3. Diamagnetism and Paramagnetism

Now that we have some understanding of the quantum origins of the magnetic dipole moment of an atom, we will proceed to gain a basic understanding of the magnetic properties of solids. It is convenient to group the magnetic properties of solids under the following headings:

(i) diamagnetism

(ii) paramagnetism

(iii) ferromagnetism, antiferromagnetism, ferrimagnetism

In this and the following sections we shall consider the dia- and paramagnetic behaviour of solids for static applied magnetic fields. The properties corresponding to group (iii) will be discussed in Sections 7 and 8.

Magnetic effects in diamagnetic and paramagnetic materials are typically a thousand to a million times less than the magnetic effects in ferromagnetic materials. Paramagnetic materials are attracted toward magnetic fields while diamagnetic materials are repelled; both attractive and repulsive forces are quite weak. (On the other hand, ferromagnetic materials are strongly attracted by a magnetic field.) Bismuth is one of the strongest diamagnetic materials, but even with it, the effect is still quite weak. Diamagnetism typically is always very weak. Substances like aluminum are called paramagnetic. They are (weakly) attracted by magnetic fields.

We want now to describe briefly the mechanisms of these two effects. First, in many substances the atoms have no permanent magnetic dipole moments, or rather, all the magnets within each atom balance out so that the net magnetic dipole moment of the atom is zero. The electron spins and orbital motions all exactly balance out, so that any particular atom has no average magnetic moment. In these circumstances, when you

turn on a magnetic field little extra currents are generated inside the atom by induction. According to Lenz's law, these currents are in such a direction as to oppose the increasing field. So the induced magnetic moments of the atoms are directed _opposite_ to the magnetic field. This is the mechanism of diamagnetism. The magnetic susceptibility (see Section 4) in this case is therefore _negative_.

In paramagnetic materials, the atoms _do_ have a permanent magnetic moment — in which the electron spins and orbits have a net circulating current that is _not_ zero. So besides the diamagnetic effect (which is _always_ present) there is also the possibility of lining up the individual permanent atomic magnetic moments _with_ the magnetic field. This is because each permanent atomic magnetic dipole experiences a torque tending to line it up parallel to the field. (The mechanism is similar to the way the permanent dipoles of a dielectric tend to line up with the electric field) As a consequence, in paramagnetic materials, the induced magnetism tends to enhance the magnetic field. That is, the magnetic susceptibility is _positive_.

Paramagnetism is generally fairly _weak_ because the _lining up forces_ are relatively _small_ compared with the forces from the _thermal motions_ which try to _derange_ the order. It also follows that paramagnetism is usually _sensitive_ to the _temperature_. (The paramagnetism arising from the spins of the electrons responsible for conduction in a metal constitutes an _exception_. We will not be discussing this phenomenon here.) For ordinary paramagnetism, the lower the temperature, the stronger the effect. There is more lining-up at low temperatures when the deranging effects of the collisions are less. We have, in the above, basically given a qualitative description that leads to Curie's law. Diamagnetism, on the other hand, is more or less independent of the temperature. In any substance whose atoms have permanent magnetic dipole moments there is a diamagnetic as well as a paramagnetic effect, but the paramagnetic effect usually dominates.

Now that a qualitative explanation of diamagnetism and para-magnetism has been given, it <u>must</u> be emphasized that magnetic effects are a <u>completely</u> quantum mechanical phenomenon. It is <u>not</u> possible to understand the magnetic effects of materials in any honest way from the point of view of classical physics. However we will mostly follow a classical approach as it does give us some useful insights regarding behavior in magnetic materials.

<u>Reference</u>: The Feynman Lectures on Physics, Volume 2.

