

## LECTURE NOTES 12

### ELEMENTARY MICROSCOPIC THEORY OF DIELECTRICS

Consider a Class-A/linear dielectric material consisting of non-polar molecules (i.e. having no permanent electric dipole moments) in gas, liquid or solid form, immersed in an external electric field  $\vec{E}_{ext}(\vec{r})$ .

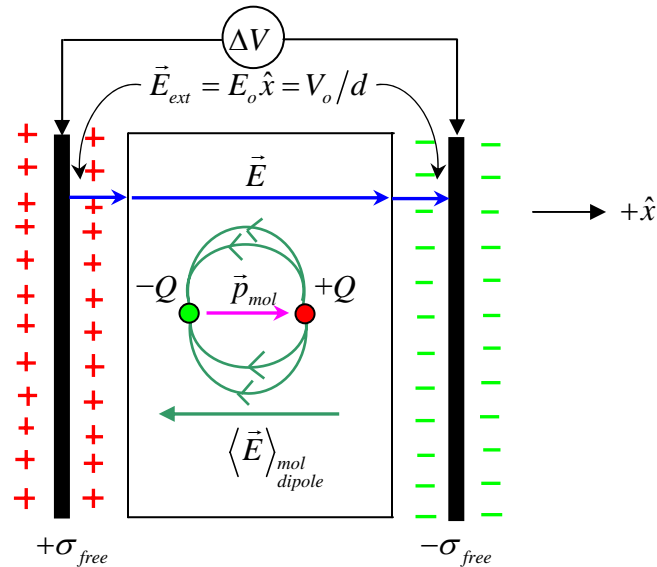
- each molecule will have an induced electric dipole moment of  $\vec{p}_{mol}$  (Coulomb-meters)
- each molecule is assumed (here, for simplicity) to be spherical in shape.

In a real Class-A/linear non-polar dielectric, e.g. at room temperature, at the microscopic level, due to the thermal energy associated with the material making up the dielectric, from one instant in time to the next at any given point  $\vec{r}$  inside the dielectric, random fluctuations of significant size can/do occur in the electric field at that point. If one simultaneously monitors a group of neighboring, microscopically nearby points in space at a particular instant in time, there are also significant, random fluctuations about an average value of the electric field in this region.

Thus, what we need to know is the time-and-space averaged local electric field as seen by a single molecule in the dielectric at the point  $\vec{r}$  - call this electric field  $\langle \vec{E}_{loc}(\vec{r}) \rangle$ . Note that this time-and-space averaged electric field does not include a contribution from the electric field associated with the induced dipole moment of the molecule in question at the point  $\vec{r}$  !!!

Conceptually, in order to determine  $\langle \vec{E}_{loc}(\vec{r}) \rangle$ , we imagine that we (momentarily) “freeze” the thermal motion of all molecules in the dielectric at a given instant in time – thus obtaining a “snapshot” of the microscopic configuration of the dielectric at that instant in time. We then imagine that we remove the molecule in question at the point  $\vec{r}$ , keeping all other molecules “frozen” in their positions and orientations at that instant in time. We then calculate the space-averaged electric field intensity inside the (assumed) spherical cavity that was occupied by the molecule in question at the point  $\vec{r}$ . We then momentarily replace the molecule, allow time to progress forward to some other instant in time, where we again freeze the motion of all molecules at this new instant in time, remove the same molecule, and repeat the space-averaged electric field calculation at the point  $\vec{r}$ . We repeat this procedure many, many times until we obtain a time-and-space-averaged value of the local electric field at the point  $\vec{r}$ ,  $\equiv \langle \vec{E}_{loc}(\vec{r}) \rangle$ .

Thus, we also expect the time-and-space averaged local electric field at the point  $\vec{r}$ ,  $\langle \vec{E}_{loc}(\vec{r}) \rangle$  to be larger than the macroscopic electric field  $\vec{E}(\vec{r})$  at the same point, precisely because  $\langle \vec{E}_{loc}(\vec{r}) \rangle$  does not include the (time-and-space-averaged) electric field of the molecule under scrutiny at the point  $\vec{r}$ ,  $\langle \vec{E}(\vec{r}) \rangle_{mol\ dipole}$  which points in the direction opposite to that of the applied external electric field,  $\vec{E}_{ext}(\vec{r})$  as shown in the figure below:



In P435 Lecture Notes 10 (p. 1-6) {again, see also Griffiths problem 3.41(a-c)}, we learned that the average electric field intensity within a sphere of radius  $R$  containing an arbitrary charge distribution, which we identify as equal to the macroscopic, microscopically time and space-averaged electric field associated with the induced molecular electric dipole moment  $\vec{p}_{mol}(\vec{r})$  of the molecule in question at the point  $\vec{r}$  is given by:

$$\left\langle \vec{E}(\vec{r}) \right\rangle_{mol\ dipole} = -\frac{\vec{p}_{mol}(\vec{r})}{4\pi\epsilon_o R^3} \text{ where } R = \text{radius of a single spherical molecule}$$

Define:  $n_{mol} \equiv \# \text{ molecules per unit volume} = \text{molecular number density } (\#/m^3).$

Then the macroscopic (i.e. microscopically space-and-time-averaged) electric dipole moment per unit volume (a.k.a. electric polarization) is:

$$\vec{P}(\vec{r}) = n_{mol} \vec{p}_{mol}(\vec{r}) \text{ and thus: } \vec{p}_{mol}(\vec{r}) = \vec{P}(\vec{r})/n_{mol}$$

Then: 
$$\left\langle \vec{E}(\vec{r}) \right\rangle_{mol\ dipole} = -\frac{\vec{p}_{mol}(\vec{r})}{4\pi\epsilon_o R^3} = -\frac{\vec{P}(\vec{r})}{4\pi\epsilon_o n_{mol} R^3} = -\frac{\vec{P}(\vec{r})}{3\epsilon_o (v_{mol} * n_{mol})} = -\frac{\vec{P}(\vec{r})}{3\epsilon_o}$$

Where:  $v_{mol} = 4\pi R^3/3 = \text{spherical volume occupied by a single spherical molecule, and}$   
note also that:  $(v_{mol} * n_{mol}) = 1.$

Thus: 
$$\left\langle \vec{E}(\vec{r}) \right\rangle_{mol\ dipole} = -\frac{\vec{P}(\vec{r})}{3\epsilon_o}$$

Thus it can be seen that the macroscopic  $\vec{E}$ -field at the point  $\vec{r}$ ,  $\vec{E}(\vec{r})$  is the linear superposition of a.) the space-and-time-averaged local electric field  $\langle \vec{E}_{loc}(\vec{r}) \rangle$  at that point, plus b.) the space-and-time averaged electric field associated with the induced electric dipole moment  $\vec{p}_{mol}(\vec{r})$  of the molecule in question at the point  $\vec{r}$ ,  $\langle \vec{E}(\vec{r}) \rangle_{mol\ dipole}$ , i.e.:

$$\vec{E}(\vec{r}) = \langle \vec{E}_{loc}(\vec{r}) \rangle + \langle \vec{E}(\vec{r}) \rangle_{mol\ dipole}$$

But  $\langle \vec{E}(\vec{r}) \rangle_{mol\ dipole} = -\frac{\vec{P}(\vec{r})}{3\epsilon_o}$  (for spherical molecules), and thus:  $\vec{E}(\vec{r}) = \langle \vec{E}_{loc}(\vec{r}) \rangle - \frac{\vec{P}(\vec{r})}{3\epsilon_o}$ .

