

## Dispersion

In an atom, the centre of mass of the negatively charged electron cloud coincides with the positively charged nucleus, so that a cancellation of charge takes place. If however, an electric field is applied, the negatively charged electron cloud shifts in the opposite direction compared to the field and a charge separation occurs, forming a dipole.

(Dipole moment =  $-e \cdot x$ )

A restoring force however develops at the same time, trying to bring back the cloud in its original equilibrium position. If we consider the entire charge of the cloud to be concentrated at the centre of mass and treat it as a particle,

(i) the force due to the applied electric field ( $E$ ) on it is  $-eE$  if a plane polarized, monochromatic light wave is incident on the atom, the electric field is of the form :  $E_0 e^{i\omega t}$  and the force due to it is  $-eE_0 e^{i\omega t}$ .

(ii) If the displacement ( $x$ ) of the charge cloud is small, the above mentioned restoring force will be proportional to the displacement and it will have the form :  $-Kx$ .

If we write  $K/m = \omega_0^2$ , then the force is :  $-m\omega_0^2 x$ .

(iii) An accelerated charge radiates which causes a loss in its energy. The loss is, as if, due to a damping force, known as radiation damping. Its expression, one can show, is :  $R d^3x/dt^3$ , where  $R = (1/4\pi\epsilon_0) (2e^2/3c^3)$ .

[The rate of energy loss =  $R (d^2x/dt^2)^2$ ]

$\Rightarrow$  Loss of energy over a period =  $\int R (d^2x/dt^2)^2 dt = \int R (d^2x/dt^2) (d^2x/dt^2) dt$

Integrating by parts, it equals :  $[R (d^2x/dt^2) (dx/dt)] - \int R (d^3x/dt^3) (dx/dt) dt$ ,

where the limits are to be imposed on the first term. If we equate this expression with the general form :  $-\int F_{\text{eff}} \cdot v dt$ , we obtain :  $F_{\text{eff}} = +R (d^3x/dt^3)$ .]

So, the equation of motion for the electron becomes :

$$m d^2x/dt^2 = -eE_0 e^{i\omega t} - m\omega_0^2 x + R d^3x/dt^3$$

Note that it's a third order differential equation, which is quite rare in Physics. However, if we expect to have an oscillatory solution of the form :  $x \sim Ae^{i\omega t}$ , then  $R d^3x/dt^3 = -\omega^2 R dx/dt$ , so, we may write :  $R d^3x/dt^3 = -\omega^2 R dx/dt$

If we further substitute :  $\omega^2 R/m = 2b$  ( $b$  is another constant), then our equation of motion becomes :

$$m d^2x/dt^2 = -eE_0 e^{i\omega t} - m\omega_0^2 x - 2mb dx/dt$$

or,  $d^2x/dt^2 + 2b dx/dt + \omega_0^2 x = -(eE_0/m) e^{i\omega t}$ ,

which is nothing but the equation for a forced, damped harmonic oscillator.

Ignoring the transient part (C.F.), the steady state solution (P.I.) is :

$$\begin{aligned} x &= 1/[D^2 + 2bD + \omega_0^2] (-eE_0/m) e^{i\omega t} \\ &= 1/[-\omega^2 + 2bi\omega + \omega_0^2] (-eE_0/m) e^{i\omega t} \\ &= 1/[(\omega_0^2 - \omega^2) + 2bi\omega] (-eE_0/m) e^{i\omega t} \end{aligned}$$

The dipole moment for each electron =  $-e \cdot x = + (e^2 E_0/m) e^{i\omega t} / [(\omega_0^2 - \omega^2) + 2bi\omega]$ .

If there are  $N$  electrons per unit volume, then the dipole moment per unit volume :

$$P = (Ne^2 E_0/m) e^{i\omega t} / [(\omega_0^2 - \omega^2) + 2bi\omega].$$

' $P$ ' is called the '**Polarization Vector**'.

The '**Susceptibility**' ( $\chi$ ) =  $P/E = (Ne^2/m) / [(\omega_0^2 - \omega^2) + 2bi\omega]$ .

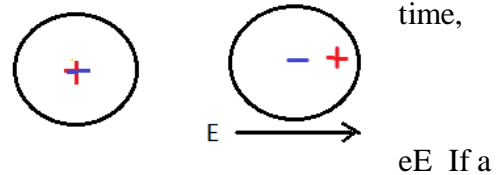
The '**Permittivity**' ( $\epsilon$ ) =  $\epsilon_0 (1 + \chi)$  and the '**Dielectric Constant**' is  $\epsilon/\epsilon_0$ , which equals :

$$\mathbf{K} = \mathbf{1} + (\mathbf{Ne}^2/m) / [(\omega_0^2 - \omega^2) + 2bi\omega],$$

which is complex now.