4. <u>Magnetization &</u>
<u>the Magnetic Susceptibility</u> Reference: Introduction to Electrodynamics by Griffiths

To review our discussions in Section 3 above, matter becomes <u>magnetized</u> in the presence of a magnetic field. That is, upon microscopic examination, it will be found to contain many tiny dipoles, with a net alignment along some direction. We have discussed two mechanisms that account for this magnetic polarization: (1) paramagnetism (the permanent magnetic dipoles associated with the atoms experience a torque tending to line them up parallel to the magnetic field) and (2) diamagnetism (the orbital speed of the electrons is altered in such a way as to change the orbital dipole moment in a direction opposite to the field). Whatever the cause, we describe the state of magnetic polarization by the vector quantity

$$\vec{M} \equiv \text{magnetic dipole moment per unit volume}.$$

$\vec{M}$ is called the <u>magnetization</u>; it plays a role analogous to the polarization $\vec{P}$ in electrostatics.

The individual electronic currents of the magnetic dipoles in a magnetized material may be considered to 'add up' resulting in both a bound surface current density, $\vec{K}_b$ as well as a bound volume current density, $\vec{J}_b$. In other words, the <u>effect</u> of magnetization is to <u>establish</u> $\vec{J}_b$ within the material and $\vec{K}_b$ on the surface. It can be shown that $\vec{J}_b$ and $\vec{K}_b$ are related to the magnetization $\vec{M}$ through the equations:

$$\vec{J_b} = \vec{\nabla} \times \vec{M} \qquad (1)$$

and

$$\vec{K_b} = \vec{M} \times \hat{n}, \qquad (2)$$

$\hat{n}$ – unit normal to the surface, etc. The field due to magnetization of the medium is just the field produced by these bound currents. Equations (1) and (2) can be quite simply obtained from a consideration of the potential due to a single dipole followed by an integration over the entire magnetized material. Interested students can look up Griffiths.

Now according to Ampere's law (of magnetostatics), if $\vec{B}(\vec{r})$ is the magnetic field at a point whose position vector is $\vec{r}$ and $\vec{J_t}(\vec{r})$ is the total volume current density at that point, then

$$\vec{\nabla} \times \vec{B}(\vec{r}) = \mu_0 \vec{J_t}(\vec{r}) \qquad (3)$$

μ_0 - permeability of free space

In magnetized materials, contribution to $\vec{B}(\vec{r})$ (where $\vec{r}$ is a position vector of a point within the material) will come from the bound currents as well as from the "free currents". The free current might flow through wires embedded in the magnetized substance or, if the latter is a conductor, through the material itself. In any event, the total current (density) can be written as

$$\vec{J_t}(\vec{r}) = \vec{J_b}(\vec{r}) + \vec{J_f}(\vec{r}), \qquad (4)$$

where $\vec{J_f}(\vec{r})$ – the free current density at $\vec{r}$. The free current is there because somebody hooked up a wire to a battery – it involves actual transport of charge. The bound current is there because of magnetization. From Eqs. (3) and (4),

$$\vec{\nabla} \times \vec{B} = \mu_0 \vec{J_t} = \mu_0 \left[\vec{J_b} + \vec{J_f} \right]$$

$$\Rightarrow \quad \vec{\nabla} \times \vec{B} = \mu_0 \left[\vec{\nabla} \times \vec{M} + \vec{J_f} \right] \quad , \quad \text{from (1)}$$

i.e.,

$$\vec{\nabla} \times \left[\frac{\vec{B}}{\mu_0} - \vec{M} \right] = \vec{J_f} \qquad (5)$$

We define the quantity $\vec{H}$ as,

$$\vec{H} = \frac{\vec{B}}{\mu_0} - \vec{M} . \qquad (6)$$

In terms of $\vec{H}$, then, Ampere's law reads

$$\vec{\nabla} \times \vec{H} = \vec{J_f} \qquad (7)$$

$\vec{H}$ is sometimes called the magnetic field intensity. (Students, you must note that $\vec{B}$ is indisputably the fundamental quantity. Can you explain why?) $\vec{H}$ permits us to express Ampere's law in terms of the free current alone – and free current is what we control directly. $\vec{H}$ plays a role in magnetostatics analogous to $\vec{D}$ in electrostatics. $\vec{D}$ originates only with free charges, (not polarization charges) while $\vec{H}$ is associated with free currents only. Bound currents, like bound (i.e. polarization) charges, come along for the ride – the material gets magnetized, and this results in bound currents; we cannot turn them on or off independently, as we can free currents.