Turning this around, the space-and-time-averaged local electric field is thus:

$$\langle \vec{E}_{loc}(\vec{r}) \rangle = \vec{E}(\vec{r}) - \langle \vec{E}(\vec{r}) \rangle_{mol\ dipole} = \vec{E}(\vec{r}) + \frac{\vec{P}(\vec{r})}{3\epsilon_o}$$

Thus, this last relation explicitly shows that the magnitude of the space-and-time averaged local electric field  $\langle \vec{E}_{loc}(\vec{r}) \rangle$  is larger than the macroscopic electric field  $\vec{E}(\vec{r})$ , since the electric polarization  $\vec{P}(\vec{r})$  (and also  $\vec{p}_{mol}(\vec{r})$ ) point in the same direction as the macroscopic electric field  $\vec{E}(\vec{r})$ . Note that  $\langle \vec{E}_{loc}(\vec{r}) \rangle$  also points in the same direction as  $\vec{E}(\vec{r})$  (and thus  $\vec{P}(\vec{r})$  and  $\vec{p}_{mol}(\vec{r})$ ), whereas the space-and-time-averaged electric field due to the induced dipole moment of the molecule in question at the point  $\vec{r}$ ,  $\langle \vec{E}(\vec{r}) \rangle_{mol\ dipole}$  points in the opposite direction to  $\vec{E}(\vec{r})$ ,  $\langle \vec{E}_{loc}(\vec{r}) \rangle$ ,  $\vec{P}(\vec{r})$  and  $\vec{p}_{mol}(\vec{r})$ .

Note also that in general:  $\langle \vec{E}_{loc}(\vec{r}) \rangle = \vec{E}(\vec{r}) - b \frac{\vec{P}(\vec{r})}{\epsilon_o}$  where  $b = 1/3$  for spherical molecules.

For molecules with shapes other than a sphere, the constant  $b = \text{some number} \sim O(1)$ .

In a linear/Class-A dielectric, the molecular charge separation is proportional to the local electric field, i.e.  $\vec{p}_{mol}(\vec{r}) = q\vec{d}_{mol}$  and  $\langle \vec{E}_{loc}(\vec{r}) \rangle$  are linearly related to each other by:

$$\vec{p}_{mol}(\vec{r}) = \alpha_{mol} \langle \vec{E}_{loc}(\vec{r}) \rangle$$

where  $\alpha_{mol} \equiv$  molecular electric polarizability (SI Units: Coulombs<sup>2</sup>/Newton/meter).

But:  $\vec{P}(\vec{r}) = n_{mol} \vec{p}_{mol}(\vec{r})$  Thus:  $\vec{P}(\vec{r}) = n_{mol} \vec{p}_{mol}(\vec{r}) = n_{mol} \alpha_{mol} \langle \vec{E}_{loc}(\vec{r}) \rangle$

But:  $\langle \vec{E}_{loc}(\vec{r}) \rangle = \vec{E}(\vec{r}) + \frac{\vec{P}(\vec{r})}{3\epsilon_o}$  Thus:  $\vec{P}(\vec{r}) = n_{mol} \alpha_{mol} \left( \vec{E}(\vec{r}) + \frac{\vec{P}(\vec{r})}{3\epsilon_o} \right)$

Then solving for the electric polarization,  $\vec{P}(\vec{r})$  in terms of the macroscopic electric field,  $\vec{E}(\vec{r})$ :

$$\vec{P}(\vec{r}) = n_{mol} \alpha_{mol} \left( \vec{E}(\vec{r}) + \frac{\vec{P}(\vec{r})}{3\epsilon_o} \right) = n_{mol} \alpha_{mol} \vec{E}(\vec{r}) + n_{mol} \alpha_{mol} \frac{\vec{P}(\vec{r})}{3\epsilon_o}$$

$$\left( 1 - \frac{n_{mol} \alpha_{mol}}{3\epsilon_o} \right) \vec{P}(\vec{r}) = n_{mol} \alpha_{mol} \vec{E}(\vec{r})$$

Thus: 
$$\vec{P}(\vec{r}) = \frac{n_{mol} \alpha_{mol}}{\left( 1 - \frac{n_{mol} \alpha_{mol}}{3\epsilon_o} \right)} \vec{E}(\vec{r})$$

But:  $\vec{P}(\vec{r}) = \epsilon_o \chi_e \vec{E}(\vec{r})$  for a linear/Class-A non-polar dielectric.

Solving for  $\chi_e$ :

$$\frac{n_{mol} \alpha_{mol}}{\left( 1 - \frac{n_{mol} \alpha_{mol}}{3\epsilon_o} \right)} \vec{E}(\vec{r}) = \epsilon_o \chi_e \vec{E}(\vec{r})$$

$$\frac{n_{mol} \alpha_{mol}}{\left( 1 - \frac{n_{mol} \alpha_{mol}}{3\epsilon_o} \right)} = \epsilon_o \chi_e$$

Thus: 
$$\chi_e = \frac{\left( \frac{n_{mol} \alpha_{mol}}{\epsilon_o} \right)}{\left( 1 - \frac{n_{mol} \alpha_{mol}}{3\epsilon_o} \right)}$$
 = electric susceptibility of a linear/Class-A non-polar dielectric (assuming spherically-shaped molecules).

