

PYL 102

Wednesday, Oct. 16, 2024

Polarization mechanism

Local E field

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

Approximate only !

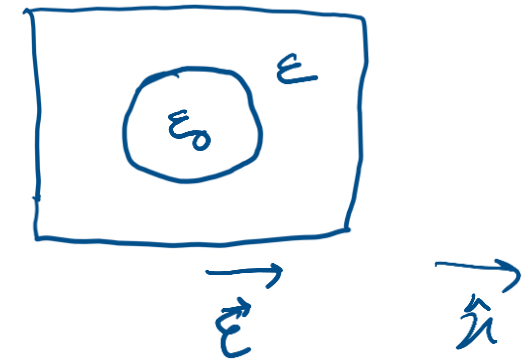
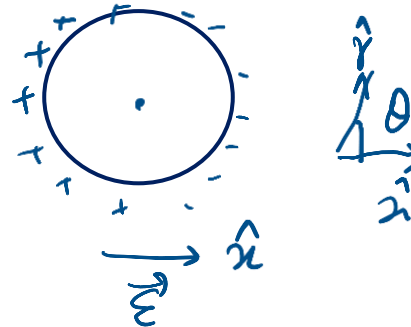
The field acting on an individual atom or molecule is assumed to be uniform within the dielectric. However, the induced polarization depends on the actual field experienced by the molecule. There are polarized molecules within the dielectric with their negative and positive charges separated so that 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.

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

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

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



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

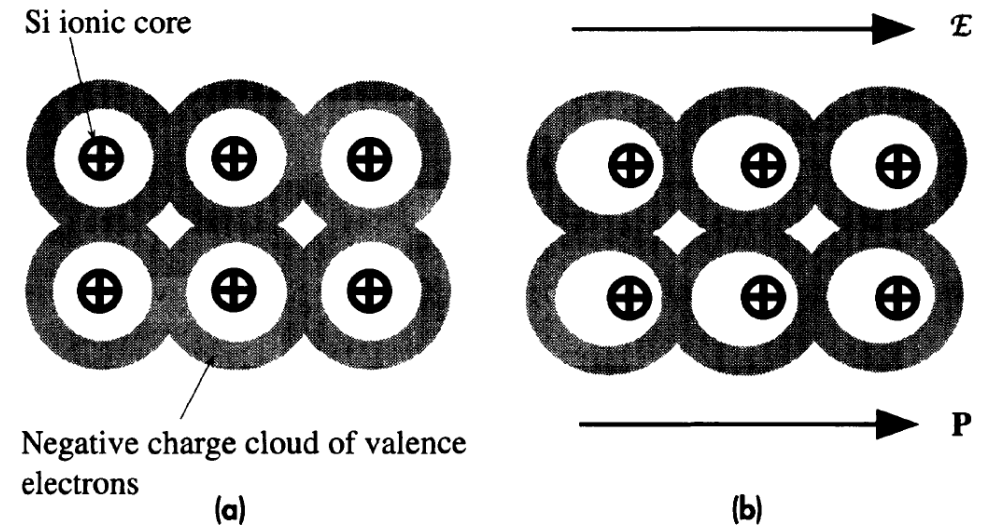
$$\alpha_e = \left(\frac{3\epsilon_0}{N} \right) \left(\frac{\epsilon_r - 1}{\epsilon_r + 2} \right) \quad \text{Clausius Mossotti equation}$$

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

Q. Why covalent crystals such as Si ($\epsilon_r = 11.9$) and Ge ($\epsilon_r = 16.0$) have large dielectric constant values?

The electronic polarization within an atom is quite small compared with the polarization due to the valence electrons in the covalent bonds within the solid.

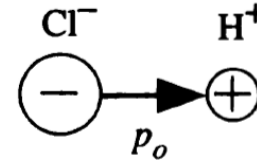
For example, in crystalline silicon, the valence electrons form bonds between the Si atoms and these valence electrons therefore are not rigidly tied to the ionic cores left in the Si atoms. Their wavefunctions are delocalized, that is, not localized to any particular Si atom. When an electric field is applied, the negative charge distribution associated with these valence electrons becomes readily shifted with respect to the positive charges of the ionic Si cores and the crystal exhibits polarization. It takes about 1-2 eV to break a covalent bond to free the valence electron, but it takes more than 10 eV to free an electron from an individual ionic Si core. Thus, the valence electrons in the bonds readily respond to an applied field and become displaced.



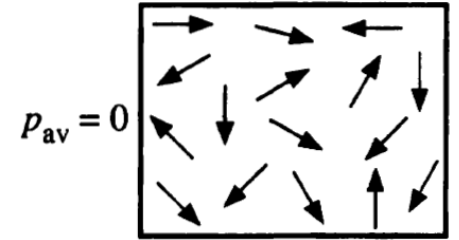
Sources of polarizability (Mechanism)

Orientational (Dipolar) Polarization: molecules with permanent dipole moment are present with random orientation.