Now from Eq. (6),

$$\vec{B} = \mu_0 \vec{H} + \mu_0 \vec{M} = \mu_0 (\vec{H} + \vec{M}) \qquad (8)$$

In paramagnetic and diamagnetic materials, the magnetization is sustained by the magnetic field $\vec{B}$; when $\vec{B}$ is removed, $\vec{M}$ disappears. In fact, for most substances the magnetization is proportional to the field, provided the field is not too strong. Custom dictates that $\vec{M}$ is written in terms of $\vec{H}$, instead of $\vec{B}$:

$$\vec{M} = \chi_m \vec{H} \qquad (9)$$

The constant of proportionality χ_m is called the magnetic susceptibility; it is a dimensionless quantity that varies from one substance to another – positive for paramagnets and negative for diamagnets.

In the last section, it was mentioned that typically both diamagnetism and paramagnetism were weak. This shows up in the generally low values of diamagnetic and paramagnetic susceptibilities – typical values are around 10^{-5}. (see table below)

Diamagnetic	Susceptibility	Paramagnetic	Susceptibility
Bismuth	-1.7×10^{-4}	Sodium	8.5×10^{-6}
Gold	-3.4×10^{-5}	Aluminum	2.2×10^{-5}
Copper	-9.7×10^{-6}	Platinum	2.7×10^{-4}
Water	-9.0×10^{-6}	Liquid Oxygen (-200°C)	3.9×10^{-3}

Materials that obey Eq.(9) are called <u>linear media</u>. From (8) and (9),

$$\vec{B} = \mu_0(\vec{H} + \vec{M}) = \mu_0(\vec{H} + \chi_m \vec{H}) = \mu_0(1 + \chi_m)\vec{H}, \qquad (10)$$

for linear media. Thus $\vec{B}$ is also proportional to $\vec{H}$. We write,

$$\vec{B} = \mu\vec{H} \qquad (11)$$

where

$$\mu = \mu_0(1 + \chi_m). \qquad (12)$$

μ is called the <u>permeability</u> of the material. In a vacuum, where there is no matter to magnetize, the susceptibility χ_m vanishes (so that $\vec{M} = 0$), and the permeability is μ_0. That's why μ_0 is called the <u>permeability of free space</u>. So in vacuum, $\mu = \mu_0$, and,

$$\vec{B} = \mu_0 \vec{H} \qquad \text{(vacuum)} \qquad (13)$$

Sometimes Eq.(12) is written as,

$$\mu = \mu_0 \mu_r \qquad (14)$$

where,

$$\mu_r = 1 + \chi_m, \qquad (15)$$

is called the <u>relative permeability</u>. From Eqs. (8) and (9), we can also write,

$$\vec{B} = \mu_0(\vec{H} + \vec{M}) = \mu_0\left(\frac{\vec{M}}{\chi_m} + \vec{M}\right) = \frac{\mu_0}{\chi_m}(1 + \chi_m)\vec{M},$$

$$\vec{M} = \frac{\chi_m}{\mu_0(1 + \chi_m)}\vec{B} = \frac{\chi_m}{\mu}\vec{B} \qquad (16)$$

You can also get this equation using Eqs. (4) and (11).

Now, so far we have mentioned that diamagnetism is very weak, and hence characterized typically by very low values of χ_m. There is, however, one important exception. It is an experimental fact that a bulk <u>superconductor</u> in a weak magnetic field will act as a <u>perfect</u> diamagnet, with <u>zero</u> magnetic field in the interior. When a specimen is placed in a magnetic field and is then cooled through the transition temperature for superconductivity, the magnetic flux originally present is <u>ejected</u> from the specimen. This is called the <u>Meissner effect</u>. → See Chapter 10, Solid State Physics by Kittel

Mathematically this means that below the transition temperature, $\vec{B} = 0$ within the superconducting specimen. Then from Eq. (8),

$$\vec{B} = 0 = \mu_0 (\vec{H} + \vec{M})$$

$$\therefore \quad \vec{M} = -\vec{H} \tag{17}$$

$\therefore$ From Eqs (9) & (17),

$$\chi_m = -1, \tag{18}$$

for a superconducting specimen below its transition temperature.

