

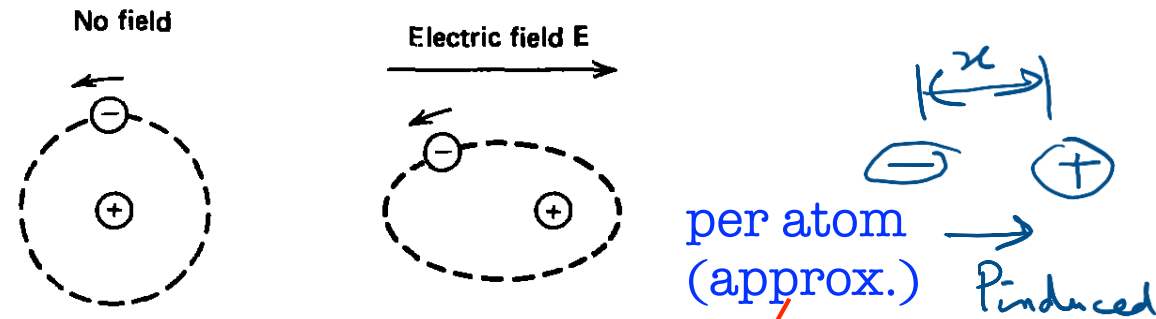
# PYL 102

Monday, Oct. 14, 2024

Dielectric properties: Clausius Mossotti eqn.

Furthermore, on average, the center of negative charge of the electrons coincides with the positive nuclear charge, which means that the atom has no net dipole moment.

When this atom is placed in an external electric field, it will develop an induced dipole moment. The electrons, being much lighter than the positive nucleus, become easily displaced by the field, which results in the separation of the negative charge center from the positive charge center. This separation of negative and positive charges and the resulting induced dipole moment are termed polarization. An atom is said to be polarized if it possesses an effective dipole moment, that is, if there is a separation between the centres of negative and positive charge distributions.



Polarizability relates the induced dipole moment to the E field causing it as  $P_{induced} = \alpha E$  where  $\alpha$  is a coefficient called the polarizability of the atom. Since the polarization of a neutral atom involves the displacement of electrons,  $\alpha_e$  is called electronic polarization.

# Polarization P

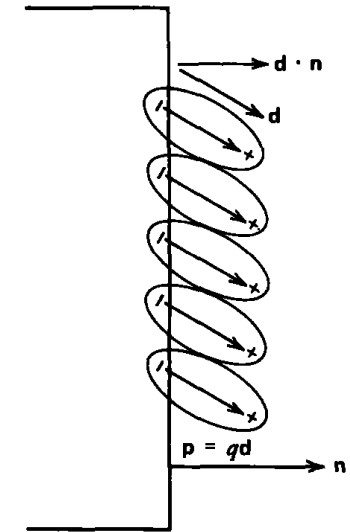
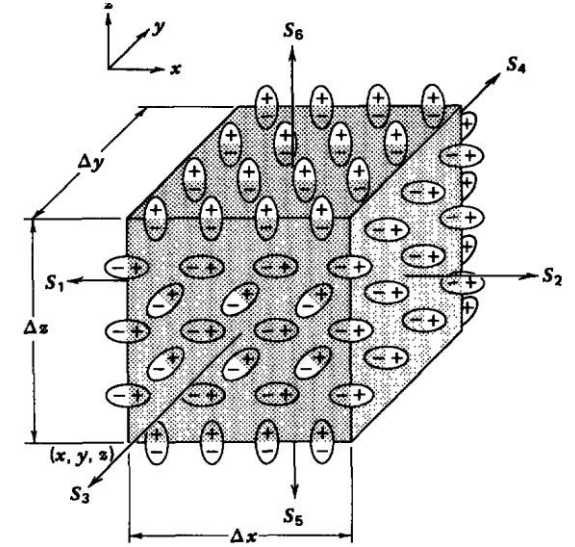
- When a material is placed in an electric field, the atoms and the molecules of the material become polarized, so we have a distribution of dipole moments in the material.
- Charges  $+Q_p$  and  $-Q_p$  appear on the opposite surfaces of a material when it becomes polarized in an electric field. These charges are bound and are a direct result of the polarization of the molecules. They are termed surface polarization charges.

