FIP10604 – Text 03
PARAMAGNETISM OF INDEPENDENT MOMENTS

Let us consider the atoms of a physical system (solid or not) as independent, i.e., not interacting with each other (an assumption to be checked a posteriori). If all the atoms are equal, the magnetization is simply the average magnetic moment of an atom multiplied by the number of atoms per unit volume. Then it suffices to study the problem of a single atom in the presence of an external magnetic field.

As we saw in Text 02, single atoms have a permanent magnetic moment given by

$$\boldsymbol{\mu} = -g\mu_B\,\mathbf{J}/\hbar\ , \tag{1}$$

that is obviously not null when $J \neq 0$. To simplify notation, we will not use the index J in the g factor (its notation in Text 02 was g_J).

The relevant energy range of magnetic-field effects is much smaller than energy differences between atomic states ($\mu_B H \simeq 5.8\times10^{-5}$ eV for $\mu_0 H = 1$ T). Therefore, each atom is in its ground state, and all degrees of freedom are "frozen" except those related to rotation of the magnetic moment to orient itself with a magnetic field. The diamagnetic effect is much weaker, as we have seen, and will not be taken into account here.

Assuming (without loss of generality) that the external magnetic field is parallel to the z axis, and choosing as zero the additive constant from the frozen degrees of freedom, the Hamiltonian is simply

$$\mathcal{H} = -\boldsymbol{\mu}\cdot\mathbf{H} = g\mu_B H J_z/\hbar\ , \tag{2}$$

and the energy eigenvalues are

$$E_{M_J} = g\mu_B H M_J\ ; \qquad M_J = -J, -J+1, \ldots, J-1, J\ . \tag{3}$$

Let us consider the time evolution of any $\mathbf{J}$ component in Heisenberg's representation,

$$J_\alpha(t) = \mathrm{e}^{i\mathcal{H}t/\hbar} J_\alpha(0)\,\mathrm{e}^{-i\mathcal{H}t/\hbar}\ ; \quad \alpha = x, y, z\ . \tag{4}$$

Using Eq. (2), it is easy to show (**EXERCISE**) that

$$\begin{aligned} J_x(t) &= J_x(0)\cos(\omega_H t) - J_y(0)\,\sin(\omega_H t)\ , \\ J_y(t) &= J_y(0)\cos(\omega_H t) + J_x(0)\,\sin(\omega_H t)\ , \\ J_z(t) &= J_z(0)\ , \end{aligned} \tag{5}$$

where

$$\omega_H = g\mu_B H/\hbar = g\frac{eH}{2m_e c}\ , \tag{6}$$

coinciding with the classical Larmor frequency when $g = 1$ (orbital contribution).

Therefore, if the atom is truly **isolated**, that is, unable to exchange energy with its surroundings, the magnetic moment **precesses** around the applied field with frequency ω_H. This does not establish a magnetization in response to the applied field, and therefore does not allow to evaluate a susceptibility.

Thermal equilibrium

The magnetization is a **thermodynamic** variable. It appears when we study a system that is not isolated but is in thermal equilibrium. The underlying assumption is that, in addition to the explicit interaction with the magnetic field, given by Eq. (2), each atom can exchange energy with some other subsystem, which plays the role of *heat reservoir* to keep the temperature constant. This process can involve atomic collisions in the case of a gas, or interaction with phonons for atoms of a solid, for example. Such interactions need not be taken into account explicitly, but we know from equilibrium Statistical Mechanics that we must evaluate an **ensemble average** of the magnetic-moment operator.

Note that the previously mentioned freezing of degrees of freedom implies that the diamagnetic response (which is only relevant for $J = 0$) is essentially independent of temperature.

Going back to Eq. (2), only the z component of the magnetic moment has nonzero average value, which is given by

$$\langle \mu_z \rangle = \operatorname{Tr} \rho \mu_z = -g\mu_B Z^{-1} \sum_{M_J=-J}^{J} M_J \, \mathrm{e}^{-\beta E_{M_J}} \, , \tag{7}$$

where $\rho = Z^{-1} \exp(-\beta\mathcal{H})$ is the density matrix in the *canonical ensemble*, $Z = \operatorname{Tr} \exp(-\beta\mathcal{H})$ is the partition function, $\beta = 1/(k_B T)$, T is the (absolute) temperature, and k_B ($= 1.38 \times 10^{-23}$ J/K) is Boltzmann's constant.

Taking into account that for N atoms in a volume V the magnetization is $M = N\langle \mu_z \rangle / V$, and using the energy eigenvalues (3), it is easy to show (**EXERCISE**) that

$$M = M_0 B_J(\beta g \mu_B J H) \, , \tag{8}$$

where

$$M_0 = \frac{N}{V} g \mu_B J \tag{9}$$

and we introduce the *Brillouin function*

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J} x\right) - \frac{1}{2J} \coth\left(\frac{1}{2J} x\right) \, . \tag{10}$$

Note that $B_J(x)$ varies between 0 and 1 as x goes from 0 to ∞. So, M_0 is the saturation magnetization, which corresponds to all atoms in the state with $M_J = -J$. It is achieved either when H is very large at finite temperature or when $T \to 0$ for a nonzero H. On the other hand, a null value of M is obtained either for $H = 0$ with $T \neq 0$ or for $T \to \infty$ with a finite H.

The smallest nonzero J, i.e., $J = 1/2$ corresponds to the simple form $B_{1/2}(x) = \tanh(x)$. In the opposite limit, $J \to \infty$, we have

$$B_\infty(x) = \coth(x) - 1/x \equiv \mathcal{L}(x) \, , \tag{11}$$

which is known as *Langevin function*. The result $M = M_0 \, \mathcal{L}(x)$ was obtained by Langevin treating the atomic magnetic moments as **classical** variables. Equation (11) thus shows a manifestation of the Correspondence Principle.

