Langevin's classical Theory of Diamagnetism

Diamagnetism is "Distortion Effect". We know that a magnetic field exerts a force on a moving charge. Thus when an external field is applied on a substance, the $\bar{e}$'s in an atom or molecule are subjected to additional force (Lorentz force), which results in perturbation of electronic motion.

The effect of a magnetic field on the electronic motion in an atom is equivalent to an additional current induced in the atom. This current is oriented in a direction s.t the magnetic dipole moment M associated with it is in the direction opposite to that of the magnetic field. Since this effect is independent of the orientation of the atom and is the same for all atoms, we conclude that the substance has acquired a magnetisation M opposite to the magnetic field B. This behaviour is called as diamagnetism and is common to all substances.

We consider the simplest case

$$i = ne = \frac{e\nu}{2\pi r} \quad \text{—①}$$

$$M = \pi r^2 i = \frac{1}{2} e\nu r. \quad \text{—②}$$

The circulating $\bar{e}$ acts like an inductance in which counter emf is produced in accordance with Lenz' Law.

Also as no resistance is encountered by the $\bar{e}$ in its motion about the nucleus, the increased velocity of the $\bar{e}$ does not diminish with time.

For a field B normal to orbit.
$$\phi = \pi r^2 B \quad \text{---} \textcircled{3}$$
as field varies with time hence.
$$emf = -\frac{d\phi}{dt} = -\pi r^2 \frac{dB}{dt} \quad \text{---} \textcircled{4}$$

The emf acts around the current loop and is equivalent to the electrostatic field ξ given as
$$emf = \int \vec{\xi} \cdot \vec{dl} = -\frac{d\phi}{dt} \quad \text{---} \textcircled{5}$$
$$\therefore \xi (2\pi r) = -\pi r^2 \frac{dB}{dt}$$
$$\vec{\xi} = -\frac{r}{2} \frac{dB}{dt} \quad \text{---} \textcircled{6}$$

This field exerts a force $e\vec{\xi}$ on the e^{-1} and this in turn produces a change dv in its velocity
$$e\xi = m \frac{dv}{dt}$$
$$\Rightarrow \frac{dv}{dt} = \frac{e\xi}{m} = -\frac{er}{2m} \frac{dB}{dt} \quad \text{---} \textcircled{7}$$

Thus as $B \to (B + \Delta B)$ we have $v \to (v + \Delta v)$ in the corresponding time.
$$\Delta v = -\frac{er}{2m} \Delta B \quad \text{---} \textcircled{8}$$
and from $\text{eqn} \textcircled{9}$
$$\Delta M = \frac{er}{2} \Delta v \quad \text{---} \textcircled{9}$$

From eqn's $\textcircled{8}$ & $\textcircled{9}$ we get
$$\Delta M = \frac{er}{2} \left(-\frac{er}{2m}\right) \Delta B$$
$$\Delta M = -\frac{e^2 r^2}{4m} \Delta B \quad \text{---} \textcircled{10}$$

writing $\Delta B = \mu_0 \Delta H$ we have.
$$\Delta M = -\frac{\mu_0 e^2 r^2}{4m} \Delta H. \quad \text{---} \textcircled{10}$$

By definition magnetic susceptibility per e^{-1} is given as
$$\Delta M = \chi_m \Delta H \quad \text{---} \textcircled{12}$$
$$\boxed{\therefore \chi_m = -\frac{\mu_0 e^2}{4m} r^2} \quad \text{---} \textcircled{A}$$

If there are N atoms per unit volume, then susceptibility in unit volume is
$$\chi = -N \frac{\mu_0 e^2}{4m} \sum r^2 \quad \text{where summation} \quad \text{---} \textcircled{13}$$
includes all Z-orbital e^{-1}'s.