All totally enclosed dipoles contribute no net charge.

Polarization  $P$  is defined as the total dipole moment per unit volume

$$P = \frac{1}{\text{volume}} [p_1 + p_2 + p_3 + \cdots + p_N]$$

where  $p_1, p_2, \dots, p_N$  are the dipole moments induced at  $N$  molecules in the volume.



✓ We can view this arrangement as one big dipole moment  $p_{\text{total}}$  from  $-Q_p$  to  $+Q_p$ . Thus  $P_{\text{total}} = Q_p d$

The magnitude of  $P = Q_p d / Ad = Q_p / A$

$\sigma_p = Q_p / A$  is the surface polarization charge density

$P = \chi \epsilon_0 E$  where  $\chi$  is called the electric susceptibility

$$P = \chi \epsilon_0 E = N P_{\text{induced}} = N \alpha_e E$$

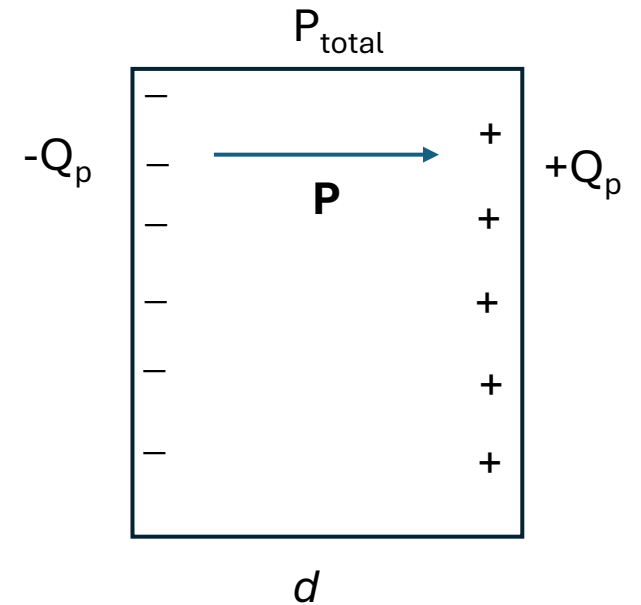
$$\chi = \frac{N \alpha_e}{\epsilon_0}$$

The field  $E$  before the dielectric was inserted is given by  $E = \frac{V}{d} = \frac{Q_0}{\epsilon_0 A} = \frac{\sigma_0}{\epsilon_0}$

where  $\sigma_0$  is the free surface charge density without any dielectric medium between the plates

After the insertion of the dielectric, this field remains the same  $V/d$ , but the free charges on the plates are different. Additional free charges  $Q - Q_0$  needed on the plates to neutralize the opposite polarity polarization charges  $Q_p$  appearing on the dielectric surfaces.

$$Q = Q_0 + Q_p$$



$$Q = Q_0 + Q_p$$

Dividing by A, defining  $\sigma = Q/A$  as the free surface charge density on the plates with the dielectric inserted