For gases (e.g. @STP), note that  $(n_{mol} \alpha_{mol} / \epsilon_o) \approx O(10^{-3}) \ll 1$ , since  $n_{mol} = \frac{\rho}{m_{mol}} N_A$  where:

$n_{mol}$  = number density of molecules (# / m<sup>3</sup>)

$\rho$  = mass density (kg / m<sup>3</sup>)

$N_A$  = Avogadro's # ( $6.022 \times 10^{23}$  molecules / mole)

$m_{mol}$  = molecular weight (# kg / mole)

Thus for non-polar gases @ STP, we can safely neglect the  $(n_{mol} \alpha_{mol} / 3\epsilon_o)$  term in the denominator of the expression for the electric susceptibility, approximating it (quite well) as:

$$\chi_e^{gas} = \frac{(n_{mol} \alpha_{mol} / \epsilon_o)}{1 - (n_{mol} \alpha_{mol} / 3\epsilon_o)} \approx \frac{n_{mol} \alpha_{mol}}{\epsilon_o} \text{ because } (n_{mol} \alpha_{mol} / \epsilon_o) \ll 1$$

And: 
$$K_e^{gas} = 1 + \chi_e^{gas} = 1 + \frac{(n_{mol} \alpha_{mol} / \epsilon_o)}{1 - (n_{mol} \alpha_{mol} / 3\epsilon_o)} \approx 1 + \frac{n_{mol} \alpha_{mol}}{\epsilon_o} \text{ because } (n_{mol} \alpha_{mol} / \epsilon_o) \ll 1$$

The table below compares theory vs. experiment for electric susceptibility  $\chi_e^{gas}$  and dielectric constant  $K_e^{gas} = 1 + \chi_e^{gas}$  for a few simple non-polar gases:

Gas	$\rho_{gas}$ (gms/cc)	$m_{mol}$ (gms/mole)	$n_{mol}$ (#/m <sup>3</sup> )	$\alpha_{mol}$ (C <sup>2</sup> /N/m)	$\chi_e^{gas} (pred)$	$K_e^{gas} (pred)$	$K_e^{gas} (expt)$
CS <sub>2</sub>	0.00339	76.0	$2.7 \times 10^{25}$	$9.55 \times 10^{-40}$	0.0029	1.0029	1.0029
O <sub>2</sub>	0.00143	32.0	$2.7 \times 10^{25}$	$1.72 \times 10^{-40}$	0.0005	1.0005	1.0005
CCl <sub>4</sub>	0.00489	153.8	$1.9 \times 10^{25}$	$1.39 \times 10^{-40}$	0.0030	1.0030	1.0030
A	0.00178	39.9	$2.7 \times 10^{25}$	$1.80 \times 10^{-40}$	0.0055	1.0055	1.0055

It can be seen that for these simple non-polar gases, the theory predictions obtained from this simple microscopic model of a linear/Class-A non-polar dielectric vs. experimental measurements of the electric susceptibility  $\chi_e^{gas}$  and dielectric constant  $K_e^{gas} = 1 + \chi_e^{gas}$  are in excellent agreement with each other.

For liquids (and solids),  $(n_{mol}\alpha_{mol}/\epsilon_o) \approx O(1)$  and thus this term cannot be neglected in the formula for the electric susceptibility.

The table below compares theory vs. experiment for electric susceptibility  $\chi_e^{liquid}$  and dielectric constant  $K_e^{liquid} = 1 + \chi_e^{liquid}$  for the liquid-form versions of the entries in the above table. The results for the liquid-form are obtained using the results from the gas-form, scaled by the ratio of volume mass densities.

Liquid	$\rho_{liquid}$ (gms/cc)	$\frac{\rho_{liquid}}{\rho_{gas}}$	$n_{mol}$ (#/m <sup>3</sup> )	$n_{mol}\alpha_{mol}/\epsilon_o$	$\chi_e^{liquid} (pred)$	$K_e^{liquid} (pred)$	$K_e^{liquid} (expt)$
CS <sub>2</sub>	1.29	381	$1.0 \times 10^{28}$	1.11	1.76	2.76	2.64
O <sub>2</sub>	1.19	832	$2.2 \times 10^{28}$	0.435	0.51	1.51	1.51
CCl <sub>4</sub>	1.59	325	$6.2 \times 10^{28}$	0.977	1.45	2.45	2.24
A	1.44	810	$2.2 \times 10^{28}$	0.441	0.52	1.52	1.54

Here the agreement of theory prediction vs. experiment is quite good.

## THE CLAUSIUS-MOSSOTTI EQUATION

We have obtained an expression for the local electric field  $\langle \vec{E}_{loc}(\vec{r}) \rangle$  inside a linear/Class-A non-polar dielectric:

$$\boxed{\langle \vec{E}_{loc}(\vec{r}) \rangle = \vec{E}(\vec{r}) + \frac{\vec{P}(\vec{r})}{3\epsilon_0}}$$

We have also obtained an expression for the electric polarization associated with this dielectric:

$$\boxed{\vec{P}(\vec{r}) = n_{mol} \alpha_{mol} \left( \vec{E}(\vec{r}) + \frac{\vec{P}(\vec{r})}{3\epsilon_0} \right)}$$

However, inside a linear/Class-A non-polar dielectric the electric displacement  $\vec{D}(\vec{r})$ , the electric field  $\vec{E}(\vec{r})$  and electric polarization  $\vec{P}(\vec{r})$  are related to each other by:

$$\boxed{\vec{D}(\vec{r}) = \vec{E}(\vec{r}) + \vec{P}(\vec{r})}$$

Thus:  $\boxed{\vec{P}(\vec{r}) = \vec{D}(\vec{r}) - \epsilon_0 \vec{E}(\vec{r})}$  but inside a linear/Class-A non-polar dielectric the electric displacement  $\vec{D}(\vec{r})$  and the electric field  $\vec{E}(\vec{r})$  are also related to each other by:  $\boxed{\vec{D}(\vec{r}) = \epsilon \vec{E}(\vec{r})}$ .

Thus:  $\boxed{\vec{P}(\vec{r}) = (\epsilon - \epsilon_0) \vec{E}(\vec{r}) = \epsilon_0 (K_e - 1) \vec{E}(\vec{r})}$  where  $\boxed{K_e \equiv \epsilon / \epsilon_0 = 1 + \chi_e}$

Thus, inside a linear/Class-A non-polar dielectric the electric polarization  $\vec{P}(\vec{r})$  and the electric field  $\vec{E}(\vec{r})$  are also related to each other by:  $\boxed{\vec{P}(\vec{r}) = \epsilon_0 \chi_e \vec{E}(\vec{r})}$

Then since:  $\vec{P}(\vec{r}) = \epsilon_0 (K_e - 1) \vec{E}(\vec{r}) = \epsilon_0 \chi_e \vec{E}(\vec{r})$  and:  $\vec{P}(\vec{r}) = n_{mol} \alpha_{mol} \left( \vec{E}(\vec{r}) + \frac{\vec{P}(\vec{r})}{3\epsilon_0} \right)$

Thus:  $\epsilon_0 (K_e - 1) \vec{E}(\vec{r}) = n_{mol} \alpha_{mol} \left( \vec{E}(\vec{r}) + \frac{\vec{P}(\vec{r})}{3\epsilon_0} \right) = n_{mol} \alpha_{mol} \left( \vec{E}(\vec{r}) + \frac{\cancel{\epsilon_0} (K_e - 1) \vec{E}(\vec{r})}{3 \cancel{\epsilon_0}} \right)$