Moreover as core e^{-1}'s have different radii hence
$$\sum r^2 = Z \langle r^2 \rangle \quad \text{---} \textcircled{14}$$
where $[\langle r^2 \rangle]^{1/2} \to$ avg radius of the e^{-1} from field axis (ie z-axis)
for an orbit in xy plane we have
$$\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle \quad \text{---} \textcircled{15}.$$
also average distance R of e^{-1} from nucleus is $\langle R^2 \rangle = \langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle$
then $\langle r^2 \rangle = \frac{2}{3} \langle R^2 \rangle \quad \text{---} \textcircled{16}$

Hence eqn $\textcircled{A}$ becomes
$$\chi = -\frac{\mu_0 N Z e^2}{6m} \langle R^2 \rangle$$
this is called as Langevins formula for susceptibility of diamagnetic substances

Importance

1) All materials have diamagnetism although it may be masked by other magnetic effects.

2) $\chi \propto Z$ thus bigger the atom, greater is its magnitude of diamagnetism.

3) χ is independent of temperature as internal structures of atoms is virtually unchanged by normal temperatures.

4) As per Langevin model, diamagnetism is attributed to the influence of magnetic field on the orbital momentum of the e^{-1}. even S-electrons do acquire small amount of orbital momentum upon the application of field.

5) $\langle R^2 \rangle$ could be calculated theoretically from the knowledge of wave fn.
For core e^{-1}'s having spherically symmetric wave fn $\psi_n (R)$ for one e^{-1} atom can be given as
$$\chi = -\frac{\mu_0 N Z e^2}{6m} \int \psi_n^*(R) R^2 \psi_n(R) dR$$

Langevin Classical theory of paramagnetism

The main outline of this theory are

i) All atoms possess a permanent magnetic moment

ii) In absence of external magnetic field there orient randomly so that nett. dipole moment is zero.

iii) When external magnetic field is applied. These dipoles tend to align || to the applied field so as to attain minimum PE state.

iv) due to thermal agitation these dipoles get aligned at an angle to the applied field (rather than ||)

P.E produced
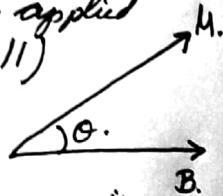
$$P.E = -\vec{\mu}.\vec{B} = -\mu B \cos\theta \quad —(1)$$

$$\Rightarrow U = -\mu B \cos\theta.$$

diff we get. $dU = \mu B \sin\theta.d\theta.$

As per B Maxwell - Boltzmann statistics no. of atoms/volume of having energy b/w $U \cdot \& (U+dU)$ is given as.

$$dn = A e^{-U/kT}.dU$$

$A \to$ const $T \to$ Absolute temperature

Substituting values of $U \& dU$

$$dn = A e^{\mu B \cos\theta/kT}.\mu B \sin\theta.d\theta \quad —(2)$$

Thus total no of dipoles/vol.

$$n = \int_{\theta=0}^{\theta=\pi} dn = A \int_0^\pi e^{\mu B \cos\theta/kT}.\mu B \sin\theta d\theta$$

$$\text{or } A = \frac{n}{\int_0^\pi e^{\mu B \cos\theta/kT}.\mu B \sin\theta.d\theta} \quad —(3)$$

Now Resultant Magnetic moment due to dn no. of dipoles is.

$$= \mu \cos\theta.dn.$$

Hence Total Average dipole moment per unit volume or Intensity of Magnetisation (M) can be given as.

$$M = \int_0^\pi \mu \cos\theta.dn = \int_0^\pi A\mu^2 B e^{\mu B \cos\theta/kT}.\sin\theta \cos\theta.d\theta$$

(from =n 2)

$$M = \frac{n\mu^2 B \int_0^\pi e^{\mu B \cos\theta/kT}.\sin\theta \cos\theta.d\theta}{\mu B \int_0^\pi e^{\mu B \cos\theta/kT}.\sin\theta.d\theta}$$

(from =n 3)

$$M = \frac{n\mu \int_0^\pi e^{\mu B \cos\theta/kT}.\sin\theta \cos\theta.d\theta}{\int_0^\pi e^{\mu B \cos\theta/kT}.\sin\theta.d\theta}$$