The speed of light within a material ( $c_m$ ) =  $1/\sqrt{(\epsilon\mu)}$  and that in vacuum ( $c$ ) =  $1/\sqrt{(\epsilon_0\mu_0)}$ .

The refractive index ( $n$ ) =  $c/c_m$ . If  $\mu \approx \mu_0$ ,  $n = \sqrt{(\epsilon/\epsilon_0)} = \sqrt{K}$ . Therefore,



$$\begin{aligned} \mathbf{n}^2 &= \mathbf{1} + (\mathbf{Ne}^2/m) / [(\omega_0^2 - \omega^2) + 2\mathbf{bi}\omega]. \\ &= \mathbf{1} + (\mathbf{Ne}^2/m)[(\omega_0^2 - \omega^2) - 2\mathbf{bi}\omega] / [(\omega_0^2 - \omega^2)^2 + 4\mathbf{b}^2\omega^2]. \end{aligned}$$

What does a complex refractive index mean? Within a material, the electric field propagates as :

$$E = E_0 \exp\{i(kx - \omega t)\} = E_0 \exp\{i\omega(x/c_m - t)\} = E_0 \exp\{i\omega(nx/c - t)\}, \text{ since, } \omega/k = c_m.$$

(The magnetic field also follows a similar expression.)

$$\text{If } n = \alpha + i\beta, \quad E = E_0 \exp\{i\omega(\alpha x/c - t)\} \times e^{-\beta\omega x/c}.$$

Thus, 'α' plays the role of the refractive index and 'β' represents damping.

If ω is far away from the resonance frequency ω<sub>0</sub>, (ω<sub>0</sub><sup>2</sup> - ω<sup>2</sup>) >> 2bω

$$\begin{aligned} \Rightarrow \mathbf{n}^2 &= \mathbf{1} + \mathbf{Ne}^2/m (\omega_0^2 - \omega^2) \\ \omega &= 2\pi n = 2\pi c/\lambda \quad \text{and} \quad \omega_0 = 2\pi c/\lambda_0 \\ \mathbf{n}^2 &= \mathbf{1} + \mathbf{Ne}^2/4\pi^2 c^2 m (1/\lambda_0^2 - 1/\lambda^2) \\ &= \mathbf{1} + \mathbf{Ne}^2 \lambda^2 \lambda_0^2 / 4\pi^2 c^2 m (\lambda^2 - \lambda_0^2) \\ &= \mathbf{1} + \mathbf{A} \lambda^2 / (\lambda^2 - \lambda_0^2), \quad \text{where } \mathbf{A} = \mathbf{Ne}^2 \lambda_0^2 / 4\pi^2 c^2 m \end{aligned}$$

This is basically the **Sellmeier Equation**.

If there are more than one resonance frequencies ω<sub>0i</sub> and hence more than one λ<sub>0i</sub>, the equation becomes :  $\mathbf{n}^2 = \mathbf{1} + \sum \mathbf{A}_i \lambda^2 / (\lambda^2 - \lambda_{0i}^2)$ .

One can write the expression :  $\mathbf{n}^2 = \mathbf{1} + \mathbf{A} \lambda^2 / (\lambda^2 - \lambda_0^2)$  as :

$$\mathbf{n}^2 = \mathbf{1} + \mathbf{A} / (1 - \lambda_0^2 / \lambda^2)$$

Expanding binomially, it becomes :  $\mathbf{n}^2 = \mathbf{1} + \mathbf{A} [1 - \lambda_0^2 / \lambda^2]^{-1} \approx \mathbf{1} + \mathbf{A} [1 + \lambda_0^2 / \lambda^2]$

$$\begin{aligned} \Rightarrow \mathbf{n} &= \{ \mathbf{1} + \mathbf{A} [1 + \lambda_0^2 / \lambda^2] \}^{1/2} \\ &\approx \mathbf{1} + \frac{1}{2} \mathbf{A} [1 + \lambda_0^2 / \lambda^2] \\ &= \mathbf{C} + \mathbf{D} / \lambda^2, \quad \text{where } \mathbf{C} = \mathbf{1} + \frac{1}{2} \mathbf{A} \quad \text{and} \quad \mathbf{D} = \frac{1}{2} \mathbf{A} \lambda_0^2 \end{aligned}$$

This is nothing but the **Cauchy Equation** for the wavelength dependence of refractive index.

