z_1}e^{-\mu B/k_B T} \tag{2}$$

Note that obviously, $P_+ + P_- = 1$: the dipole must be either parallel or anti-parallel to the magnetic field.

Let us look at the asymptotic behavior:

- In the limit $\mu B/k_B T \ll 1$ - corresponding to either a very weak magnetic field and / or high temperature: for $x \ll 1$, $e^x \approx 1 + x$. Thus, both P_+ and $P_- \rightarrow 1/2$.

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- In the other extreme, $\mu B/k_B T \gg 1$ - corresponding to very strong magnetic field and/or very low temperatures: $e^{-\mu B/k_B T} \to 0$, and we get $P_+ \to 1$, $P_- \to 0$. Namely, *all dipoles are aligned with the magnetic field.*

This is shown in Figure 1. The conclusion is therefore that **strong magnetic field tend to increase the order, while thermal motion decreases order (increases disorder)**. This is very typical to many thermal problems !.

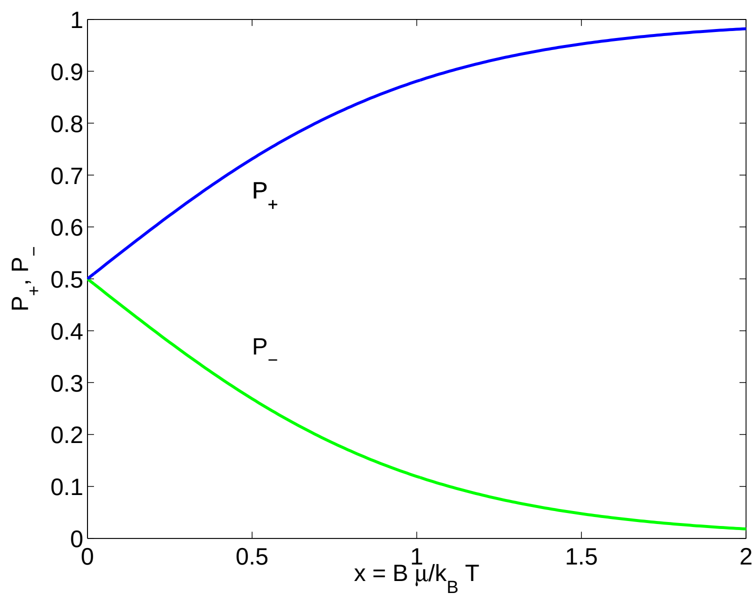

Fig. 1.— The probabilities P_+ and P_- that the magnetic dipole μ put in a magnetic field be oriented parallel or antiparallel to the magnetic field, as a function of the temperature, T and the magnetic field, B.

Once we know the probability of a dipole being parallel or anti-parallel to the magnetic field, we can find the mean magnetic moment $\overline{\mu}$ for given magnetic field and temperature:

$$\overline{\mu} = \mu P_+ + (-\mu) P_- = \frac{\mu}{Z_1}(e^{\mu B/k_B T} - e^{-\mu B/k_B T}) = \mu \tanh\left(\frac{\mu B}{k_B T}\right) \quad (3)$$

Similarly, we can find the mean energy of the dipole:

$$\overline{E}_1 = (-\mu B)P_+ + (\mu B)P_- = (-\mu B)(P_+ - P_-) = -\mu B \tanh\left(\frac{\mu B}{k_B T}\right) \quad (4)$$

Alternatively, we could obtain the average energy using the partition function:

$$\overline{E}_1 = -\frac{\partial \ln Z_1}{\partial \beta} = -\frac{1}{Z_1}\frac{\partial Z_1}{\partial \beta}, \quad (5)$$

using Equation 1, $Z_1 = e^{\mu B/k_B T} + e^{-\mu B/k_B T} = e^{\mu B\beta} + e^{-\mu B\beta}$, we find

$$\overline{E}_1 = -\frac{1}{Z_1}\left(\mu B e^{\mu B/k_B T} - \mu B e^{-\mu B/k_B T}\right) = -\mu B \tanh\left(\frac{\mu B}{k_B T}\right), \tag{6}$$

which is similar, of course to the result obtained in Equation 4.