$\therefore \epsilon_0 (K_e - 1) = n_{mol} \alpha_{mol} \left( 1 + \frac{(K_e - 1)}{3} \right) = n_{mol} \alpha_{mol} \left( \frac{3 + (K_e - 1)}{3} \right) = n_{mol} \alpha_{mol} \frac{(K_e + 2)}{3}$

or:  $\boxed{\left( \frac{K_e - 1}{K_e + 2} \right) = \left( \frac{n_{mol} \alpha_{mol}}{3\epsilon_0} \right)}$  or equivalently:  $\boxed{\left( \frac{\chi_e}{\chi_e + 3} \right) = \left( \frac{n_{mol} \alpha_{mol}}{3\epsilon_0} \right)}$

If the Class-A/linear non-polar dielectric is a compound dielectric composed of  $N$  different types of (spherical) non-polar molecules, then we obtain the so-called Clausius-Mossotti Equation:

$$\left( \frac{K_e - 1}{K_e + 2} \right) = \frac{1}{3\epsilon_o} \sum_{i=1}^N n_i^{mol} \alpha_i^{mol} \leftarrow \text{Clausius-Mossotti Equation}$$

The Clausius-Mossotti Equation relates the dielectric constant  $K_e = (\epsilon/\epsilon_o) = (1 + \chi_e)$  for a Class-A/linear non-polar dielectric material (n.b. assumed to have spherically-shaped molecular electric dipoles) to the mass density  $\rho$  (kg/m<sup>3</sup>) of the Class-A dielectric material and the molecular electric polarizability,  $\alpha_{mol}$ .

If  $n_{mol} = \frac{\rho}{m_{mol}} N_A$  then for a single molecular species the Clausius-Mossotti equation becomes:

$$\left( \frac{K_e - 1}{K_e + 2} \right) = \left( \frac{n_{mol} \alpha_{mol}}{3\epsilon_o} \right) \quad \text{then:} \quad \left( \frac{K_e - 1}{K_e + 2} \right) = \frac{\rho N_A \alpha_{mol}}{3\epsilon_o m_{mol}} \quad \text{or:} \quad \frac{1}{\rho} \left( \frac{K_e - 1}{K_e + 2} \right) = \left( \frac{N_A \alpha_{mol}}{3\epsilon_o} \right) \frac{1}{m_{mol}}$$

We define:  $P_{molar} = \text{molar electric polarization} \equiv \left( \frac{N_A}{3\epsilon_o} \right) \alpha_{mol}$

Then:  $\frac{1}{\rho} \left( \frac{K_e - 1}{K_e + 2} \right) = \frac{P_{molar}}{m_{mol}}$

n.b. The RHS of this equation (and thus also the LHS) is independent of the mass density  $\rho$  !!!  
 {This is true for a wide variety of gases and also non-polar liquids (approximately  $\sim 50$ )}

For the single molecular species the Clausius-Mossotti Equation:  $\left( \frac{K_e - 1}{K_e + 2} \right) = \frac{n_{mol} \alpha_{mol}}{3\epsilon_o}$

Note that if  $n_{mol} \rightarrow \frac{3\epsilon_o}{\alpha_{mol}}$  then the RHS of C-M Equation  $n_{mol} \left( \frac{\alpha_{mol}}{3\epsilon_o} \right) \rightarrow \left( \frac{3\epsilon_o}{\alpha_{mol}} \right) \left( \frac{\alpha_{mol}}{3\epsilon_o} \right) \rightarrow 1$

Thus, when  $n_{mol} \rightarrow \left( \frac{3\epsilon_o}{\alpha_{mol}} \right)$ , then  $\left( \frac{K_e - 1}{K_e + 2} \right) \rightarrow 1$ , i.e.  $K_e \rightarrow \infty$  !!!

Physically, this corresponds to (spherical) molecules that become infinitely polarizable!!

For gases and liquids, the molecular electric polarizabilities  $\alpha_{mol}$  are relatively small,

so  $n_{mol} \rightarrow \left( \frac{3\epsilon_o}{\alpha_{mol}} \right)$  never actually happens for gases and/or liquids.

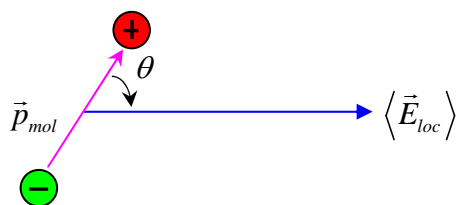
For crystalline solids, this simple model of molecular polarization is simply too crude – it doesn't work / doesn't agree well with crystal data...

## Polar Dielectrics and the Langevin Equation

Polar dielectrics (e.g. water, calcite, quartz, . . .) have permanent molecular electric dipole moments. Molecules consisting of two (or more) dissimilar atoms can exhibit permanent electric dipole moments. Diatomic molecules such as O<sub>2</sub>, N<sub>2</sub>, etc. with identical atoms cannot, due to symmetry considerations – there is no asymmetric way to arrange charge with identical atoms!!!

The potential energy of a single molecule with a permanent electric dipole moment  $\vec{p}_{mol}(\vec{r})$  inside a polar dielectric is:

$$W_1 = P.E._1 = -\vec{p}_{mol}(\vec{r}) \cdot \langle \vec{E}_{loc}(\vec{r}) \rangle \quad (\text{n.b. } W_1 = P.E._1 \text{ is a } \underline{\text{minimum}} \text{ when } \vec{p}_{mol} \parallel \langle \vec{E}_{loc} \rangle)$$



## The Langevin Equation

In a gaseous or liquid dielectric, the thermal energy of the medium (due to it being at finite temperature) causes collisions between the molecules, which tend to destroy / randomize any net alignment of the polar molecules with the local field  $\langle \vec{E}_{loc} \rangle$  (i.e. thermal energy / thermal agitation depolarizes the macroscopic alignment of such molecules). However, the local electric field  $\langle \vec{E}_{loc} \rangle$  exerts a restoring force (via a torque) on the electric dipoles between collisions.

Thus a partial net macroscopic alignment, or electric polarization will exist, i.e. a net  $\vec{P}$  (electric dipole moment per unit volume) will exist, macroscopically.

For no applied external electric field (i.e.  $\vec{E}_{ext} = 0$ ) the dipoles are oriented at random. If there are  $n_{mol}$  molecules per unit volume, then for random orientation of dipoles, the fraction  $dn_{mol}/n_{mol}$  of polar molecules within angles  $\theta$  and  $(\theta + d\theta)$  {see figure above} is just:

$$\frac{dn_{mol}}{n_{mol}} = \frac{d\Omega}{\Omega} = \frac{2\pi \overbrace{\sin \theta d\theta}^{d \cos \theta}}{4\pi} = \frac{1}{2} \sin \theta d\theta$$

where  $n_{mol} = \#$  polar molecules per unit volume and  $dn_{mol} = \#$  polar molecules per unit volume within  $\theta$  and  $(\theta + d\theta)$ . The factor of  $2\pi$  arises from azimuthal ( $\varphi$ ) symmetry – the dot product  $\vec{p}_{mol} \cdot \langle \vec{E}_{loc} \rangle$  only cares about the (polar) angle  $\theta$  between  $\vec{p}_{mol}$  and  $\langle \vec{E}_{loc} \rangle$ . Note that random orientations are flat probability distributions in  $(\varphi, \cos \theta)$  with  $\varphi$  ranging over  $0 \leq \varphi \leq 2\pi$  and  $\cos \theta$  ranging over  $-1 \leq \cos \theta \leq 1$  (i.e. where the polar angle variable  $\theta$  ranges over  $0 \leq \theta \leq \pi$ ).