Paramagnetic susceptibility

For a fixed temperature, the Brillouin function approaches zero as the magnetic field intensity is reduced. In this regime, we have a linear relation between magnetization and field, the linear coefficient being the magnetic susceptibility. Using the expansion

$$\coth(x) = \frac{1}{x} + \frac{x}{3} + O(x^3)\ , \tag{12}$$

we obtain

$$B_J(x) = \frac{J+1}{3J} x + O(x^3)\ , \tag{13}$$

and therefore

$$M = M_0 \frac{J+1}{3J} \beta g \mu_B J H + O(H^3)\ . \tag{14}$$

This yields the form $M = \chi H$ in the limit $H \to 0$, with the susceptibility χ satisfying the so-called *Curie's law*

$$\chi = \frac{C}{T} \tag{15}$$

(originally obtained empirically), where the *Curie constant* C is given by

$$C = \frac{N}{V} \frac{g^2 \mu_B^2 J(J+1)}{3 k_B}\ . \tag{16}$$

Equation (15) shows that

- the paramagnetic susceptibility diverges when $T \to 0$, indicating that in the absence of thermal motion each atom tends to acquire a nonzero average magnetic moment for an arbitrarily small applied field;
- the paramagnetic susceptibility vanishes for $T \to \infty$, reflecting the fact that in extreme thermally induced disorder a finite magnetic field is not effective to align the magnetic moments.

Plots of χ and χ^{-1} as functions of temperature for an ideal paramagnetic substance are shown in Figure 1. Note that the inverse susceptibility gives a straight line passing through origin, whose slope is the reciprocal of the Curie constant. Measured values of this constant give information about the total angular momentum of the atoms, since it depends explicitly on the eigenvalue of $\mathbf{J}^2$. It is usual to define the *effective magnetic moment* of a single atom as

$$\mu_{\text{eff}} = g \mu_B \sqrt{J(J+1)}\,, \tag{17}$$

so that the Curie constant can be written in the form

$$C = \frac{N}{V} \frac{\mu_{\text{eff}}^2}{3\, k_B}\,. \tag{18}$$

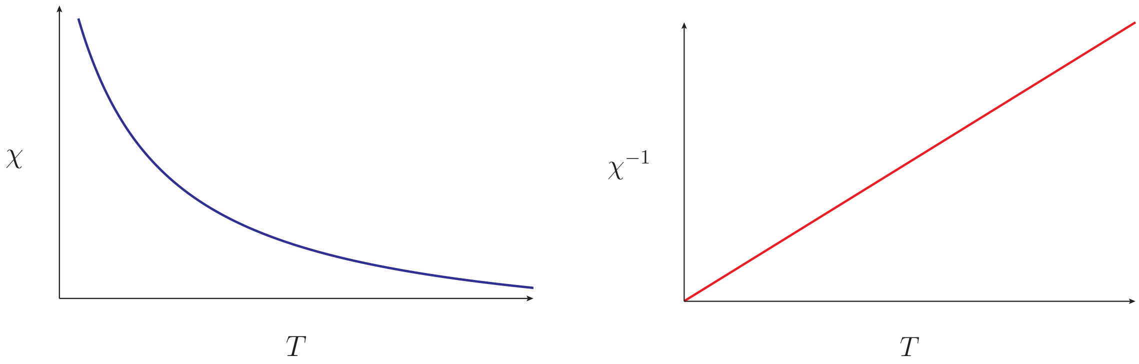

Figure 1: Schematic plots of the susceptibility (left) and inverse susceptibility (right) as functions of temperature for a paramagnetic system that obeys Curie's law.

The Curie law is a theoretical prediction for an idealized system, comprising independent magnetic moments. Pure paramagnetic behavior in real solids is observed only in alloys containing magnetic ions diluted in a nonmagnetic matrix, or in a few transition-metal or rare-earth salts. Examples of the latter are $CrK(SO_4)_2.12H_2O$, $Fe(NH_4)(SO_4)_2.12H_2O$, and $Gd_2(SO_4)_3.8H_2O$, whose magnetic moments are due to ions Cr^{3+}, Fe^{3+}, and Gd^{3+}, respectively. These compounds are electric insulators, with a large number of atoms per unit cell, so that their magnetic ions are quite distant, essentially not interacting with each other.

Relation to Linear Response Theory

The susceptibility as described by Eqs. (15) and (16) can be obtained from the definition of initial susceptibility (see Text 01) applied to an isotropic system in the presence of static and uniform field,

$$\chi = \left.\frac{\partial M}{\partial H}\right|_{H=0} . \tag{19}$$

The first equality of Eq. (7) is generic, and can be used for a general Hamiltonian of the form $\mathcal{H} = \mathcal{H}_0 - \mu_z H$, where $\mathcal{H}_0$ is independent of H. A similar equation can be written for the square of the magnetic moment. Then it is easy to show that

$$\chi = \frac{N}{V}\beta\left[\langle\mu_z^2\rangle_0 - \langle\mu_z\rangle_0^2\right] , \tag{20}$$

where $\langle\ldots\rangle_0$ indicates the average at zero field. Note that the Eq. (20) reproduces the susceptibility (15)-(16) when we take into account that for independent magnetic moments we have $\mu_z = -g\mu_B J_z/\hbar$, $\langle J_z\rangle_0 = 0$ and $\langle J_z^2\rangle_0 = \langle \mathbf{J}^2\rangle_0/3 = J(J+1)\hbar^2/3$.

Equation (20) is a special case of a more general relationship from Linear Response Theory, in which the generalized-susceptibility components are determined by correlation functions of components of the magnetic-moment operator evaluated in the absence of applied external field. We will have opportunity to use this more general relation later on.