1.2. Macroscopic collection of dipoles

After calculating the probabilities, mean magnetic moment and mean energy of a single dipole, let us look now at macroscopic paramagnet, which can be thought of as a collection of N dipoles. Remember, that we neglect the interactions between the dipoles. Thus, the total energy is just the sum of energies:

$$\overline{E} = N\overline{E}_1 = -N\mu B \tanh\left(\frac{\mu B}{k_B T}\right) \tag{7}$$

Similarly, the total magnetic moment (or **magnetization**) is

$$M = N\overline{\mu} = N\mu \tanh\left(\frac{\mu B}{k_B T}\right). \tag{8}$$

Let us look at the asymptotic behavior of the magnetization:

- In the limit $\mu B/k_B T \ll 1$ - corresponding to either a very weak magnetic field and / or high temperature: for $x \ll 1$, $\tanh x \approx x$. Thus,

  $$M \approx N\mu\left(\frac{\mu B}{k_B T}\right) = \frac{N\mu^2 B}{k_B T}. \tag{9}$$

  We see that $M \propto B$, and $M \propto T^{-1}$.

- In the other extreme, $\mu B/k_B T \gg 1$ - corresponding to very strong magnetic field and/or very low temperatures: $\tanh x = (e^x - e^{-x})/(e^x + e^{-x}) \approx e^x/e^x = 1$ (for $x \gg 1$), implying $M \approx N\mu$. This, again corresponds to the situation in which *all dipoles are aligned with the magnetic field.*

The magnetization M is plotted in Figure 2.

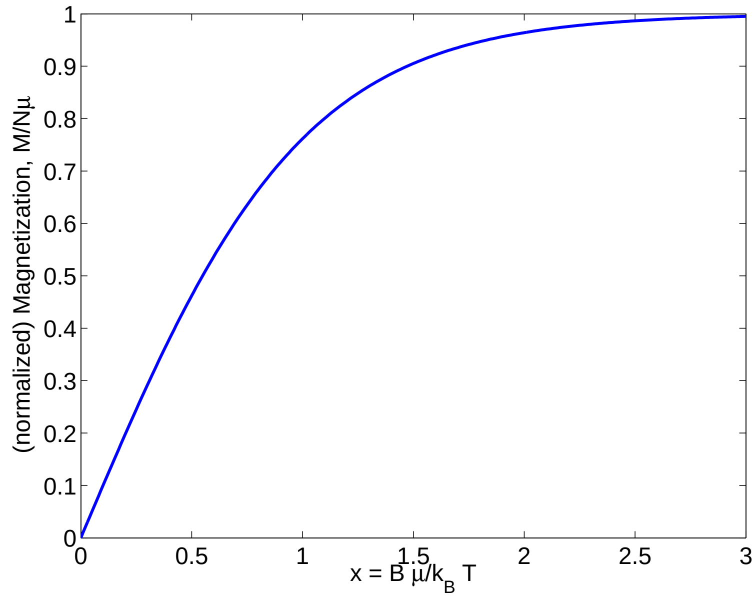

Fig. 2.— The (normalized) magnetization M as a function of the temperature and the magnetic field.

2. Isolated paramagnetic solid.

Although it is much more practical to discuss systems having constant temperatures than constant energy, we will discuss now the example of paramagnet at constant energy; the idea is to demonstrate the concepts we learned using a fairly simple system.

Recall that the energy of a paramagnet is determined by the number n of dipoles aligned parallel to the magnetic field, out of the total N dipoles in the system: $E_{tot} = E_{tot}(n) = -\mu B n + \mu B(N-n) = (N-2n)\mu B$. The statistical weight of this state is

$$\Omega(n) = \frac{N!}{n!(N-n)!}. \tag{10}$$

The entropy, $S(n) = k_B \ln \Omega(n)$ gets a useful form when using Stirling's formula, $\ln(n!) \approx n \ln n - n$ (which is valid for large n),

$$S(n) \approx k_B \left(N \ln N - n \ln n - (N-n) \ln(N-n) \right). \tag{11}$$

Using this expression for the entropy and the entropy-based definition of the temperature, we get

$$\begin{aligned} \tfrac{1}{T} = \tfrac{\partial S}{\partial E} &= \tfrac{\partial S}{\partial n} \tfrac{dn}{dE} \\ &= \left[k_B \ln \left(\tfrac{N-n}{n} \right) \right] \cdot \left[\tfrac{-1}{2\mu B} \right]. \end{aligned} \tag{12}$$

Solving for n, we find

$$\begin{aligned} \frac{n}{N} &= \tfrac{1}{1+e^{-2\mu B/k_BT}} = \tfrac{e^{\mu B/k_BT}}{e^{\mu B/k_BT}+e^{-\mu B/k_BT}} \\ &= \tfrac{1}{Z_1}e^{\mu B/k_BT} = P_+. \end{aligned} \tag{13}$$

This should not be really surprising; n/N is just the probability P_+ that a dipole is in the "Parallel aligned" state.