Non superconducting materials only ↑

5. <u>Induced Magnetic Moment & Magnetic Susceptibility in Diamagnetism</u>

Diamagnetic materials have atoms or ions with complete shells, so they do not have a net magnetic dipole moment. Their diamagnetic behavior is due to the fact that a magnetic field acts to distort the orbital motion. We will study this using classical physics and then remark on the quantum result.

Let us now establish the fact that the effect of a magnetic field on the orbital motion of an electron is such as to produce a diamagnetic susceptibility. Consider an electron, (e^-) rotating about the nucleus in a circular orbit of radius r with uniform linear speed v_0 — Figure 4. Assuming the electronic charge to be $-e$, the 'loop' current is given by.

Figure 4
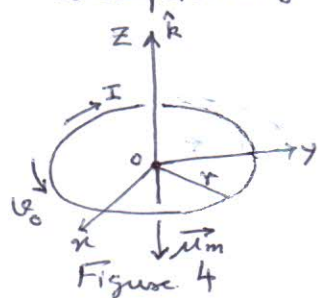
$$I = \frac{e}{T}, \qquad \left.\begin{array}{c} \\ \\ \end{array}\right\} \tag{1}$$

where

$$v_0 T = 2\pi r$$

$$I = \frac{e v_0}{2\pi r} \tag{2}$$

Accordingly the orbital dipole moment is,

$$\mu_m = I \cdot \pi r^2 = \frac{e v_0}{2\pi r} \cdot \pi r^2 = \frac{e v_0 r}{2} \tag{3}$$

If ω_0 is the angular speed of the electron, then $v_0 = \omega_0 r$ and

$$\mu_m = \frac{e \omega_0 r^2}{2} \tag{4}$$

If we consider the orbit to lie on the xy-plane and choose the positive

References : i) Griffiths ii) Dekker iii) Kittel iv) Feynman (Vol. II)

z-direction as shown in Figure 4 ($\hat{k}$ – unit vector along positive z axis), then

$$\vec{\mu}_m = \frac{e v_0 r}{2} (-\hat{k}) \qquad (5)$$

The centripetal force sustaining the circular orbit of the electron is provided by the Coulomb attraction of the nucleus. Assuming its magnitude to be F_0,

$$F_0 = \frac{m v_0^2}{r}, \qquad \left(F_0 = \frac{Ze \cdot e}{4\pi \varepsilon_0 r^2} ; \; Ze - \text{nuclear charge} \right) \qquad (6)$$

where m – mass of the electron.

Let us now apply a magnetic field $\vec{B}$ in the positive z-direction, i.e.,

$$\vec{B} = B\hat{k} \qquad (7)$$

Figure 5

This gives rise to an <u>additional force</u> $-e\vec{v} \times \vec{B}$ on the electron directed towards the center of the orbit (i.e, radially inwards) at all points on the orbit. Then assuming the radius of the orbit to remain unchanged at r, the magnitude of the centripetal force is now <u>increased</u> to $F_0 + e v B$, so that,

$$F_0 + e v B = \frac{m v^2}{r}, \qquad (8)$$

where v is the new speed of the electron. Clearly <u>$v > v_0$</u> since the centripetal force has <u>increased</u> due to $\vec{B}$, while r remains the same. The magnitude of the new magnetic dipole moment is,

$$\mu'_m = \frac{e v r}{2} \qquad \left(= \frac{e \omega r^2}{2}, \; v = \omega r \right) \qquad (9)$$

and

$$\vec{\mu}'_m = \frac{e v r}{2} (-\hat{k}) \qquad (10)$$

Therefore the <u>induced</u> dipole moment due to $\vec{B}$ is,

$$\Delta \vec{\mu}_m = \vec{\mu}'_m - \vec{\mu}_m = \frac{e r}{2}(v - v_0)(-\hat{k}), \qquad (11)$$
the applied field