If the permanent dipoles are then subjected to an externally-applied electric field  $\vec{E}_{ext}$  and are also in thermal equilibrium with each other, then number  $dn_{mol}$  of molecules per unit volume possessing a particular potential energy  $W$  is given by the Boltzmann distribution law:

$$dn_{mol} = \int_{\text{constant}} e^{-W/k_B T} \quad \text{where } k_B = \text{Boltzmann's Constant} = 1.381 \times 10^{-23} \text{ J/K}$$

$$T = \text{Absolute Temperature (Kelvin degrees)}$$

For a single polar molecule in a gas of identical particles:  $W_1 = -\vec{p}_{mol} \cdot \langle \vec{E}_{loc} \rangle = -\vec{p}_{mol} \langle E_{loc} \rangle \cos \theta$

The number of polar electric dipoles / unit volume within  $\theta$  and  $(\theta + d\theta)$  is:

$$\begin{aligned} dn_{mol} &= C e^{+\left(\frac{\vec{p}_{mol} \cdot \langle \vec{E}_{loc} \rangle}{k_B T}\right)} \sin \theta d\theta = C e^{+\left(\frac{p_{mol} \langle E_{loc} \rangle \cos \theta}{k_B T}\right)} \sin \theta d\theta \\ &= C e^{u \cos \theta} \sin \theta d\theta \quad \text{where } \boxed{u \equiv \frac{p_{mol} \langle E_{loc} \rangle}{k_B T}} \end{aligned}$$

The constant  $C$  is a normalization constant such that the total # of molecules / unit volume  $n_{mol}$  is given by:

$$\boxed{n_{mol} = C \int_0^\pi e^{u \cos \theta} \sin \theta d\theta}$$

Now the polar molecules whose permanent electric dipole moments lie within  $\theta$  and  $(\theta + d\theta)$  possess a total electric dipole moment per unit volume in the direction of the local electric field of:

$$dP = dn_{mol} p_{mol} \cos \theta = n_{mol} p_{mol} \frac{e^{u \cos \theta} \sin \theta \cos \theta d\theta}{\int_0^\pi e^{u \cos \theta} \sin \theta d\theta}$$

Thus the NET electric dipole moment per unit volume (= electric polarization)  $P$  is given by:

$$P = \int dP = n_{mol} p_{mol} \langle \cos \theta \rangle = n_{mol} p_{mol} \frac{\int_0^\pi e^{u \cos \theta} \sin \theta \cos \theta d\theta}{\int_0^\pi e^{u \cos \theta} \sin \theta d\theta}$$

We define:  $\boxed{t \equiv u \cos \theta}$  thus:  $t = \left( \frac{p_{mol} \langle E_{loc} \rangle}{k_B T} \right) \cos \theta = u \cos \theta$

Then:  $P = \frac{n_{mol} p_{mol}}{u} \langle t \rangle = \frac{n_{mol} p_{mol}}{u} \frac{\int_{-u}^{+u} e^t t dt}{\int_{-u}^{+u} e^t dt} = \frac{n_{mol} p_{mol}}{u} \frac{[te^t - e^t]_{-u}^{+u}}{e^t \Big|_{-u}^{+u}}$

Or:  $\boxed{P = n_{mol} p_{mol} \left[ \coth \left( \frac{p_{mol} \langle E_{loc} \rangle}{k_B T} \right) - \left( \frac{k_B T}{p_{mol} \langle E_{loc} \rangle} \right) \right]} \Leftarrow \text{Langevin Equation}$

At room temperature ( $T \sim 300\text{K}$ ) the  $\langle \text{thermal energy} \rangle$  is:

$$\boxed{k_B T \sim 4 \times 10^{-21} \text{ Joules} \left( \sim \frac{1}{40} \text{ eV (electron-Volt)} \right)} \quad (1 \text{ eV} = 1.602 \times 10^{-19} \text{ Joules})$$

Typical permanent/polar molecular electric dipole moments are on the order of  $|\vec{p}_{mol}| \sim O(10^{-31})$  Coulomb-meters, and for a typical value of  $\langle E_{loc} \rangle \sim 10^7 V/m$ , then:

$$\Rightarrow u(T) = \frac{p_{mol} \langle E_{loc} \rangle}{k_B T} \approx 2 \times 10^{-3} (\ll 1) \quad @ \quad T = T_{room} \sim 300K$$

Now since  $u(T)$  is quite small in this situation, we can expand the Langevin Equation in a Taylor series expansion, retaining terms up to order  $u^3$ :

$$\coth(u) \approx \frac{1}{u} + \frac{u}{3} - \frac{u^3}{45} + \frac{2u^5}{945} + \dots$$

$$\text{Then: } P \approx n_{mol} p_{mol} \left[ \frac{2+u^2}{2u \left[ 1 + \left( \frac{u^2}{6} \right) \right]} - \frac{1}{u} \right] \approx n_{mol} p_{mol} \left[ \frac{1}{2u} (2+u^2) \left( 1 - \frac{u^2}{6} \right) - \frac{1}{u} \right]$$

$$\text{Or: } P(\vec{r}) \approx \frac{n_{mol} p_{mol} u(\vec{r})}{3} = \frac{n_{mol} p_{mol}^2 \langle E_{loc}(\vec{r}) \rangle}{3k_B T}$$

$$\text{Thus: } P(\vec{r}) \approx \frac{n_{mol} p_{mol}^2 \langle E_{loc}(\vec{r}) \rangle}{3k_B T} \quad \text{for } T \sim 300K \quad \{ \text{i.e. } p_{mol} \langle E_{loc} \rangle \ll k_B T \}$$

$\Rightarrow$  When  $p_{mol} \langle E_{loc} \rangle \ll k_B T$  the electric polarization  $P(r)$  in a polar dielectric is linearly proportional to the local electric field  $E_{loc}(r)$ .