$$\sigma = \epsilon_0 E + \sigma_p$$

$$\text{since } \sigma_p = P \text{ and } P = \chi \epsilon_0 E$$

$$\sigma = \epsilon_0 (1 + \chi) E$$

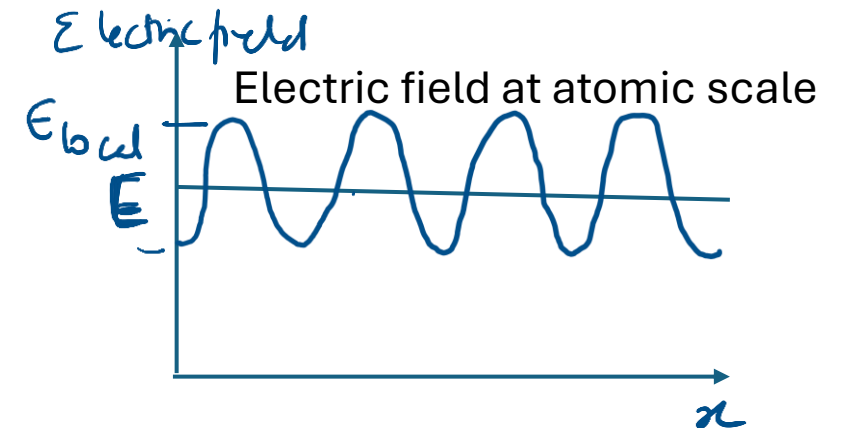
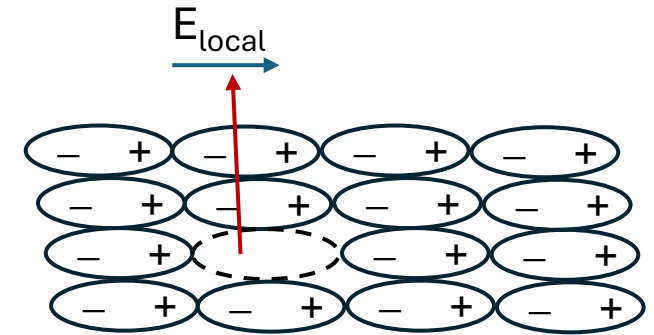
The relative permittivity is defined as  $\epsilon_r = \frac{Q}{Q_0} = \frac{\sigma}{\sigma_0}$

$$\epsilon_r = 1 + \chi$$

$$\epsilon_r = 1 + \frac{N \alpha_e}{\epsilon_0}$$

microscopic polarization  $\alpha_e$  determines the macroscopic property  $\epsilon_r$

The electric field inside a polarized dielectric at the atomic scale is not uniform. The local field is the actual field that acts on a molecule. It can be calculated by removing that molecule and evaluating the field at that point from the charges on the plates and the dipoles surrounding the point.



# Local E field

$$\epsilon_r = 1 + \frac{N\alpha_e}{\epsilon_0}$$

Approximate only !

The field acting on an individual atom or molecule is assumed to be uniform within the dielectric. However, the induced polarization depends on the actual field experienced by the molecule. There are polarized molecules within the dielectric with their negative and positive charges separated so that the field is not constant on the atomic scale as we move through the dielectric.

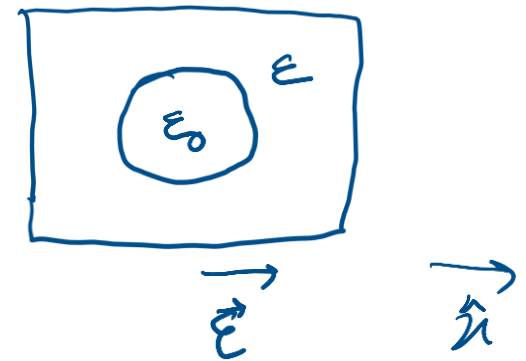
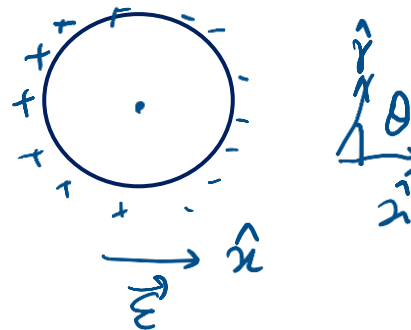
The actual field experienced by a molecule in a dielectric is defined as the local field and it depends not only on the free charges on the plates but also on the arrangement of all the polarized molecules around this point.



