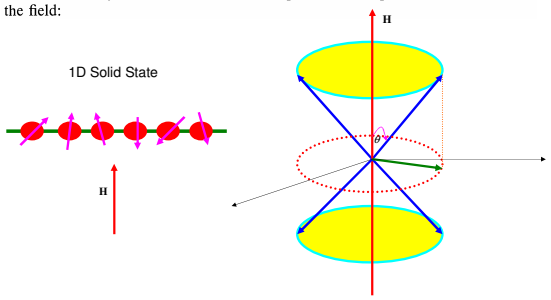
# The statistics of paramagnetism

Next, we study a system of $N$ magnetic dipoles, each having a magnetic moment $\boldsymbol{\mu}$. In the presence of an external magnetic field $\boldsymbol{H}$, the dipoles will experience a torque tending to align them in the direction of the field. If there were nothing else to check this tendency, the dipoles would align themselves precisely in this direction and we would achieve a complete magnetization of the system. In reality, however, thermal agitation in the system offers resistance to this tendency and, in equilibrium, we obtain only a *partial* magnetization. Clearly, as $T \to 0$ K, the thermal agitation becomes ineffective and the system exhibits a complete orientation of the dipole moments, whatever the strength of the applied field; at the other extreme, as $T \to \infty$, we approach a state of complete randomization of the dipole moments, which implies a vanishing magnetization. At intermediate temperatures, the situation is governed by the parameter $(\mu H/kT)$.

The model adopted for this study consists of $N$ identical, localized (and, hence, distinguishable), practically static, mutually non-interacting and freely orientable dipoles. It is obvious that the only energy we need to consider here is the potential energy of the dipoles which arises from the presence of the external field $\boldsymbol{H}$ and is determined by the orientations of the dipoles with respect to the direction of the field:




$$E = \sum_{i=1}^{N} E_i = -\sum_{i=1}^{N} \boldsymbol{\mu}_i \cdot \mathbf{H} = -\sum_{i} \mu H \; Cos\theta_i = -\mu H \sum_{i} Cos\theta_i$$

$$Q_N(\beta) = \sum_{E} \exp(-\beta E) = \sum_{\{\theta_i\}} \exp\left(\beta\mu H \sum_{i=1}^{N} Cos\theta_i\right)$$

$$= \sum_{\{\theta_i\}} \prod_{i=1}^{N} \exp(\beta\mu H \; Cos\theta_i) = \prod_{i=1}^{N} \sum_{\{\theta_i\}} \exp(\beta\mu H \; Cos\theta_i)$$

$$= [Q_1(\beta)]^N = \left[\sum_{\{\theta_i\}} \exp(\beta\mu H \; Cos\theta_i)\right]^N$$

$$M_z = N\langle \mu \; Cos\theta \rangle = N \frac{\sum_{\theta} \mu \; Cos\theta \; \exp(\beta\mu H \; Cos\theta)}{\sum_{\theta} \exp(\beta\mu H \; Cos\theta)} = \frac{N}{\beta} \frac{\partial}{\partial H} \ln Q_1(\beta)$$

$$\left\langle \sum_{i=1}^{N} \mu \; Cos\theta_i \right\rangle_{\{\theta_i\}} = \frac{1}{\beta} \frac{\partial}{\partial H} \ln Q_N(\beta) \qquad \left\langle \sum_{i=1}^{N} \mu \; Cos\theta_i \right\rangle_{\{\theta_i\}} = N\langle \mu \; Cos\theta \rangle$$

Thus, to determine the degree of magnetization in the system all we have to do is to evaluate the single-dipole partition function (3).