Let $\frac{\mu B}{kT} = x$; $\cos\theta = y \Rightarrow -\sin\theta.d\theta = dy$

When $\theta = 0$ $\cos\theta = 1 \Rightarrow y = +1$

When $\theta = \pi$ $\cos\theta = -1 \Rightarrow y = -1.$

$$M = \frac{n\mu \int_{+1}^{-1} e^{xy}.y \, dy}{\int_{+1}^{-1} e^{xy} dy}$$
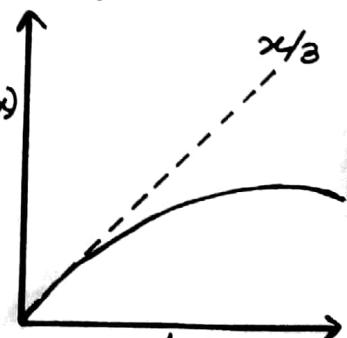
$$= n\mu \left[\frac{e^x + e^{-x}}{e^x - e^{-x}} - \frac{1}{x}\right] = n\mu\left[\coth x - \frac{1}{x}\right]$$

$$\boxed{M = n\mu \, L(x)} \quad —(4).$$

→ Langevin function.

Conclusion

The variation of $L(x)$ w.r.t x is as shown

fig (a)

Case-I

$\frac{\mu B}{kT}$ is very large $\Rightarrow x >> 1$

Thus T is small and B is large.

$$|L(x)|_{x\to\infty} = \left[\coth x - \frac{1}{x}\right]_{x\to\infty} = \left[\frac{e^x + e^{-x}}{e^x - e^{-x}} - \frac{1}{x}\right]_{x\to\infty}$$

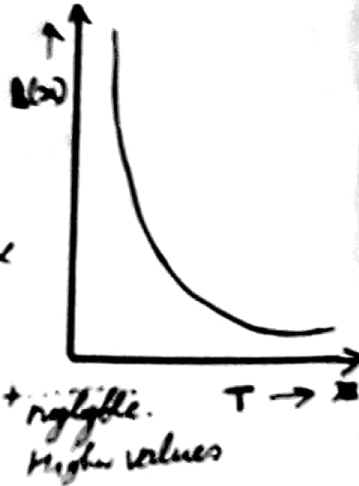$$= \left[\frac{1 + e^{-2x}}{1 - e^{-2x}} - \frac{1}{x}\right]_{x\to\infty} \simeq 1$$

$$\Rightarrow M = n\mu = M_S \to \text{saturated value of magnetisation}$$

Hence there is complete alignment of Dipoles parallel to applied field.

Case–II

$$\frac{\mu B}{kT} \ll 1$$

$$\mu B \ll kT \Rightarrow x \ll 1$$

Here Temp T is large
& B is small.

Thus $\coth x = \frac{1}{x} + \frac{x}{3} + \text{negligible}$.
higher values

$$M = n\mu \frac{x}{3} = \frac{n\mu}{3} \cdot \frac{\mu B}{kT} = \frac{n\mu^2 B}{3kT}$$

$$M = \frac{n\mu^2 \mu_0 H}{3kT} \qquad (B = \mu_0 H)$$

$$\frac{M}{H} = \chi_m = \left(\begin{array}{c}\text{magnetic} \\ \text{susceptibility}\end{array}\right) = \frac{n\mu^2 \mu_0}{3kT} = \frac{C}{T}$$

here $C = \frac{n\mu^2 \mu_0}{3k}$ is called as

Curie Constant also called as

"CURIE LAW"

As given in fig (b) Magnetic Susceptibility
(χ_m) of paramagnetic substances
is inversely proportional to absolute
Temperature

Draw backs of Langevins Theory

1) It does not explain the paramagnetic
properties Vs temperature in case of
highly compressed, solid salts &
crystals.

2) This theory is restricted to gases
only. wherein inter atomic
interaction is negligible.

3) Does not explain the relationship
b/w dia & paramagnetism.