i.e., the induced dipole moment is in a direction <u>opposite</u> to $\vec{B}$. This is the <u>essence</u> of diamagnetic behavior. Let us now calculate its magnitude.
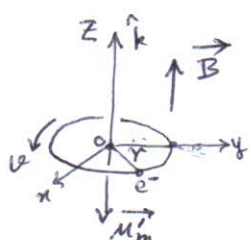
Subtracting (6) from (8),

$$e \mathcal{U} B = \frac{m \mathcal{U}^2}{r} - \frac{m \mathcal{U}_o^2}{r} = \frac{m}{r} (\mathcal{U} + \mathcal{U}_o)(\mathcal{U} - \mathcal{U}_o) \equiv \frac{m}{r} (\mathcal{U} + \mathcal{U}_o) . \Delta \mathcal{U} \qquad (12)$$

Even for the largest fields that can be obtained in the laboratory ($B \sim 100 T$), $\Delta \mathcal{U} (\equiv \mathcal{U} - \mathcal{U}_o)$ is small compared to $\mathcal{U}_o$. Then Eq.(12) can be approximated by,

$$e \mathcal{U}_o B = \frac{m}{r} (\mathcal{U}_o + \mathcal{U}_o) . \Delta \mathcal{U}$$

$$\Rightarrow \qquad e \mathcal{U}_o B = \frac{m}{r} . 2 \mathcal{U}_o . \Delta \mathcal{U} ,$$

i.e.,

$$\Delta \mathcal{U} (\equiv \mathcal{U} - \mathcal{U}_o) = \frac{e B}{2 m} r \qquad (13)$$

Note: Since $\mathcal{U} = \omega r$ & $\mathcal{U}_o = \omega_o r$, $\mathcal{U} - \mathcal{U}_o = (\omega - \omega_o) r$, i.e.,

$$\Delta \mathcal{U} = \Delta \omega . r$$

where $\qquad (14)$

$$\Delta \omega = \frac{e B}{2 m}$$

The quantity $\frac{eB}{2m}$ is known as the Larmor frequency. For its physical significance, see Section 18-3, Dekker.

From Eqs.(11) and (13), the magnitude of the induced magnetic dipole moment is,

$$\Delta \mu_m = \frac{e r}{2} (\mathcal{U} - \mathcal{U}_o) = \frac{e r}{2} . \frac{e B}{2 m} . r = \frac{e^2 r^2}{4 m} B . \qquad (15)$$

Then

$$\Delta \vec{\mu}_m = \frac{e r}{2} (\mathcal{U} - \mathcal{U}_o) (-\hat{k}) = \frac{e^2 r^2}{4 m} B (-\hat{k}) = - \frac{e^2 r^2}{4 m} \vec{B} , \qquad (16)$$

since $\vec{B} = B \hat{k}$.

- **Students**: **Show** that $\Delta \vec{\mu}_m$ will be opposite to applied field $\vec{B}$, and Eq.(16) will hold if we had chosen $\vec{B} = - B \hat{k}$.

Equation (16) shows explicitly that the induced magnetic dipole moment is _opposite_ in direction to the applied field $\vec{B}$. It is critical to understand this if we wish to understand diamagnetism. Diamagnetism is the result of Lenz's law operating on an atomic scale. Upon the application of a magnetic field, the electronic currents in each atom are modified in such a way that they tend to weaken the effect of this field.

Now suppose the atom has Z electrons; then Eq.(16), which was

developed for one electron must be suitably modified. However first we would like to write Eq.(16) a bit differently. Figure 5 shows the nucleus to be at the origin of the coordinate system with a single electron rotating about the nucleus in a circular orbit of radius r. This motion is confined to the xy-plane with the applied magnetic field $\vec{B}$ along the z-axis. Now clearly this picture of a circular orbit is both simplistic and unrealistic. In an atom, the motion of an electron around the nucleus is in three dimensions, not two as envisaged in Figures 4 and 5. Further the nature of the motion is quite complicated. So to be physically realistic, we need to replace r^2 in Eq.(16) by $\langle r^2 \rangle$ where $\langle r^2 \rangle$ is the mean square of the perpendicular distance of the electron from the Z-axis (remember that the nucleus is at the origin, and $\vec{B}$ is along the Z-axis). So Eq.(16) becomes,

$$\Delta \vec{\mu}_m = - \frac{e^2 \langle r^2 \rangle}{4m} \vec{B} \qquad (17)$$

where,

$$\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle . \qquad (18)$$

Now the mean square distance of the electron from the nucleus is

$$\langle \varkappa^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle . \qquad (19)$$