First, we do it classically (after Langevin, 1905a,b). Using $(\sin\theta \, d\theta \, d\phi)$ as the elemental solid angle representing a small range of orientations of the dipole, we get

$$Q_1(\beta) = \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} \exp(\beta\mu H \; Cos\theta) \; Sin\theta \; d\theta \; d\varphi$$

$$\beta\mu H \; Cos\theta = u$$

$$-\beta\mu H \; Sin\theta \; d\theta = du$$

$$= 2\pi \int \exp(u) \; \frac{du}{(-\beta\mu H)} = -\frac{2\pi}{\beta\mu H} \; \exp(u)$$

$$= -\frac{2\pi}{\beta\mu H} \exp(\beta\mu H \; Cos\theta) \Big|_0^{\pi}$$

$$= -\frac{2\pi}{\beta\mu H} [\exp(-\beta\mu H) - \exp(\beta\mu H)]$$

$$= 4\pi \; \frac{Sin(\beta\mu H)}{\beta\mu H}$$

$$\langle \mu \rangle = \bar{\mu} = \frac{\sum_{\theta} \mu_\theta \; \exp(\beta\mu H \; Cos\theta)}{\sum_{\theta} \exp(\beta\mu H \; Cos\theta)}$$

$$\mu_\theta = \mu \; Cos\theta$$

$$= \frac{\sum_{\theta} \mu \; Cos\theta \; \exp(\beta\mu H \; Cos\theta)}{\sum_{\theta} \exp(\beta\mu H \; Cos\theta)}$$

$$= \frac{1}{\beta} \frac{\partial}{\partial H} \ln \left\{ \sum_{\theta} \exp(\beta\mu H \; Cos\theta) \right\}$$

$$= \frac{1}{\beta} \frac{\partial}{\partial H} \ln Q_1(\beta)$$

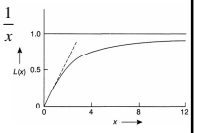
$$= \frac{1}{\beta} \frac{\partial}{\partial H} \ln \left\{ 4\pi \; \frac{Sin(\beta\mu H)}{\beta\mu H} \right\}$$

$$= \frac{1}{\beta} \frac{\partial}{\partial H} \left\{ \ln [Sin(\beta\mu H)] - \ln \frac{(\beta\mu H)}{4\pi} \right\}$$

$$= \frac{1}{\beta} \left\{ \frac{\beta\mu \; Cosh(\beta\mu H)}{Sinh(\beta\mu H)} - \frac{\beta\mu / 4\pi}{\beta\mu H / 4\pi} \right\}$$

$$= \frac{1}{\beta} \frac{\partial}{\partial H} \left\{ \ln [Sin(\beta\mu H)] - \ln \frac{(\beta\mu H)}{4\pi} \right\}$$

$$L(x) = Coth(x) - \frac{1}{x}$$




$$\langle \mu \rangle = \mu \; L(x)$$

$$M = N \; \bar{\mu} = N\mu \; L(x) \qquad (x = \beta\mu \; H)$$

$$if \quad x >> 1 \quad \Rightarrow \quad \frac{\mu H}{kT} >> 1 \quad \Rightarrow \mu H >> kT$$

$$L(x)\Big|_{x>>1} \to 1$$

$$\langle \mu \rangle = \mu \quad \Rightarrow M = N\langle \mu \rangle \approx N\mu$$ ☺

$$if \quad x << 1 \quad \Rightarrow \quad \frac{\mu H}{kT} << 1 \quad \Rightarrow \mu H << kT$$

$$L(x)\Big|_{x<<1} \to \frac{x}{3} - \frac{x^3}{45} + \cdots \quad \Rightarrow \quad L(x)\Big|_{x<<1} \sim \frac{x}{3}$$

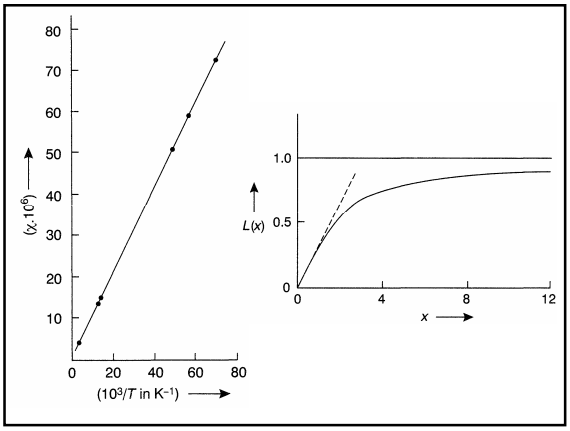
$$\langle \mu \rangle = \mu \; L(x) = \mu \left(\frac{x}{3}\right) = \mu \left(\frac{\beta\mu H}{3}\right) = \frac{1}{3}\beta\mu^2 H$$