3. Negative temperature.

Recall that we defined the temperature of the system in terms of its entropy or statistical weight by $1/T = \partial S/\partial E = k_B(\partial\Omega/\partial E)$. We stated that the absolute temperature is always positive: this follows from the fact that both S and Ω are monotonic increasing functions of E.

However, clearly, the results of Equation 12 implies that this is not always the case. For if

$$\frac{N-n}{n} > 1 \quad \rightarrow \ln\left(\frac{N-n}{n}\right) > 0 \quad \rightarrow \frac{1}{T} < 0, \tag{14}$$

and so T is negative !.

But what does it mean ? When looking at Equation 12, we see that formally, $T < 0$ if $n < N/2$, namely fewer than 1/2 of the dipoles are aligned with the magnetic field, or more than 1/2 are anti-parallel to the magnetic field.

When $n = N/2$, $\ln(N - N/2/(N/2)) = \ln 1 = 0$, and thus $1/T = 0$ or $T \rightarrow \infty$. Recall that $E_{tot} = (N - 2n)\mu B$, and thus **a negative temperature is "hotter" than $T = \infty$:** it is a more energetic state of the system. Clearly, a negative temperature state cannot be obtained in any ordinary way by placing the system in a heat bath.

From a mathematical point of view, negative temperature implies that the entropy S decreases when the energy E increases. This is demonstrated in Figure 3. It can happen in systems in which there is a state with finite maximum energy, $E_{\max}$. Strictly speaking, this *does not* exist in nature, since there are no states with an upper bound on the energy - the kinetic energy can always grow !. However, it **can** occur, if we isolate one aspect of the system, such as the magnetic moment, as we have done here. (This is true if this particular aspect of the system interacts very weakly with other aspects). This is exactly what we have here, when we discuss magnetic moment, ignoring all other aspects of the system such as vibrations, etc.

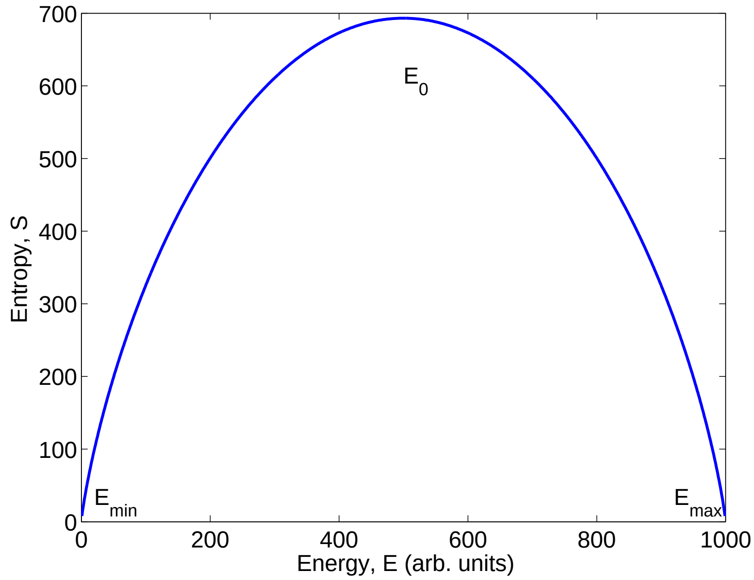

Fig. 3.— For a system having negative temperature, the entropy S is an increasing function of the energy E for $E_{\rm min} < E < E_0$. In this regime, the temperature is $T = (\partial S/\partial E)^{-1}$ is positive. However, for $E_0 < E < E_{\rm max}$, the entropy decreases as E increases, hence the temperature is negative.

Historically, negative temperature was first realized by Purcell and Pound in 1951 using Lithium Fluoride crystal. The idea was to align all dipoles using a strong magnetic field, and then to reverse the field quickly. It takes some time for the molecules to re-align, and during that time, the majority are anti-aligned with the field. During this time, the population is **inverted**, and the **spin temperature is negative**.

If we put a thermometer in contact with a negative temperature system, what we get is that the system is in fact very hot, giving up energy to *any* system at positive temperature put into contact with it. It decays into normal state through infinite temperature.