Now for a linear/Class-A polar dielectric we also have the relation:  $\vec{P}(\vec{r}) = \epsilon_o \chi_e \vec{E}(\vec{r})$

$$\text{But: } \langle \vec{E}_{loc}(\vec{r}) \rangle = \vec{E}(\vec{r}) + \frac{\vec{P}(\vec{r})}{3\epsilon_o} \quad \text{or: } \vec{E}(\vec{r}) = \langle \vec{E}_{loc}(\vec{r}) \rangle - \frac{\vec{P}(\vec{r})}{3\epsilon_o} \quad \text{for spherical polar molecules.}$$

$$\text{Thus: } \vec{P}(\vec{r}) = \epsilon_o \chi_e \vec{E}(\vec{r}) = \epsilon_o \chi_e \left( \langle \vec{E}_{loc}(\vec{r}) \rangle - \frac{\vec{P}(\vec{r})}{3\epsilon_o} \right)$$

$$\text{Or: } \vec{P}(\vec{r}) = \frac{\epsilon_o \chi_e}{\left( 1 + \frac{\chi_e}{3} \right)} \langle \vec{E}_{loc}(\vec{r}) \rangle = 3\epsilon_o \left( \frac{K_e - 1}{K_e + 2} \right) \langle \vec{E}_{loc}(\vec{r}) \rangle \quad \text{then using: } P(\vec{r}) \approx \frac{n_{mol} p_{mol}^2 \langle E_{loc}(\vec{r}) \rangle}{3k_B T}$$

$$\text{We see that: } \frac{n_{mol} p_{mol}^2 \langle E_{loc}(\vec{r}) \rangle}{3k_B T} \approx 3\epsilon_o \left( \frac{K_e - 1}{K_e + 2} \right) \langle \vec{E}_{loc}(\vec{r}) \rangle$$

$$\text{or: } \left( \frac{K_e - 1}{K_e + 2} \right) \approx \frac{n_{mol} p_{mol}^2}{9\epsilon_o k_B T} \quad \text{when } p_{mol} \langle E_{loc} \rangle \ll k_B T, \text{ i.e. when } T \sim 300K.$$

We can solve the above relation for the dielectric constant  $K_e$  and electric susceptibility

$\chi_e = K_e - 1$  associated with a polar dielectric. Defining:  $a \equiv \frac{n_{mol} P_{mol}^2}{9 \epsilon_0 k_B T}$ , then for  $T \approx 300K$

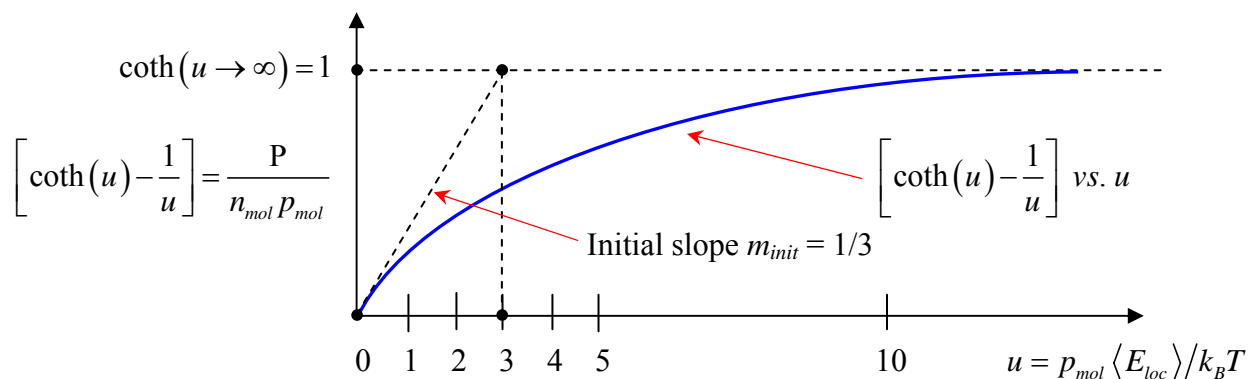
(i.e.  $p_{mol} \langle E_{loc} \rangle \ll k_B T$ ):

$$K_e = \left( \frac{1+2a}{1-a} \right) = \left( \frac{1 + \frac{2n_{mol} P_{mol}^2}{9 \epsilon_0 k_B T}}{1 - \frac{n_{mol} P_{mol}^2}{9 \epsilon_0 k_B T}} \right) \geq 1 \quad \text{and:} \quad \chi_e = K_e - 1 = \left( \frac{1+2a}{1-a} \right) - 1 = \left( \frac{3a}{1-a} \right) = \left( \frac{\frac{n_{mol} P_{mol}^2}{3 \epsilon_0 k_B T}}{1 - \frac{n_{mol} P_{mol}^2}{9 \epsilon_0 k_B T}} \right) \geq 0$$

$\Rightarrow$  When  $p_{mol} \langle E_{loc} \rangle \ll k_B T$ , dielectric constant  $K_e$  and electric susceptibility  $\chi_e$  of a polar dielectric are inversely proportional to the absolute temperature  $T$ . Note that non-polar dielectrics have no such temperature dependence! For polar gases, where  $\chi_e \sim 0$  and  $K_e \sim 1$ , note that:

$$\chi_e^{gas} \approx \frac{n_{mol} P_{mol}^2}{3 \epsilon_0 k_B T} \geq 0 \quad \text{and} \quad K_e^{gas} = 1 + \chi_e^{gas} \approx 1 + \frac{2n_{mol} P_{mol}^2}{9 \epsilon_0 k_B T} \geq 1$$

A plot of the Langevin Function  $\left[ \coth(u) - \frac{1}{u} \right] = \frac{P}{n_{mol} P_{mol}}$  versus  $u = \frac{p_{mol} \langle E_{loc} \rangle}{k_B T}$  is shown below:



### The Debye Equation for Polar Dielectrics

Consider a real polar dielectric – i.e. one in which both permanent and induced molecular electric dipoles are taken into account. Then by the principle of linear superposition:

$$\vec{P}_{TOT}(\vec{r}) = \vec{P}_{induced}(\vec{r}) + \vec{P}_{polar}(\vec{r})$$

Now:  $\vec{P}_{induced}(\vec{r}) = n_{mol} \vec{p}_{mol, induced}(\vec{r})$   $n_{mol}$  = number density of molecular dipoles ( $\#/m^3$ )

$\vec{p}_{mol, induced}(\vec{r})$  = induced electric dipole moment at point  $\vec{r}$

Induced electric dipole moment per unit volume

But: 
$$\boxed{\vec{P}_{induced}^{mol}(\vec{r}) = \underbrace{\alpha_{mol}}_{\text{molecular polarizability}} \langle \vec{E}_{loc}(\vec{r}) \rangle} \Rightarrow \therefore \boxed{\vec{P}_{induced}(\vec{r}) = n_{mol} P_{induced}^{mol}(\vec{r}) = n_{mol} \alpha_{mol} \langle \vec{E}_{loc}(\vec{r}) \rangle}$$

And (from the Langevin Equation):

$$\boxed{\vec{P}_{polar}(\vec{r}) \approx \frac{n_{mol} P_{mol}^2}{3k_B T} \langle \vec{E}_{loc}(\vec{r}) \rangle \text{ for } T \sim 300\text{K (i.e. } P_{mol} \langle E_{loc} \rangle \ll k_B T)}$$

$$\therefore \vec{P} = \vec{P}_{TOT}(\vec{r}) = \vec{P}_{induced}(\vec{r}) + \vec{P}_{polar}(\vec{r}) = n_{mol} \alpha_{mol} \langle \vec{E}_{loc}(\vec{r}) \rangle + \frac{n_{mol} P_{mol}^2}{3k_B T} \langle \vec{E}_{loc}(\vec{r}) \rangle$$

But: 
$$\boxed{\langle \vec{E}_{loc}(\vec{r}) \rangle = \vec{E}(\vec{r}) - \langle \vec{E}_{molecular\ dipoles}(\vec{r}) \rangle = \vec{E}(\vec{r}) + \frac{\vec{P}(\vec{r})}{3\epsilon_o}}$$

n.b. This is an important (but simplifying) assumption here - because it implicitly assumes  $b = 1/3$  spherical-shaped molecules...