If we consider spherically symmetric atoms (i.e., the electronic charge distribution surrounding the nucleus of the atom is spherically symmetric), we have

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle \qquad (20)$$

so that

$$\langle r^2 \rangle = 2 \langle x^2 \rangle \quad \& \quad \langle \varkappa^2 \rangle = 3 \langle x^2 \rangle \qquad (21)$$

$$\therefore \langle r^2 \rangle = \frac{2}{3} \langle \varkappa^2 \rangle \qquad (22)$$

From (17) and (22),

$$\Delta \vec{\mu}_m = - \frac{e^2 \langle \varkappa^2 \rangle}{6m} \vec{B}, \qquad (23)$$

i.e., the magnitude of the induced dipole moment is,

$$\Delta \mu_m = \frac{e^2 \langle r^2 \rangle}{6m} B \qquad (24)$$

We are still left with the problem: What _is_ the mean square radius, $\langle r^2 \rangle$? Classical mechanics _cannot_ supply an answer. We must go back and start over with quantum mechanics. In an atom we _cannot_ really say _where_ an electron is, but only know the _probability_ that it will be at some place. If we interpret $\langle r^2 \rangle$ to mean the average of the square of the distance from the center for the _probability distribution_, the magnitude of the diamagnetic moment given by quantum mechanics is _just the same_ as given in Eq. (24). Now Eq. (24), of course, is the moment for one electron. The total induced diamagnetic moment is given by the sum over all the Z (say) electrons of the atom and hence will have the magnitude.

$$\mu_{ind}^{dia} = Z \Delta \mu_m = \frac{Z e^2 \langle r^2 \rangle}{6m} B \qquad (25)$$

&

$$\vec{\mu}_{ind}^{dia} = -\frac{Z e^2 \langle r^2 \rangle}{6m} \vec{B} \qquad (26)$$

Then if $\vec{M}$ is the magnetization, N is the number of atoms per unit volume, and $\vec{\mu}_{ind}^{dia}$ is the average induced diamagnetic moment per atom, then

$$\vec{M} = N \vec{\mu}_{ind}^{dia} = -\frac{N Z e^2 \langle r^2 \rangle}{6m} \vec{B} \qquad (27)$$

If χ_m^{dia} is the diamagnetic susceptibility, then

$$\vec{B} = \mu_0 (\vec{H} + \vec{M}), \quad \vec{M} = \chi_m^{dia} \vec{H}, \qquad (28)$$

so

$$\vec{B} = \mu_0 (\vec{H} + \chi_m^{dia} \vec{H}) = \mu_0 (1 + \chi_m^{dia}) \vec{H},$$

i.e.,

$$\vec{B} \approx \mu_0 \vec{H}, \qquad (29)$$

since $\chi_m^{dia} \sim 10^{-5} \ll 1$. Therefore from Eqs. (27) and (29),

$$\vec{M} = -\frac{N Z e^2 \langle r^2 \rangle}{6m} \mu_0 \vec{H}, \qquad (30)$$

and with $\vec{M} = \chi_m^{dia} \vec{H}$ we get the diamagnetic susceptibility as,

$$\chi_m^{dia} = -\frac{N Z e^2 \langle r^2 \rangle \mu_0}{6 m} \qquad (31)$$

This is the classical Langevin result. With $\langle r^2 \rangle \sim 10^{-20} \, m^2$, $N \sim 5 \times 10^{28} / m^3$, one obtains $|\chi_m^{dia}| \sim 10^{-6} Z \sim 10^{-5}$ — compare this with experimental values given in page 12. Diamagnetism associated with free electrons in a metal is not discussed here — not in your syllabus.

