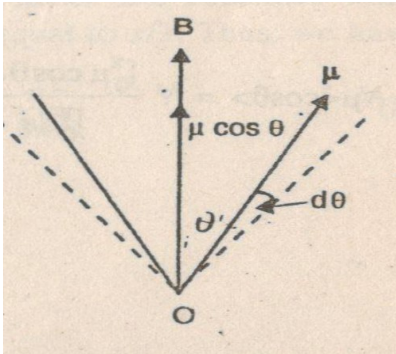
Langevin's classical theory of Paramagnetism:

Langevin considered a paramagnetic gas containing N atoms per unit volume each having a permanent magnetic moment μ. The mutual interaction between the magnetic dipoles was assumed to be negligible. In the presence of a magnetic field H, these dipoles tend to orient themselves in the direction of the field in order to minimize their energy. However, the thermal energy at ordinary temperature resists such an alignment of dipoles. In thermal equilibrium, let assume that the dipoles orient themselves at an angle θ with the direction of the applied field as shown in the figure below.



The potential energy of each dipole in this position is given by

$$E = -\mu . H = -\mu H \cos\theta$$

Using Maxwell-Boltzmann distribution law, the number of magnetic dipoles having this particular orientation is proportional to

$$exp\left(-\frac{E}{k_B T}\right) \text{ or } \quad exp\left(\frac{\mu H\cos\theta}{k_B T}\right)$$

Also, according to statistical mechanics, the probability for a magnetic dipole to make an angle between θ and $(\theta + d\theta)$ with the magnetic field, or the number of dipoles, dn, having axes within the solid angle $d\Omega$ lying between two hollow cones of semi-angles θ and $(\theta + d\theta)$ (see the figure above) is given by

$$dn \propto exp\left(\frac{\mu H\cos\theta}{k_B T}\right) d\Omega = A\, exp\left(\frac{\mu H\cos\theta}{k_B T}\right) 2\pi \sin\theta\, d\theta$$

where A is a constant. Each one of these dipoles contributes a component of magnetic moment $\mu\ cos\theta$ to the magnetization, whereas the components perpendicular to the field direction cancel each other. Hence the average component of magnetic moment of each atom along the field direction is given by

$$\langle\mu\rangle = \frac{\int_0^\pi \mu\cos\theta\, dn}{\int_0^\pi dn} = \frac{A\int_0^\pi \mu\cos\theta\, exp\left(\mu H\cos\theta / k_B T\right) 2\pi \sin\theta\, d\theta}{A\int_0^\pi exp\left(\mu H\cos\theta / k_B T\right) 2\pi\sin\theta\, d\theta}$$

$$= \frac{\int_0^{\pi} \mu \cos\theta \exp\left(\mu H \cos\theta / k_B T\right) \sin\theta d\theta}{\int_0^{\pi} \exp\left(\mu H \cos\theta / k_B T\right) \sin\theta d\theta}$$

Let $y = \frac{\mu H}{k_B T}$ and $x = \cos\theta$ then $dx = -\sin\theta \, d\theta$

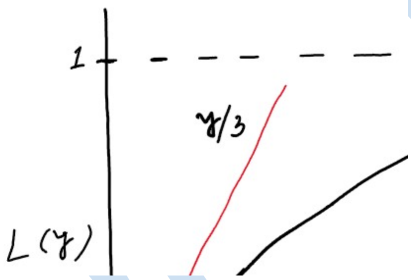
When $\theta \to 0$then $x \to 1$ and if $\theta \to \pi$then $x \to -1$

Therefore,

$$\langle \mu \rangle = \frac{\mu \int_{-1}^{1} x e^{yx} dx}{\int_{-1}^{1} e^{yx} dx} = \frac{\mu \left[\frac{x}{y} e^{yx} - \frac{1}{y^2} e^{yx}\right]_{-1}^{1}}{\left[\frac{e^{yx}}{y}\right]_{-1}^{1}}$$

$$= \frac{\mu\left[\frac{e^{y}}{y} + \frac{e^{-y}}{y} - \frac{e^{y}}{y^2} + \frac{e^{-y}}{y^2}\right]}{\frac{e^{y}}{y} - \frac{e^{-y}}{y}} = \mu\left\{\left(\frac{e^{y}+e^{-y}}{e^{y}-e^{-y}}\right) - \frac{1}{y}\right\} = \mu\left[\coth y - \frac{1}{y}\right] = \mu L(y)$$

Where $L(y)$ is called the Langevin function and variation of $L(y)$ with $y \left(= \frac{\mu H}{k_B T}\right)$is shown below,



Now, the average magnetic moment of each atom along the field direction multiplied by the number of atoms per unit volume, N, gives the magnetization$M = N\mu L(y)$.

Case I: For large values of y, i.e. when $y >> 1$

i.e.$(\mu H >> k_B T)$ when applied magnetic field strength is high and the specimen is kept at very low temperature; then $L(y) \to 1$and magnetization becomes maximum $M = N\mu = M_S$. This is the saturation condition which corresponds to the complete alignment of the magnetic dipoles in the field direction. $M_S$is called saturation magnetization.

Therefore, susceptibility per unit volume $\chi = \frac{M}{H} = \frac{N\mu}{H}$ is independent of temperature.

Case II: For small values of y, i.e. when $y << 1$

i.e. $(\mu H << k_B T)$ at normal magnetic field strengths and ordinary temperatures, the curve is almost linear and coincides with the tangent to the curve at the origin which is equal to $y/3$.

$L(y) = \left\{\left(\frac{e^{y}+e^{-y}}{e^{y}-e^{-y}}\right) - \frac{1}{y}\right\}$ and if $y << 1$ then

$$L(y) = \left\{ \left(\frac{\left[1 + y + y^2/_{2!} + y^3/_{3!} + \ldots\ldots\right] + \left[1 - y + y^2/_{2!} - y^3/_{3!} + \ldots\ldots\right]}{\left[1 + y + y^2/_{2!} + y^3/_{3!} + \ldots\ldots\right] - \left[1 - y + y^2/_{2!} - y^3/_{3!} + \ldots\ldots\right]} \right) - \frac{1}{y} \right\}$$

$$\cong \frac{2\left[1 + y^2/_{2!} + \ldots\right]}{2\left[y + y^3/_{3!} + \ldots\right]} - \frac{1}{y} \cong \frac{1 + y^2/_2}{y\left(1 + y^2/_6\right)} - \frac{1}{y}$$

$$\cong \frac{1}{y}\left(1 + y^2/_2\right)\left(1 - y^2/_6\right) - \frac{1}{y}$$ (Neglecting higher order terms of *y*)

$$\cong \frac{1}{y}\left(1 + \frac{y^2}{2} - \frac{y^2}{6}\right) - \frac{1}{y} = \frac{1}{y}\left(1 + \frac{y^2}{3}\right) - \frac{1}{y} = \frac{y}{3}$$

Thus magnetization per unit volume $M = N\mu L(y) = N\mu \frac{y}{3} = N\mu \frac{\mu H}{3k_B T} = \frac{N\mu^2 H}{3k_B T}$

Hence magnetic susceptibility per unit volume becomes

$$\chi = \frac{M}{H} = \frac{N\mu^2}{3k_B T} = \frac{C}{T}$$ where $C = \frac{N\mu^2}{3k_B}$ is known as Curie constant.

This expression is known as Curie law, which shows that paramagnetic susceptibility is inversely proportional to temperature [for the condition$(\mu H << k_B T)$].