However, for linear/Class-A dielectrics we also have: 
$$\boxed{\vec{P}(\vec{r}) = \epsilon_o \chi_e \vec{E}(\vec{r}) = \epsilon_o (K_e - 1) \vec{E}(\vec{r})}$$

Then: 
$$\boxed{\langle \vec{E}_{loc}(\vec{r}) \rangle = \vec{E}(\vec{r}) + \frac{\vec{P}(\vec{r})}{3\epsilon_o} = \left(1 + \frac{\cancel{\epsilon_o} (K_e - 1)}{3\cancel{\epsilon_o}}\right) \vec{E}(\vec{r}) = \left(1 + \frac{(K_e - 1)}{3}\right) \vec{E}(\vec{r}) = \left(\frac{K_e + 2}{3}\right) \vec{E}(\vec{r})}$$

Thus we obtain an important relationship between the space-and-time-averaged local electric field  $\langle \vec{E}_{loc}(\vec{r}) \rangle$  and the macroscopic electric field,  $\vec{E}(\vec{r})$ :

$$\boxed{\langle \vec{E}_{loc}(\vec{r}) \rangle = \left(\frac{K_e + 2}{3}\right) \vec{E}(\vec{r})} \quad \text{or:} \quad \boxed{\vec{E}(\vec{r}) = \left(\frac{3}{K_e + 2}\right) \langle \vec{E}_{loc}(\vec{r}) \rangle}$$

Again, it can be seen from this relation that  $\langle \vec{E}_{loc}(\vec{r}) \rangle$  is parallel to  $\vec{E}(\vec{r})$  but because  $K_e \geq 1$  we also see that  $|\langle \vec{E}_{loc}(\vec{r}) \rangle| > |\vec{E}(\vec{r})|$ .

From the above relation(s) for the electric polarization, we see that:

$$\boxed{\vec{P} = n_{mol} \alpha_{mol} \langle \vec{E}_{loc}(\vec{r}) \rangle + \frac{n_{mol} P_{mol}^2}{3k_B T} \langle \vec{E}_{loc}(\vec{r}) \rangle = \epsilon_o (K_e - 1) \vec{E}(\vec{r}) = 3\epsilon_o \left(\frac{K_e - 1}{K_e + 2}\right) \langle \vec{E}_{loc}(\vec{r}) \rangle}$$

Or: 
$$\boxed{\left(\frac{K_e - 1}{K_e + 2}\right) = \left(\frac{n_{mol}}{3\epsilon_o}\right) \left(\alpha_{mol} + \frac{P_{mol}^2}{3k_B T}\right)} \Leftarrow \text{Debye Equation for Class-A polar dielectrics}$$

Compare this to:

$$\left( \frac{K_e - 1}{K_e + 2} \right) = \left( \frac{n_{mol}}{3\epsilon_o} \right) \alpha_{mol} \quad \Leftarrow \text{Clausius-Mossotti Equation for Class-A non-polar dielectrics}$$

Thus we see that the Debye Equation essentially is the C-M Equation, just with an additional term on the RHS, depending on  $1/T$  due to the contribution arising from the polar molecules, as seen from the Langevin equation for polar molecules at finite temperature.

Let us now multiply both sides of the Debye equation by:  $\left( \frac{m_{mol}}{\rho} \right)$   $\leftarrow$  molecular mass (kg/mole)

Recall that:

$$n_{mol} = \# \text{ density of molecules } \left( \frac{\#}{m^3} \right) = \frac{\rho}{m_{mol}} N_A \quad N_A = \text{Avogadro's number } 6.022 \times 10^{23} \text{ molecules/mole}$$

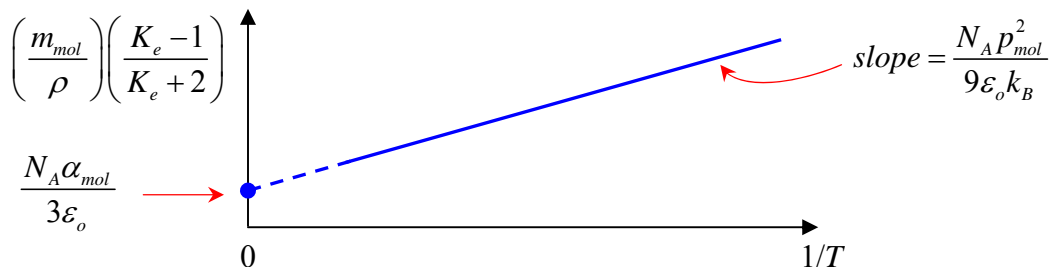
Rearranging the above relation for polar dielectrics, we obtain the molar polarization as :

$$P_{molar} \equiv \frac{m_{mol}}{\rho} \left( \frac{K_e - 1}{K_e + 2} \right) = \left( \frac{N_A}{3\epsilon_o} \right) \left( \alpha_{mol} + \frac{p_{mol}^2}{3k_B T} \right) \quad \Leftarrow \text{Debye Equation for polar molecules}$$

Again, note that the RHS of this equation is independent of mass density (hence so is the LHS). Note also that this equation is that for a straight line, i.e.  $y(x) = mx + b$  with  $x = 1/T$ , and

$$y(x) = P_{molar} (1/T) \equiv \frac{m_{mol}}{\rho(T)} \left( \frac{K_e(T) - 1}{K_e(T) + 2} \right), \quad \text{slope } m = \left( \frac{N_A p_{mol}^2}{9\epsilon_o k_B} \right) \text{ and intercept } b = \left( \frac{N_A \alpha_{mol}}{3\epsilon_o} \right)$$

as shown in the figure below:



Note also that the ratio of slope/intercept, many things cancel, except:  $\frac{m}{b} = \frac{p_{mol}^2}{3k_B \alpha_{mol}}$

In real life, it is only possible to reliably measure  $\alpha_{mol}$  and  $p_{mol}$  for gases, or for dilute solutions of polar molecules in non-polar solvents.

