



Debye Equation:

Here we consider molecules which possess a permanent dipole moment  $\mu$  such as a water molecule or chlorobenzene molecule in an electrostatic field.

In the absence of an electric field the individual dipoles point in random directions so that the net electric moment per unit volume is zero. When an electric field is applied it affects the polar molecules in two ways

(i) It induces an extra dipole moment in the molecule due to the forces acting on the electron.

(ii) The electric field tends to line up the individual dipoles to produce a net dipole moment per unit volume

However, in the present discussion we overlook the induced dipole moment and consider only the permanent dipole moment due to which molecules align in the field.

At ordinary temp. and fields the collision of molecules during the thermal motion keep them away from perfect alignment, but there is always some orientational polarisation.

Given:

$\mu$  = permanent electric dipole moment of each molecule.



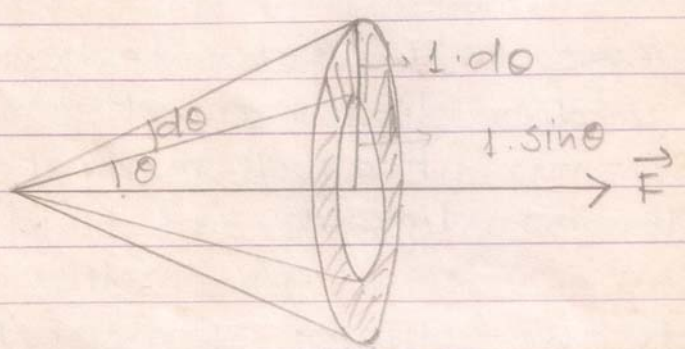
$F$  = Strength of the applied field.  
 $T$  = Temperature.

Consider a molecule, whose permanent electric dipole moment vector is inclined to the field direction at an angle  $\theta$ .

The P.E of this molecule in the electric field  $U = -MF \cos\theta$

According to Maxwell, Boltzman distribution law " the number of molecules distributed with the axes of their dipoles ; pointing in all directions within a solid angle  $d\Omega$  contained in the direction laying between  $\theta$  &  $\theta + d\theta$ '

$$dn = A e^{-u/kT} d\Omega = A e^{-(-MF \cos\theta)/kT} d\Omega$$



Shaded area = solid angle  $d\Omega = (2\pi \cdot 1 \sin\theta)(1) = 2\pi \sin\theta d\theta$

$$\therefore dn = A e^{-u/kT} 2\pi \sin\theta d\theta \quad \text{--- (1)}$$



Integrating eq<sup>n</sup> (1) to include all directions we get the total number of molecules present per unit volume =  $n$

$$\therefore n = \int dn = \int_0^{\pi/2} A e^{MF \cos \theta / KT} \cdot 2\pi \sin \theta d\theta \quad (2)$$

The dipole moment of each of that 'dn' molecules lying within the solid angle in the direction of the field =  $M \cos \theta$

$\therefore$  Dipole moment of the 'dn' molecules in the field direction =  $dn \cdot M \cos \theta = A e^{\frac{MF \cos \theta}{KT}} M \cos \theta d\theta$  — (3)

Integrating eq<sup>n</sup> (3) to include all possible values of ' $\theta$ ' we get the total dipole moment per unit volume in the direction of the field.

$$\therefore \sum p = \int A e^{MF \cos \theta / KT} M \cos \theta \cdot 2\pi \sin \theta d\theta \quad (4)$$

The average dipole moment in the field direction is therefore:

$$\bar{m} = \frac{\sum m}{Z} = \frac{\int A e^{MF \cos \theta / KT} M \cos \theta d\Omega}{\int A e^{MF \cos \theta / KT} d\Omega} \quad (5)$$

Now the solid angle  $d\Omega$  covering all directions in which the inclination of the dipoles to the directions of the field lies between  $\theta$  and ' $\theta + d\theta$ ' is given by,



$d\Omega = \text{Area of the ring between angles } \theta \text{ \& } \theta + d\theta$

$$\frac{2\pi r^2 \sin\theta \cdot r d\theta}{r^2} = 2\pi \sin\theta d\theta$$

$$= \frac{2\pi r^2 \sin\theta \cdot r d\theta}{r^2} = 2\pi \sin\theta d\theta$$

In equation (4) putting  $\cos\theta = \alpha$  ;  $\sin\theta d\theta = -d\alpha$   
 $\therefore d\Omega = -2\pi d\alpha$  putting  $\frac{\mu F}{kT} = x$   
 from equation (4) :-

$$\frac{\bar{m}}{\mu} = \frac{\int e^{x\alpha} \alpha d\alpha}{\int e^{x\alpha} d\alpha}$$

Now as  $\theta$  varies from 0 to  $\pi$ ,  $\alpha$  will vary from +1 to -1

$$\therefore \frac{\bar{m}}{\mu} = \frac{\int_{-1}^{+1} \alpha e^{x\alpha} d\alpha}{\int_{-1}^{+1} e^{x\alpha} d\alpha} = \frac{\left[ \frac{\alpha}{x} e^{x\alpha} - \frac{1}{x^2} e^{x\alpha} \right]_{-1}^{+1}}{\left[ \frac{1}{x} e^{x\alpha} \right]_{-1}^{+1}}$$

$$= \frac{\frac{1}{x} (e^x + e^{-x}) - \frac{1}{x^2} (e^x - e^{-x})}{\frac{1}{x} (e^x - e^{-x})} = \frac{e^x + e^{-x}}{e^x - e^{-x}}$$

$$= \coth x - \frac{1}{x}$$

$$= L(x)$$

$$\therefore \frac{\bar{m}}{\mu} = L(x)$$

The function  $L(x)$  was derived by Langerin in calculating mean magnetic moment of gas molecules carrying permanent magnetic