6. <u>Induced Magnetic Moment & Magnetic Susceptibility in Paramagnetism</u>

Paramagnetism requires the existence of permanent magnetic dipoles, and the paramagnetic behavior is the analogue of the orientational polarization associated with permanent electric dipoles.

The classical theory of paramagnetism is just like the theory of orientational polarization that we discussed during our study of dielectric properties. One assumes that each of the atoms in the paramagnetic specimen has a permanent magnetic dipole moment $\vec{\mu}_m^o$, which always has the same magnitude μ_m^o, but which can point in any direction. Suppose that the paramagnetic specimen has N such (identical) atoms per unit volume. Without an external magnetic field, the magnetic moments of these atoms will be oriented at random, due to thermal motions and the specimen as a whole will have no resulting magnetization. In the presence of a magnetic field $\vec{B}$, a torque $\vec{\mu}_m^o \times \vec{B}$ is exerted on each magnetic dipole of moment $\vec{\mu}_m^o$, tending to orient it towards $\vec{B}$. This ordering tendency is countered by the thermal motion of the dipoles. In the classical theory, the dipoles are assumed to be freely rotating. From the above discussion, the close analogy with orientational polarization is quite apparent. Our calculations will closely follow this analogy.

The potential energy of each magnetic dipole $\vec{\mu}_m^o$ in the magnetic field $\vec{B}$ is,

$$U = -\vec{\mu_m^o} \cdot \vec{B} = -\mu_m^o B \cos\theta, \qquad (1) \quad \text{See Figure 6.}$$

where $\mu_m^o = |\vec{\mu_m^o}|$ & $B = |\vec{B}|$. According to statistical mechanics, the probability $P(\theta)d\theta$ for a magnetic dipole to make an angle between θ and $\theta + d\theta$ with the magnetic field $\vec{B}$ is,

Figure 6

$$P(\theta)d\theta = \frac{\sin\theta \, d\theta \, e^{-U/kT}}{\int_0^\pi \sin\theta \, d\theta \, e^{-U/kT}} \qquad (2)$$

From Eqs. (1) and (2),

$$P(\theta)d\theta = \frac{\sin\theta \, d\theta \, e^{\mu_m^o B \cos\theta / kT}}{\int_0^\pi \sin\theta \, d\theta \, e^{\mu_m^o B \cos\theta / kT}}, \qquad (3)$$

where k – Boltzmann constant & T – temperature of the paramagnetic specimen. The average component of the dipole moment in the direction of the field $\vec{B}$ is given by

$$\langle \mu_m \rangle = \langle \mu_m^o \cos\theta \rangle = \mu_m^o \langle \cos\theta \rangle, \qquad (4)$$

where,

$$\langle \cos\theta \rangle = \int_0^\pi \cos\theta \, P(\theta) d\theta = \frac{\int_0^\pi \cos\theta \, \sin\theta \, d\theta \, e^{\mu_m^o B \cos\theta / kT}}{\int_0^\pi \sin\theta \, d\theta \, e^{\mu_m^o B \cos\theta / kT}}, \qquad (5)$$

i.e.,

$$\langle \cos\theta \rangle = \frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a} \equiv L(a) \qquad (6)$$

where $L(a)$ is the familiar Langevin function. and,

$$a = \frac{\mu_m^o B}{kT} \qquad (7)$$

$$\therefore \quad \langle \mu_m \rangle = \mu_m^o \langle \cos\theta \rangle = \mu_m^o L(a) \qquad (8)$$

Clearly $\langle \mu_m \rangle$ can be interpreted as the average induced dipole moment per atom in the direction of $\vec{B}$. $\langle \vec{\mu_m} \rangle$ & $\vec{B}$ have the same direction, because the dipole moments tend to orient along $\vec{B}$. That is, the susceptibility is positive.