$$M = N\langle \mu \rangle \approx \frac{1}{3}\beta\mu^2 NH = \left(\frac{\mu^2 N}{3kT}\right) H$$

$$\chi_m = \lim_{H \to 0} \left(\frac{\partial M}{\partial H}\right) \approx \frac{\mu^2 N}{3kT}$$

$$\chi_m = \frac{C}{T} \qquad C = \frac{\mu^2 N}{3k}$$

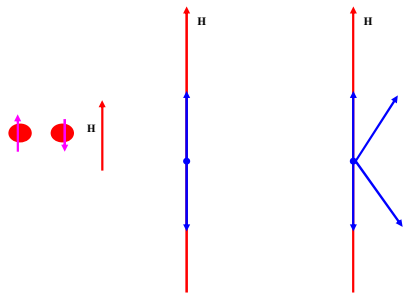
Equation (12) is the *Curie law* of paramagnetism, the parameter $C$ being the *Curie constant* of the system. Figure 3.7 shows a plot of the susceptibility of a powdered sample of copper–potassium sulphate hexahydrate as a function of $T^{-1}$; the fact that the plot is linear and passes almost through the origin vindicates the Curie law for this particular salt.




We shall now treat the problem of paramagnetism quantum-mechanically. The major modification here arises from the fact that the magnetic dipole moment $\boldsymbol{\mu}$ and its component $\mu_z$ in the direction of the applied field cannot have *arbitrary* values.

If J = 1/2, then m = -1/2, 1/2

If J = 3/2 then m = -3/2, -1/2, 1/2, 3/2




Quite generally, we have a direct relationship between the magnetic moment $\boldsymbol{\mu}$ of a given dipole and its angular momentum $\boldsymbol{l}$:

$$\boldsymbol{\mu} = \left(g\frac{e}{2mc}\right)\boldsymbol{l}, \tag{13}$$

with

$$l^2 = J(J+1)\hbar^2; \quad J = \tfrac{1}{2}, \tfrac{3}{2}, \tfrac{5}{2}, \ldots \quad \text{or} \quad 0, 1, 2, \ldots \tag{14}$$

The quantity $g(e/2mc)$ is referred to as the *gyromagnetic ratio* of the dipole while the number $g$ is known as *Lande's g-factor*. If the net angular momentum of the dipole is due solely to electron spins, then $g = 2$; on the other hand, if it is due solely to orbital motions, then $g = 1$. In general, however, its origin is mixed; $g$ is then given by the formula

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}, \tag{15}$$

$S$ and $L$ being, respectively, the spin and the orbital quantum numbers of the dipole. Note that there is no upper or lower bound for the values that $g$ can have!

Combining (13) and (14), we can write

$$\mu^2 = g^2\mu_B^2 J(J+1), \tag{16}$$

where $\mu_B(=e\hbar/2mc)$ is the *Bohr magneton*. The component $\mu_z$ of the magnetic moment in the direction of the applied field is, on the other hand, given by

$$\mu_z = g\mu_B m, \quad m = -J, -J+1, \ldots, J-1, J. \tag{17}$$

Thus, a dipole whose magnetic moment $\mu$ conforms to expression (16) can have no other orientations with respect to the applied field except the ones conforming

$$Q_1(\beta) = \sum_{m=-J}^{J} \exp(\beta g \mu_B m H)$$

$$x = \beta(g\mu_B J)H$$

$$Q_1(\beta) = \sum_{m=-J}^{J} e^{mx/J} = \frac{e^{-x}\left\{e^{(2J+1)x/J} - 1\right\}}{e^{x/J} - 1} = \frac{\exp\left\{(2J+1)\frac{x}{2J}\right\} - \exp\left\{-(2J+1)\frac{x}{2J}\right\}}{\exp\left\{\frac{x}{2J}\right\} - \exp\left\{-\frac{x}{2J}\right\}}$$