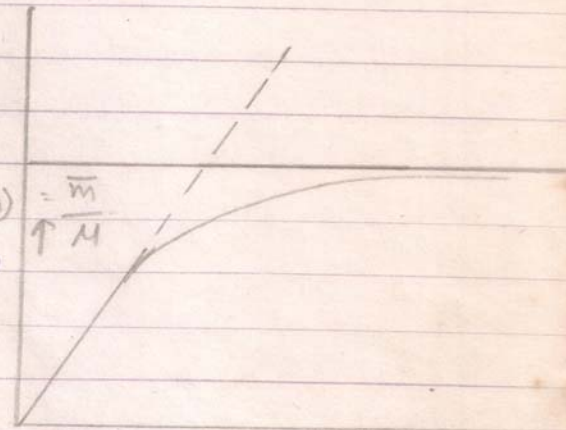


moment and is consequently called Langevin function.

When  $L(x)$  is plotted against  $x$  i.e.  $\bar{m}$  is plotted against  $\frac{\mu F}{kT}$  the curve is found to be almost linear for very small values of  $\frac{\mu F}{kT}$  (i.e. very small

$kT$  values of  $F$  & large values of  $T$ ), while for large values of  $\frac{\mu F}{kT}$  it approaches one.

for small values of  $x$ ,  $L(x)$  can be expanded in the series.



$$L(x) = \frac{x}{3} - \frac{x^3}{45} + \dots \quad x = \frac{\mu F}{kT} \rightarrow$$

As under normal experimental conditions  $x$  is very small, only the first term of this series is considered. Therefore

$$L(x) = \frac{x}{3}$$

$$\text{or } \frac{\bar{m}}{\mu} = \frac{\mu F}{3kT} \quad (5) \quad \text{or } \bar{m} = \frac{\mu^2 F}{3kT} \quad (6)$$

The effect of this average dipole moment produced by the alignment of the dipole in the field direction is added to the induced moment which has been temporarily disregarded.

Therefore the total mean dipole moment



in the field direction is

$$m' = m + \bar{m} = \alpha \epsilon_0 F + \frac{\mu^2 F}{3kT}$$

$$= \left( \alpha + \frac{\mu^2}{3kT} \right) \epsilon_0 F \quad (7)$$

While  $\alpha$  is the polarisability by distortion and  $\frac{\mu^2}{3kT}$  the polarisability by orientation, Thus for a polar molecule the effective polarisability is given by

$$\alpha_{\text{eff}} = \alpha + \frac{\mu^2}{3kT} \quad (8)$$

This is known as Langvin-Debye equation. Therefore in the case of polar molecules on replacing  $\alpha$  by  $\alpha_{\text{eff}}$  (i.e. on applying Debye correction) take the form.

$$\bar{A} = \frac{\epsilon - \epsilon_0}{\epsilon + 2\epsilon_0} = \frac{\bar{M}}{3} \left( \alpha + \frac{\mu^2}{3kT} \right) \quad (8)$$

$$P = \frac{\epsilon - \epsilon_0}{\epsilon + 2\epsilon_0} V = \frac{Z}{3} \left( \alpha + \frac{\mu^2}{3kT} \right) \quad (9)$$

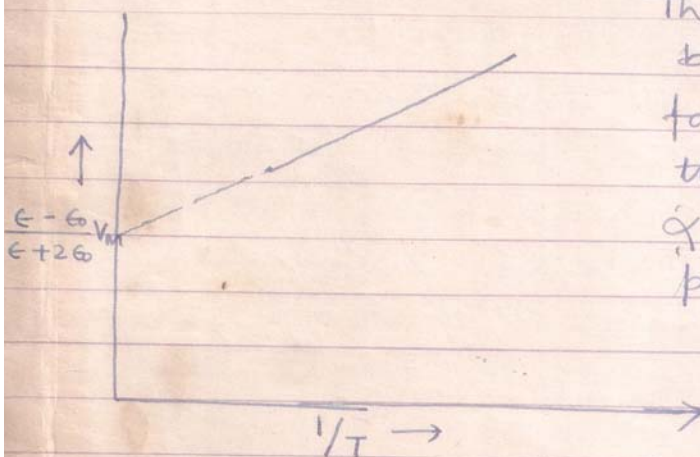
$$P_m = \frac{\epsilon - \epsilon_0}{\epsilon + 2\epsilon_0} V_m = \frac{N}{3} \left( \alpha + \frac{\mu^2}{3kT} \right) \quad (10)$$

Any of these three equations may be called Debye Equation.



The Debye equation shows that the permittivity or dielectric constant of a polar dielectric depends on temperature. From the practical point of view this is only feature which distinguishes a polar dielectric from non-polar dielectric.

The equations derived above strictly hold only for gases at pressures which are so low that the interactions between the molecules may be neglected. They have however, been applied to polar molecules in dilute solutions of non-polar solvents and also to polar liquids.



The Debye eq<sup>2</sup> can be employed for determining the polarisability  $\alpha'$  and the permanent dipole moment  $\mu$  of a molecule by

plotting  $\frac{\epsilon - \epsilon_{\infty}}{\epsilon + 2\epsilon_{\infty}} V_m$  against  $1/T$ . The intercept of the straight line thus obtained on the ordinate is  $\frac{N\mu^2}{3}$  and its slope is  $\frac{NK}{9\epsilon_0}$ . Where  $N$  is the Avogadro's no. and  $K$  is the Boltzmann constant.