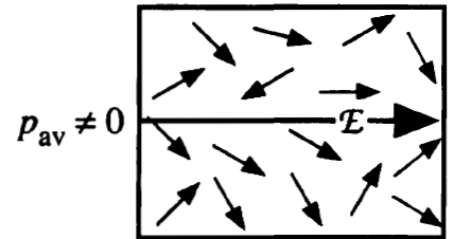
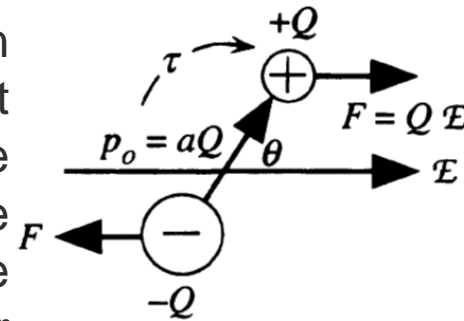
For example, the HCl molecule has a permanent dipole moment p_0 . In the absence of a field, thermal agitation of the molecules results in zero net average dipole moment per molecule. A dipole such as HCl placed in a field experiences a torque that tries to rotate it to align p_0 with the field E . In the presence of an applied field, the dipoles try to rotate to align with the field against thermal agitation. There is now a net average dipole moment per molecule along the field. If all the molecules were to simply rotate and align with the field, the polarization of the solid would be $P = N p_0$, where N is the number of molecules per unit volume. However, due to their thermal energy, the molecules move around randomly and collide with each other and with the walls of the container. These collisions destroy the dipole alignments. Thus, the thermal energy tries to randomize the orientations of the dipole moments.



(a)



(b)



There is, nonetheless, a net average dipole moment per molecule that is finite and directed along the field. Thus, the material exhibits net polarization, which leads to a dielectric constant that is determined by this orientational polarization.

The average dipole potential energy is $V = -\mathbf{p}_o \cdot \mathbf{E} = -p_o E \cos\theta$

For orientational polarization to be effective, this energy must be greater than the average thermal energy, $5/2 kT$ per molecule as in the present case of five degrees of freedom.

As the PE depends on the orientation, there is a certain probability of finding a dipole oriented at this angle as determined by the Boltzmann distribution. The fraction f of molecules oriented at angle θ is proportional to $\exp(-V/kT)$.

Probability of finding it along θ direction $f \propto e^{p_o E \cos\theta / kT}$

The initial orientation of the dipole should be considered in three dimensions and not as in the two-dimension. In three dimensions we use solid angles, and the fraction f then represents the fraction of molecules pointing in a direction defined by a small solid angle $d\Omega$.

The whole sphere around the dipole corresponds to a solid angle of 4π .

Average orientational dipole polarization

$$P_{av} = \frac{\int_0^{4\pi} p_0 \cos\theta f d\Omega}{\int_0^{4\pi} f d\Omega}$$

The result of this integration is a special function called the Langevin function which is denoted as $L(u)$

$$p_{av} = p_0 L(u), u = \frac{p_0 E}{kT}$$

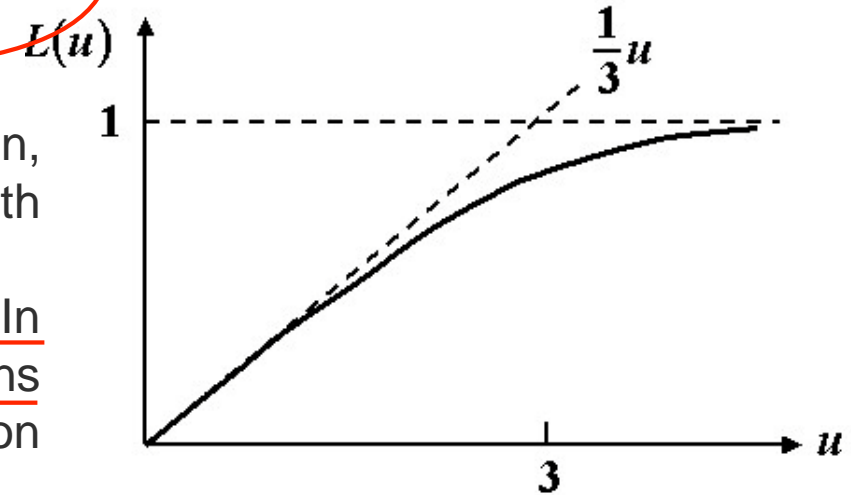
At the highest fields $L(u)$ tends toward saturation at unity. Then, $p_{av} = p_0$, which corresponds to nearly all the dipoles aligning with the field, so increasing the field cannot increase p_{av} anymore.