Now μ_m^o is of the order of 1 Bohr magneton, i.e., $\mu_m^o \sim 10^{-23}$ Amp·m², so that for a magnetic field of 1 Tesla, $\mu_m^o B \simeq 10^{-23}$ Joule. At room temperature $(T \approx 300K)$, $kT \simeq 400 \times 10^{-23}$ Joule. So if the magnetic field is not too high and the temperature not too low, the condition $\mu_m^o B / kT \ll 1$ is satisfied. And when $\dfrac{\mu_m^o B}{kT} = a \ll 1$, then $L(a) \approx a/3$, i.e.,

$$L(a) \simeq \frac{a}{3} = \frac{\mu_m^o B}{3kT} , \qquad a \ll 1 \qquad (9)$$

From (8) and (9), for $\mu_m^o B \ll kT$,

$$\langle \mu_m \rangle = \mu_m^o L(a) = \frac{\mu_m^{o2} B}{3kT} \qquad (10)$$

Since $\langle \vec{\mu_m} \rangle$ & $\vec{B}$ have the same direction, we can write,

$$\langle \vec{\mu_m} \rangle = \frac{\mu_m^{o2} \vec{B}}{3kT} \qquad (11)$$

Now with N atoms per unit volume, the magnetization $\vec{M}$ is given by,

$$\vec{M} = N \langle \vec{\mu_m} \rangle = \frac{N \mu_m^{o2} \vec{B}}{3kT} , \qquad (12)$$

for $\mu_m^o B \ll kT$. Now, $\vec{B} = \mu_o (\vec{H} + \vec{M}) = \mu_o (\vec{H} + \chi_m^{para} \vec{H})$, i.e.,

$$\vec{B} = \mu_o (1 + \chi_m^{para}) \vec{H} \qquad (13)$$

But the paramagnetic susceptibility $\chi_m^{para} \sim 10^{-5} \ll 1$, i.e.,

$$\vec{B} \approx \mu_o \vec{H} \qquad (14)$$

∴ From (12) and (14),

$$\vec{M} = \frac{N \mu_m^{o2} \mu_o}{3kT} \vec{H} = \chi_m^{para} \vec{H} , \qquad (15)$$

so that the paramagnetic susceptibility is given by,

$$\chi_m^{para} = \frac{N \mu_m^{o2} \mu_o}{3kT} = \frac{C}{T} \qquad (16)$$

where

$$C = \frac{N \mu_m^{o2} \mu_o}{3k} \qquad (17)$$

The constant C is known as the Curie constant, and (16) is known
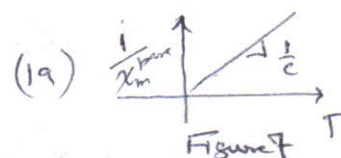
as the <u>Curie law</u>. Remember that the Curie law holds only in the region $\mu_m^o B \ll kT$.

Quantum mechanics essentially leads to the same expression for χ_m^{para} (i.e., $\chi_m^{para} = \dfrac{N \mu_m^{o^2} \mu_o}{3kT}$) if we set,

$$\mu_m^o = \mu_m^J = g \mu_B \sqrt{J(J+1)} \quad , \qquad\qquad (18)$$

i.e. we use the quantum mechanical expression for the permanent magnetic dipole moment μ_m^o using Eq. (34) on page 7. Next, from (16),

$$\frac{1}{\chi_m^{para}} = \frac{T}{C} \qquad\qquad (19)$$

Figure 7

So a plot of $\dfrac{1}{\chi_m^{para}}$ vs T should yield a straight line. See Figure 5, p 305 of Kittel (8th Ed.) for a nice plot for a gadolinium salt, $Gd (C_2H_3SO_4)_3 \cdot 9H_2O$.

Now, the discussion above shows that paramagnetism is temperature dependent, unlike diamagnetism. (However there is also a class of paramagnetism called Van Vleck paramagnetism where the susceptibility is independent of temperature — not in your syllabus.)

References : 1. Solid State Physics by Dekker (Chapter 18)
            2. Solid State Physics by Kittel (Chapter 11)
            3. Feynman Lectures on Physics Vol II (Chapters 34 & 35)