$$\vec{E} = \frac{q}{4\pi\epsilon_0 r^2} \hat{r} \quad (\text{E field point charge})$$

$$d\vec{E} = \frac{dq}{4\pi\epsilon_0 r^2} \hat{r}$$

$$\sigma = \frac{dq}{dS} = \frac{q}{A}$$



$$dE_x = \frac{\sigma ds \cos\theta}{4\pi\epsilon_0 r^2}$$

$$\sigma = \vec{P} \cdot \hat{n} = P \cos\theta$$

$$dE_n = \frac{P \cos^2\theta}{4\pi\epsilon_0 r^2} ds$$

$$ds = r^2 \sin\theta \cdot r d\theta \cdot d\phi$$

$$dE_n = \frac{P \cos^2\theta \sin\theta r^2 d\theta d\phi}{4\pi\epsilon_0 r^2}$$

$$E = \int dE_n = \frac{P}{4\pi\epsilon_0} \int_0^{2\pi} d\phi \int_0^\pi \cos^2\theta \sin\theta d\theta = \frac{P}{2\epsilon_0} \int_0^\pi \cos^2\theta \sin\theta d\theta$$

$$\Rightarrow \boxed{E = \frac{P}{3\epsilon_0}} \text{ electric field within center of cavity}$$

per atom  
(exact)

The local field acting on a molecule

$$\vec{E}_{\text{local}} = E + \frac{P}{3\epsilon_0}$$

★ [Lorentz field]

$$\boxed{\vec{P} = \alpha \vec{E}_{\text{local}}}$$

The induced polarization in the molecule now depends on this local field rather than the average field  $E$ .

$$\vec{P} = N \vec{p} = N \alpha_e \vec{E}_{\text{loc}} = N \alpha_e \left( \vec{E} + \frac{\vec{P}}{3 \epsilon_0} \right)$$

$$\Rightarrow N \alpha_e \vec{E} = \vec{P} \left( 1 - \frac{N \alpha_e}{3 \epsilon_0} \right)$$

$$\vec{P} = \epsilon_0 \chi \vec{E}$$

$$\Rightarrow N \alpha_e \vec{E} = \epsilon_0 \chi \vec{E} \left( 1 - \frac{N \alpha_e}{3 \epsilon_0} \right) \Rightarrow \epsilon_0 \chi = N \alpha_e \left( 1 + \frac{\chi}{3} \right)$$

$$\Rightarrow \alpha_e = \left( \frac{3 \epsilon_0}{N} \right) \left( \frac{\chi}{3 + \chi} \right)$$

$$\epsilon_r = 1 + \chi$$

$\Rightarrow$

$$\alpha_e = \left( \frac{3 \epsilon_0}{N} \right) \left( \frac{\epsilon_r - 1}{\epsilon_r + 2} \right)$$

Exact :  
Clausius Mossotti equation

This equation allows the calculation of the macroscopic property  $\epsilon_r$  from microscopic polarization phenomena  $\alpha_e$ . The local E field depends on the arrangement of polarized molecules around the point of interest and hence depends on the crystal structure.





Exp: The electronic polarizability of the Ar atom is  $1.7 \times 10^{-40} \text{ F m}^2$ . What is the static dielectric constant of solid Ar (below 84 K) if its density is  $1.8 \text{ g cm}^{-3}$ ?

To calculate  $\epsilon_r$  we need the number of Ar atoms per unit volume  $N$  from the density  $d$ . If  $M_{\text{at}} = 39.95$  is the relative atomic mass of Ar and  $N_a$  is Avogadro's number, then

$$N = \frac{N_a d}{M} = \frac{6.02 \times 10^{23} \times 1.8 \times 10^{-3}}{39.95} = 2.71 \times 10^{21} \text{ cm}^{-3} \approx 2.71 \times 10^{28} \text{ m}^{-3}$$

$$\epsilon_0 = 1 + \frac{N \alpha_e}{\epsilon_0} = 1 + \frac{2.71 \times 10^{28} \times 1.7 \times 10^{-40}}{8.85 \times 10^{-12}} = 1.52$$

Using Clausius Mossotti eqn.

$$\alpha = \left( \frac{3 \epsilon_0}{N} \right) \left( \frac{\epsilon_r - 1}{\epsilon_r + 2} \right) \Rightarrow \epsilon_r = 1.63$$

The two values are different by about 7 percent.