### Clausius – Mossotti Equation

[Applicable for gases like H<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, etc., at low density, which don't have a large permanent dipole moment]

From the knowledge of electrostatics, we know that the electric displacement vector is defined as :

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P},$$

where **P** is the polarization vector, which is the dipole moment per unit volume of a material.

For a linear dielectric,

$$\mathbf{P} \propto \mathbf{E} \Rightarrow \mathbf{P} = \epsilon_0 \chi \mathbf{E}.$$

So,

$$\mathbf{D} = \epsilon_0 \mathbf{E} (1 + \chi).$$

One writes ε for ε<sub>0</sub>(1 + χ), so that **D** becomes ε**E**

$$\Rightarrow \mathbf{P} = \mathbf{D} - \epsilon_0 \mathbf{E} = \epsilon \mathbf{E} - \epsilon_0 \mathbf{E} = \epsilon_0 (\epsilon_r - 1) \mathbf{E}$$

At the molecular level, the dipole moment **p** induced *on a molecule* is also proportional to the electric field. However a molecule experiences an electric field at its position, which is not quite the applied (external) electric field **E** mentioned above. This is called the local (Lorentz) field **E<sub>loc</sub>**. Thus, for a molecule,

$$\mathbf{p} \propto \mathbf{E}_{loc} \Rightarrow \mathbf{p} = \alpha \mathbf{E}_{loc},$$

where α is called the molecular polarizability. We wish to look for an expression for α, in terms of macroscopic parameters, but for that, we shall first have to express **E<sub>loc</sub>** in terms of **E**.

Consider a molecule 'A' within a dielectric. We have drawn a sphere 'S' such that the molecule A can distinguish the other individual molecules within the sphere S, but the molecules outside S are so far away, that they form a continuum, with a permittivity ε. There are four electric fields experienced by A and **E<sub>loc</sub>** is the vector sum of these four fields.

- 1) The applied or the external electric field  $\mathbf{E}$ .
- 2) The field due to the molecular dipoles within  $S$ . Now, the electric field due to a dipole  $\mathbf{p}_k$  is given by :  $1/4\pi\epsilon_0 [\mathbf{p}_k/r_k^3 - 3(\mathbf{p}_k \cdot \mathbf{r}_k) \mathbf{r}_k/r_k^5]$
- 3) The field due to the induced charges on the outer surface of the dielectric. This can be neglected if the dielectric is considered infinite, so that the outer surface is very far away.
- 4) The field due to the induced charges on the surface of the spherical cavity  $S$ .

[If the dielectric is uniformly polarized (i.e.,  $\mathbf{P}$  is constant), the volume density of induced charge  $\rho = -\nabla \cdot \mathbf{P} = 0$ .]

- 3) The electric field due to a dipole  $\mathbf{p}_k$  at a position  $\mathbf{r}_k$  (with respect to the dipole) is given by :

$$\mathbf{E}_k = 1/(4\pi\epsilon) [\mathbf{p}_k/r_k^3 - 3(\mathbf{p}_k \cdot \mathbf{r}_k) \mathbf{r}_k/r_k^5].$$

If the applied electric field is along  $z$ , then, we assume, that all the dipoles moments  $\mathbf{p}_k$  are along  $z$  and all of them have the same magnitude  $p$ .

In that case :

$$E_{kx} = 1/(4\pi\epsilon) [0 - 3(p z_k) x_k/r_k^5].$$

$$E_{ky} = 1/(4\pi\epsilon) [0 - 3(p z_k) y_k/r_k^5].$$

$$E_{kz} = 1/(4\pi\epsilon) [p/r_k^3 - 3(p z_k) z_k/r_k^5].$$

Consider all the dipoles at a fixed distance  $r_k = r$  from  $A$ . Now, summing over all such dipoles :

$$\text{we get : } \sum E_{kx} = \sum E_{ky} = 0,$$

$$\text{since, } \sum z_k x_k = \sum z_k y_k = \sum x_k y_k = 0.$$

[For every  $z_k$ , there are  $x_k$ 's with opposite signs and so on.]

$$\sum E_{kz} = 1/(4\pi\epsilon) [p/r^3 - 3(p z_k) z_k/r^5].$$

$$\text{Now, } \sum x_k^2 = \sum y_k^2 = \sum z_k^2, \text{ [by symmetry]} = 1/3 \sum r_k^2$$

$$\Rightarrow \sum E_{kz} = 1/(4\pi\epsilon) [p/r^3 - 3p(1/3)r^2/r^5] = 0.$$

**Thus the field due to the dipoles within the cavity do not contribute.**

- 4) The induced surface charge density on the surface of  $S$  is :  $\sigma = \mathbf{P} \cdot \mathbf{n} = -P \cos\theta$

[since  $\mathbf{P}$  is along  $z$  and  $\mathbf{n}$  is towards the centre  $A$ ].

