FoP3B Part I Lecture 7: Paramagnetism

As seen previously most elements in the periodic table are either diamagnetic or paramagnetic, i.e. weakly magnetic. A paramagnetic solid is characterised by no *long range order* of the magnetic moments, so that the overall magnetisation is zero in the absence of an external **B**-field. Here we will explore paramagnetism using both classical and quantum physics.

Langevin theory of paramagnetism

The classical theory of paramagnetism is due to Paul Langevin. Since there is no long range order we assume that the magnetic moments are randomly oriented in space and can lie anywhere on a unit sphere (Figure 1). If the **B**-field is along the *z*-axis magnetic moments with angles between θ and $\theta + d\theta$ to the applied field will cover an area $(2\pi\sin\theta)d\theta$ on the unit sphere. The energy of a magnetic moment $\boldsymbol{\mu}$ is $E = -\boldsymbol{\mu}\cdot\mathbf{B} = -\mu B\cos\theta$. Furthermore, since the magnetic moments are independent of one another, a fact that is consistent with the lack of any long range order, classical Maxwell-Boltzmann statistics should apply. The probability of a magnetic moment at angle θ to the applied field is therefore proportional to $\exp(-E/kT) = \exp(\mu B\cos\theta/kT)$. The average moment $\langle\mu_z\rangle$ is:

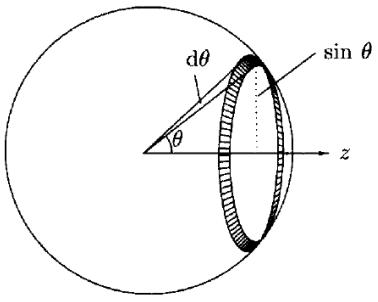

Figure 1

$$\langle\mu_z\rangle = \frac{\int_0^\pi (\mu\cos\theta)e^{\frac{\mu B\cos\theta}{kT}}(2\pi\sin\theta)d\theta}{\int_0^\pi e^{\frac{\mu B\cos\theta}{kT}}(2\pi\sin\theta)d\theta} = \mu\frac{\int_{-1}^1 xe^{yx}dx}{\int_{-1}^1 e^{yx}dx}$$

where $y = \mu B/kT$ and $x = \cos\theta$. Hence

$$\frac{\langle\mu_z\rangle}{\mu} = \coth y - \frac{1}{y} = L(y)$$

$L(y)$ is called the **Langevin function**.

For determining magnetic susceptibility (χ), we are interested in weak magnetic fields, so that $y\to 0$ and $\lim_{y\to 0}\coth y = \frac{y}{3} + \frac{1}{y}$. Therefore, $\frac{\langle\mu_z\rangle}{\mu} = \frac{y}{3} = \frac{\mu B}{3kT}$. For n moments per unit volume the magnetisation $M = n\langle\mu_z\rangle$ and the *saturation* magnetisation $M_s = n\mu$ (the saturation magnetisation is the largest magnetisation possible and occurs when all magnetic moments are parallel to the **B**-field). It follows that $\frac{M}{M_S} = \frac{\langle\mu_z\rangle}{\mu} = \frac{\mu B}{3kT}$. Furthermore, for a weak magnetic material $B = \mu_0(H+M) \approx \mu_0 H$, and $\chi = M/H = \mu_0 M/B$. We therefore finally obtain:

$$\chi = \frac{n\mu_0\mu^2}{3kT}$$

Note that the paramagnetic susceptibility is temperature dependent, unlike diamagnetic susceptibility. The $\chi \propto 1/T$ dependence is known as **Curie's law**.