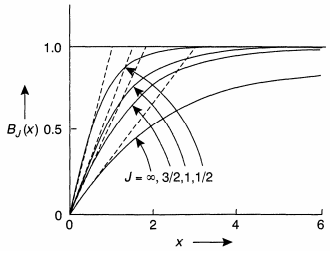
$$= Sinh\left\{\left(1+\frac{1}{2J}\right)x\right\} \Big/ Sinh\left\{\frac{1}{2J}x\right\}$$

$$\langle \mu_z \rangle = \frac{1}{\beta}\frac{\partial}{\partial H} \ln Q_1(\beta) = (g\mu_B J)\left\{\left(1+\frac{1}{2J}\right) Coth\left\{\left(1+\frac{1}{2J}\right)x\right\} - \frac{1}{2J}\, Coth\left\{\frac{1}{2J}x\right\}\right\}$$

$$\langle \mu_z \rangle = \overline{\mu}_z = (g\mu_B J)\; B_J(x)$$

$$B_J(x) = \left(1+\frac{1}{2J}\right) Coth\left\{\left(1+\frac{1}{2J}\right)x\right\} - \frac{1}{2J}\, Coth\left\{\frac{1}{2J}x\right\}$$

Brillouin Function (of order J)




$$if \quad x \gg 1 \;\Rightarrow B_J(x) \to 1$$

$$if \quad x \ll 1 \quad \Rightarrow \quad B_J(x) \to \frac{1}{3}\left(1+\frac{1}{J}\right)x + \cdots$$

$$M = N\langle \mu_z \rangle = N(g\mu_B J)\left\{\frac{1}{3}\left(1+\frac{1}{J}\right)x\right\}$$

$$= N(g\mu_B J)\left\{\frac{1}{3}\left(1+\frac{1}{J}\right)\beta(g\mu_B J)H\right\}$$

$$= \frac{N(g\mu_B J)^2}{3kT}\left(1+\frac{1}{J}\right)H = \frac{Ng^2\mu_B^2\, J(J+1)}{3kT}\, H = \frac{N\mu^2}{3kT}\, H$$

$$\chi \propto \frac{1}{T}$$

$$C_J = \frac{Ng^2\mu_B^2\, J(J+1)}{3k} = \frac{N\mu^2}{3k}$$

*if* $J=\frac{1}{2}$ , $L=0$ , $S=\frac{1}{2}$

$$\langle\mu\rangle=\bar{\mu}=\mu\frac{\exp(\beta\mu H)-\exp(-\beta\mu H)}{\exp(\beta\mu H)+\exp(-\beta\mu H)}$$

$$=\mu\ \frac{Sinh(\beta\mu H)}{Cosh(\beta\mu H)}$$

$$=\mu\ \tanh(\beta\mu H)=\mu\ \tanh(x)$$

$$x=\beta\mu H$$

*for* $x>>1 \quad\Rightarrow\quad \tanh(x)\to 1$

$$M=N\langle\mu\rangle=N\mu\ \tanh\left(\frac{\mu H}{kT}\right)=N\mu$$

*for* $x<<1$

$$\langle\mu\rangle=\mu\ \frac{1+\beta\mu H-(1-\beta\mu H)}{1+\beta\mu H+1-\beta\mu H}$$

$$=\mu\ \frac{2\beta\mu H}{2}=\beta\mu^2 H$$

$$M=N\langle\mu\rangle=N\beta\mu^2 H=N\frac{\mu^2 H}{kT}$$

$$C_{1/2}=\frac{N\mu^2}{k}=3C_{cla}$$

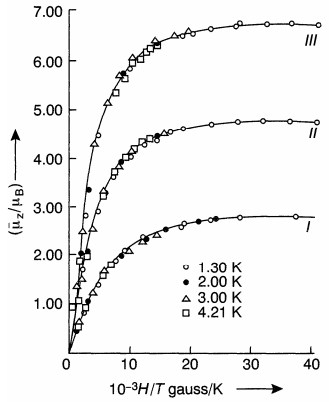



FIG. 3.9. Plots of $\bar{n}_z/\mu_B$ as a function of $H/T$. The solid curves represent the theoretical results, while the points mark the experimental findings of Henry (1952). Curve I is for potassium chromium alum ($J=\frac{1}{2}, g=2$), curve II for iron ammonia alum ($J=\frac{1}{2}, g=2$) and curve III for gadolinium sulphate octahydrate ($J=\frac{7}{2}, g=2$).