The field at  $A$ , due to the charges on  $dS$

$$= \sigma dS (-\mathbf{n}) / 4\pi\epsilon r^2 = +P \cos\theta dS (\mathbf{n}) / 4\pi\epsilon_0 r^2.$$

[Note that the dipoles are placed in *vacuum* within the sphere, so **permittivity here is  $\epsilon_0$** ]

The  $z$ -component of this field is :  $P \cos^2\theta dS / r^2$ ,

So that, that the total field due to the charges on  $S$

$$= \iint P \cos^2\theta r^2 \sin\theta d\theta d\phi / 4\pi\epsilon_0 r^2$$

$$= P / (4\pi\epsilon_0) \iint \cos^2\theta \sin\theta d\theta d\phi$$

$$= 2\pi P / (4\pi\epsilon_0) \int \cos^2\theta \sin\theta d\theta$$

Integrating between the limits  $0$  to  $\pi$ , we get :

$$2\pi P / (4\pi\epsilon_0) \times 2/3 = \mathbf{P/3\epsilon_0}.$$

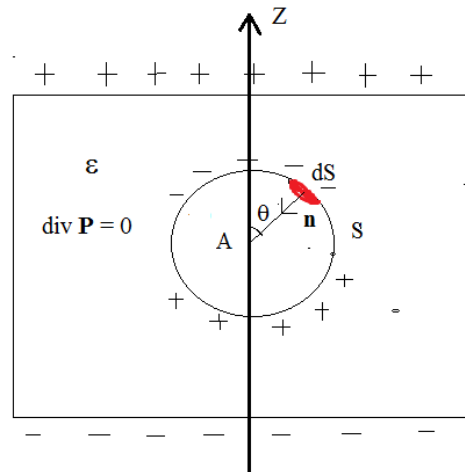
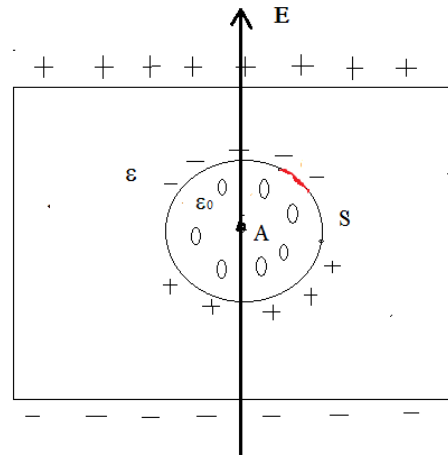
Thus the total field experienced by the dipole at  $A$  :

$$\mathbf{E}_{loc} = \mathbf{E}_{ex} + \mathbf{P/3\epsilon_0}.$$

So now, dipole moment  $\mathbf{p}$  for a molecule (like that at  $A$ ) =  $\alpha \mathbf{E}_{loc} = \alpha (\mathbf{E}_{ex} + \mathbf{P/3\epsilon_0})$

For  $N$  molecules per unit volume, the polarization  $\mathbf{P} = N\mathbf{p} = \alpha N (\mathbf{E}_{ex} + \mathbf{P/3\epsilon_0})$ ,

but,  $\mathbf{P} = \mathbf{D} - \epsilon_0 \mathbf{E} = \epsilon_0 (\epsilon_r - 1) \mathbf{E}$



$$\begin{aligned}
\Rightarrow (\epsilon_r - 1)\epsilon_0 \mathbf{E}_{ex} &= \alpha N \{ \mathbf{E}_{ex} + (\epsilon_r - 1)\epsilon_0 \mathbf{E}_{ex} / 3\epsilon_0 \} \\
\Rightarrow (\epsilon_r - 1)\epsilon_0 &= \alpha N \{ 2\epsilon_0 + \epsilon_r \epsilon_0 \} / 3\epsilon_0 = \alpha N \{ 2 + \epsilon_r \} / 3 \\
\Rightarrow \alpha N &= 3\epsilon_0 \{ (\epsilon_r - 1) / (\epsilon_r + 2) \}
\end{aligned}$$

**This is the well-known Clausius – Mossotti relation.**