Quantum Mechanical theory of paramagnetism

The quantum mechanical analysis of paramagnetism is similar to the Langevin theory, with the key difference being that the angular momentum component along the *z*-axis, and therefore its

associated magnetic moment, is a discrete, rather than continuous, variable. For an atom with *LS* coupling the paramagnetic Hamiltonian term is $\gamma g_J \mathbf{B} \cdot \mathbf{J}$. We will first consider the simplest case of atoms where $L = 0$, $S = ½$ and $J = L + S = ½$ (e.g. a hydrogen atom). The J_z component is $m_J\hbar$, where $m_J = ½, -½$. Therefore, $\mu_z = -g_J\gamma J_z$ and $g_J = \frac{3}{2} + \frac{S(S+1)-L(L+1)}{2J(J+1)} = 2$. μ_z values are therefore $\pm\gamma\hbar$ or $\pm\mu_B$. The average magnetic moment is:

$$\langle \mu_z \rangle = \frac{-\mu_B e^{\frac{\mu_B B}{kT}} + \mu_B e^{-\frac{\mu_B B}{kT}}}{e^{\frac{\mu_B B}{kT}} + e^{-\frac{\mu_B B}{kT}}} = \mu_B \tanh\left(\frac{\mu_B B}{kT}\right)$$

The exponential terms in the above Equation are the Maxwell-Boltzmann probabilities of finding a magnetic moment with energy $\pm\mu_B B$. Again assuming small **B**-fields and using the fact that $\tanh(y) \approx y$ for small values of y, gives $\frac{M}{M_s} = \frac{\langle \mu_z \rangle}{\mu_B} = \frac{\mu_B B}{kT}$. From $\chi = \mu_0 M/B$ we get:

$$\chi = \frac{n\mu_0\mu^2}{kT}$$

The susceptibility for a $J = ½$ solid is therefore very similar to the Langevin result apart from a missing factor '3' in the denominator. We can also calculate χ for other (i.e. larger) values of J using a similar procedure, but because $m_J = J, J\text{-}1, \ldots, -J$ can now take many more values we need to consider the additional μ_z contributions to $\langle \mu_z \rangle$.

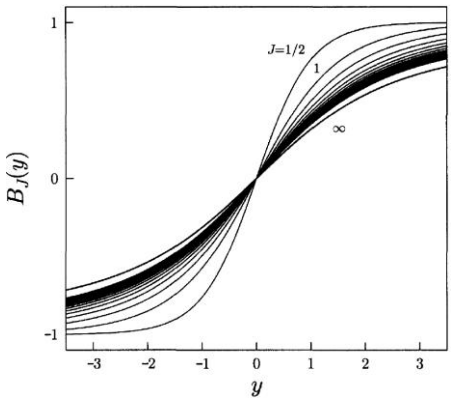

Figure 2

It is easy to show that:

$$\frac{M}{M_s} = B_J(y) \quad ; \quad y = \frac{g_J \mu_B J B}{kT}$$

where $B_J(y)$ is the **Brillouin function**:

$$B_J(y) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}y\right) - \frac{1}{2J}\coth\left(\frac{y}{2J}\right)$$

The Brillouin function is plotted in Figure 2 for all allowed values of J from $J = ½$ to ∞ (the latter corresponds to the Langevin case where magnetic moment is a continuous variable; in fact $B_J(y) \rightarrow L(y)$ for $J \rightarrow \infty$ giving the same result as Langevin theory).

Thermodynamic properties of paramagnetism and adiabatic cooling

Using the results for a $J = ½$ solid as an example we can calculate the thermodynamic properties of a paramagnet. Figure 3a shows the magnetisation M as a function of $(kT/\mu_B B)$; it shows that as the temperature is decreased for a given **B**-field, or alternatively magnetic field increased at constant temperature, the magnetisation gradually increases towards the saturation value M_s. This is because low temperature and strong **B**-fields both favour alignment of the magnetic moments. The energy of the solid $E = -MB$ is simply a mirror reflection of the magnetisation curve (Figure 3b). From the energy we can calculate the specific heat, using the relation $C = \left(\frac{\partial E}{\partial T}\right)_B$, as shown in Figure 3c. The specific heat shows a maximum, known as the **Schottky anomaly**. Its interpretation is straightforward: to the right of the maximum the magnetic moments are misaligned by thermal effects. At high enough temperature the moments are as

disordered as they can be, so that increasing the temperature further will not make any significant difference and the heat capacity will approach zero. To the left of the Schottky anomaly the moments become more aligned with decreasing temperature, until perfect order is reached and the heat capacity approaches zero. Finally, from the heat capacity the entropy of the solid can also be calculated using $S = \int \frac{dE}{T} = \int \frac{C}{T} dT$ (Figure 3d). Note that since heat capacity is defined for a constant **B**-field we can construct an entropy curve similar to Figure 3d for each value of the magnetic field.