In the low field region, p_{av} increases linearly with the field. In practice, the applied fields are such that all dipolar polarizations fall into this linear behavior region where the Langevin function

$L(u) \sim \frac{1}{3} u$. Therefore, $p_{av} = \frac{p_0^2 E}{3kT}$

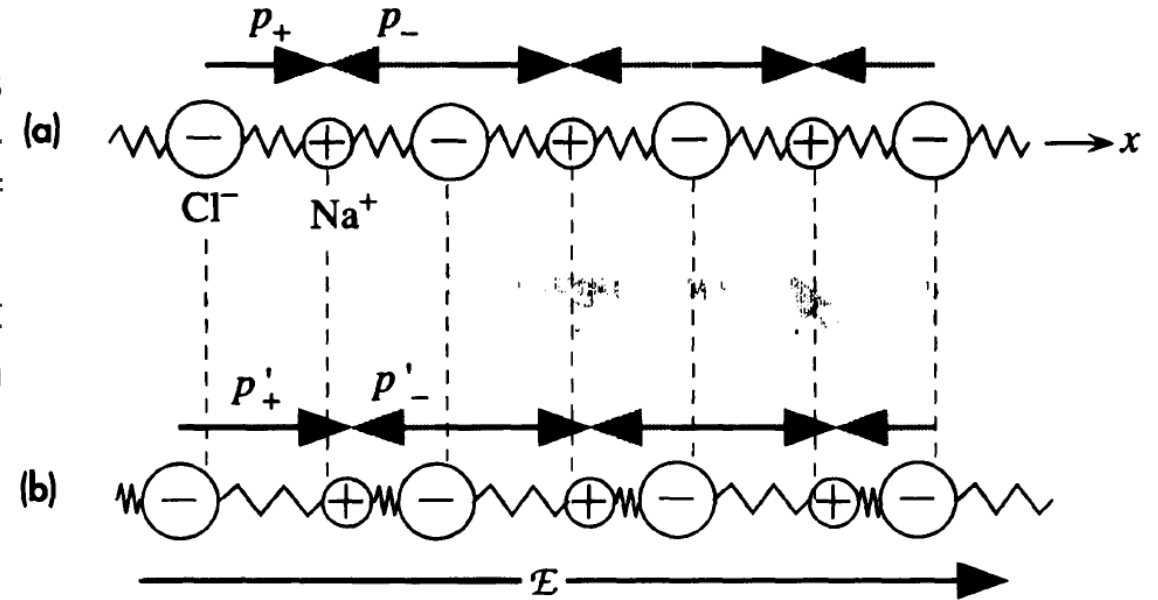
The dipolar or orientational polarizability is then:

$$\alpha_d = \frac{p_0^2}{3kT}$$



Ionic Polarization

This type of polarization occurs in ionic crystals such as NaCl, KCl, etc. The ionic crystal has ions, for example, Na^+ and Cl^- , located at well defined lattice sites, so each pair of oppositely charged neighboring ions has a dipole moment. In the absence of an applied field, the solid has no net polarization because the dipole moments in the $+x$ direction has the same magnitude as in the $-x$ direction.



In the presence of a field E along the x direction, the net dipole moment is now no longer zero. The net dipole moment per ion pair is now $(p'_+ - p'_-)$, which depends on the electric field E .

The ionic polarizability α_i is defined in terms of the local field experienced by the ions.

$$P_{av} = \alpha_i \cdot E_{local}$$

The larger α_i the greater the induced dipole moment. Generally, α_i is larger than the electronic polarizability α_e by a factor of 10 or more, which leads to ionic solids having large dielectric constants.

Each ion also has a core of electrons that become displaced in the presence of an applied field with respect to their positive nuclei and therefore also contribute to the polarization of the solid. This electronic polarization simply adds to the ionic polarization. Its magnitude is much smaller than the ionic contribution in these solids.

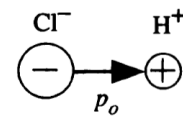
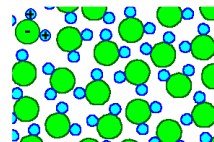
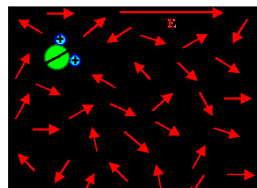
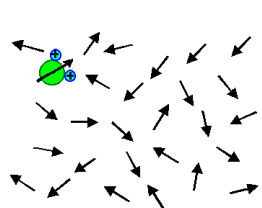
Total Polarization

In the presence of electronic, ionic, and dipolar polarization mechanisms, the average induced dipole moment per molecule will be the sum of all the contributions in terms of the local field. Each effect adds linearly to the net dipole moment per molecule,

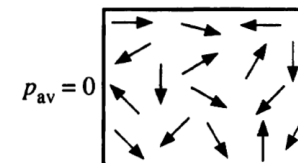
$$p_{av} = \alpha_e E_{loc} + \alpha_i E_{loc} + \alpha_d E_{loc}$$

Clausius-Mossotti equation does not work with dipolar dielectrics and the calculation of the local field is quite complicated. The dielectric constant under electronic and ionic polarizations can be obtained from:

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3\epsilon_0} (N_i \alpha_i + N_e \alpha_e)$$



(a)



(b)