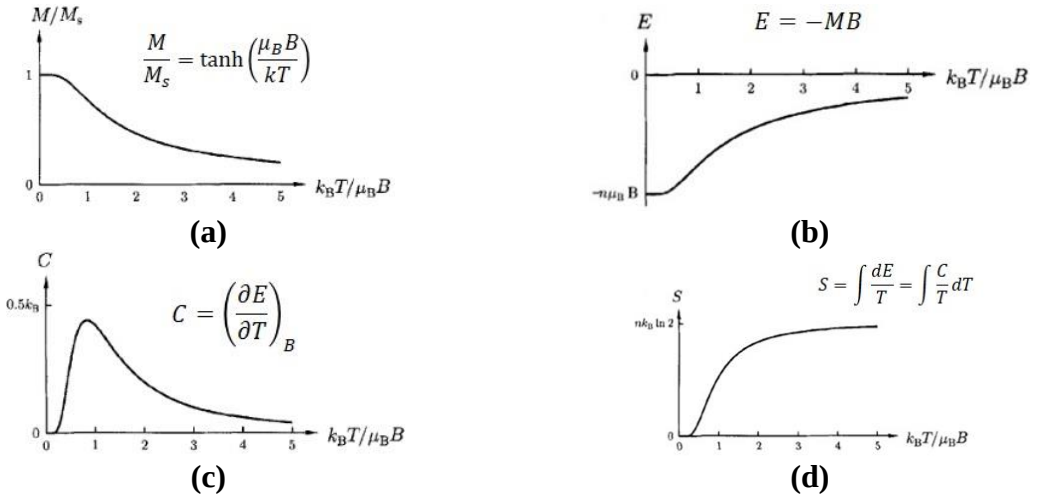

Figure 3: (a) magnetisation, (b) energy, (c) heat capacity and (d) entropy curves for a J = ½ solid

The thermodynamic properties enable a method to cool paramagnetic solids down to extremely low temperatures, as much as a few milli-Kelvin above absolute zero. The procedure is outlined in Figure 4 which shows entropy as a function of temperature for different **B**-fields. The sample is first cooled to a low temperature T_i (e.g. liquid Helium at 4.2 K) in zero **B**-field (point *a*). Next *isothermal magnetisation* is carried out by switching the magnetic field on. The sample entropy and energy decrease due to alignment of the magnetic moments in the **B**-field (*a*→*b*). Since the process is isothermal the energy is transferred to the thermal bath (e.g. liquid He).

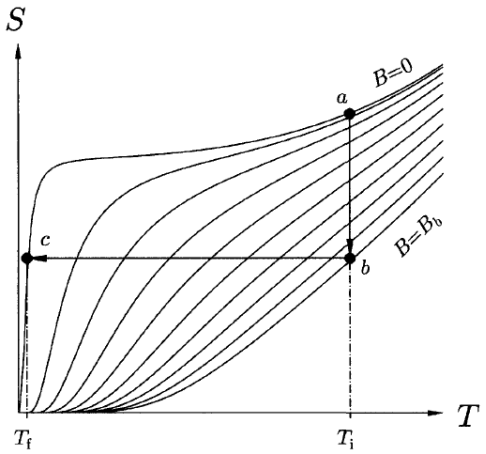

Figure 4

The sample is then isolated from its environment to enable the process of *adiabatic demagnetisation*, where the magnetic field is switched off. Since there is no energy transfer the entropy change $\Delta S = \int \frac{dE}{T} = 0$ is zero (*b*→*c*).The increase in entropy due to spin misalignment under zero **B**-field must therefore be balanced by a simultaneous decrease in entropy caused by phonon annihilation. The destruction of phonons causes the sample temperature to decrease to T_f, which is lower than T_i.