### Ferro-Electricity:

In a certain crystalline solids, the condition  $\left(\frac{K_e - 1}{K_e + 2}\right) = \frac{n_{mol}\alpha_{mol}}{3\epsilon_o} \approx 1$  is satisfied, i.e.  $K_e \rightarrow \infty$  and

$\chi_e = (K_e - 1) \rightarrow \infty!$  In this situation, such materials exhibit permanent polarization (e.g. permanently polarized materials, such as electrets).

Thus,  $\frac{n_{mol}\alpha_{mol}}{3\epsilon_o} \approx 1$  can be taken as a necessary condition for permanent polarization to occur.

### The Making of a “Ferro-Electret”:

Suppose the (absolute) temperature  $T$  is very high (i.e. let  $T \rightarrow \infty$ ). No permanent polarization  $\vec{P}_{\text{permanent dipoles}}$  can exist, because the thermal energies  $\sim k_B T$  are  $\gg p_{mol} \langle E_{loc} \rangle$ , randomizing the (net) polarization orientation. However,  $\exists$  (there exists) a temperature  $T_c$  (known as the Curie Temperature) at (or below) which a ferro-electric material spontaneously generates a net permanent electric polarization  $\vec{P}$  (this is precisely what happens e.g. for ferro-magnets, spontaneously developing a permanent magnetization  $\vec{M}$  (= magnetic dipole moment per unit volume). This spontaneous electrically-polarized state is relatively stable and can exist for a very long time!!!

#### Examples of Ferro-Electric Materials:

Barium Titanate ( $\text{BaTiO}_3$ ), Curie Temperature  $T_c \approx 120^\circ\text{C}$

Lead Zirconate ( $\text{PbZrO}_3$ )

Potassium Tantalum Niobate ( $\text{KTaNbO}_3$ ) has  $K_e = 34,000$  @  $0^\circ\text{C}$ !!!

Lead Titanate ( $\text{PbTiO}_3$ )

Certain (organic) polymers such as Kynar  $\text{\textcircled{R}}$  Film = Polyvinylidene Flouride (*a.k.a.* PVDF)

#### Examples of Ferro-Magnetic Materials:

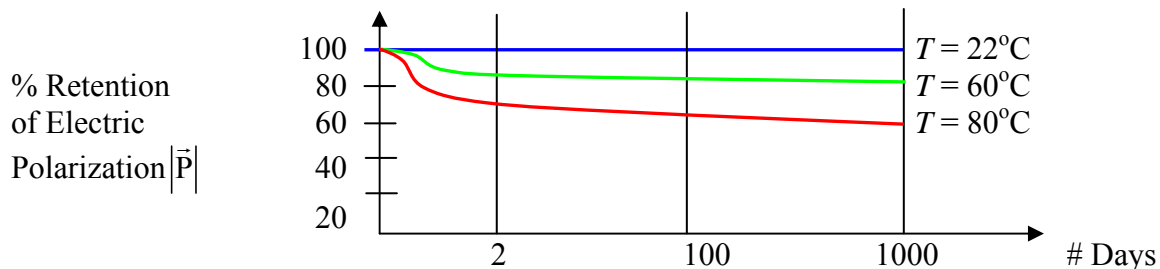
Iron ( $T_c \sim 770^\circ\text{C}$ )

AlNiCo Alloys

Samarium-Cobalt

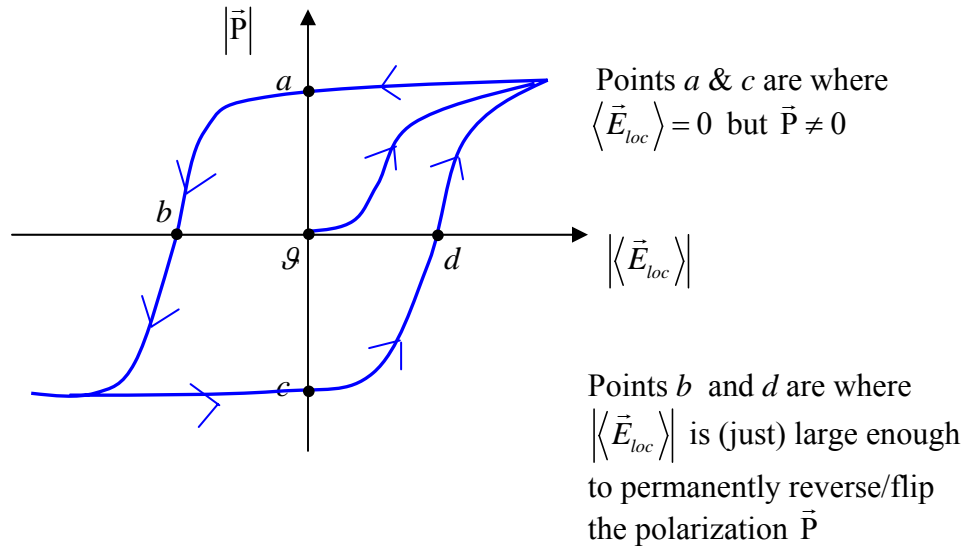
Other rare earth magnets using Neodymium, e.g. Neodymium-Boron...

### Thermal Stability of Kynar $\text{\textcircled{R}}$ (PVDF) Film

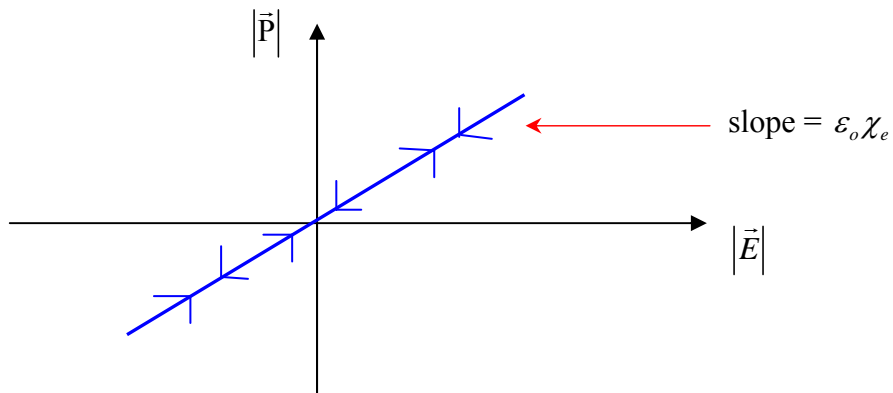


A polarized ferro-electric material is stable against a reversed external electric field, provided it is not too large. The electric polarization  $\vec{P}$  of such a material, exhibits hysteresis (= “to lag behind”)

“Typical” hysteresis curve of  $|\bar{P}|$  vs.  $\langle \bar{E}_{loc} \rangle$  for a ferro-electric material:



Compare the above curve for a ferro-electric material with that for a class-A dielectric (where  $\bar{P} = \epsilon_o \chi_e \bar{E}$  is valid):



For ferro-electric materials, we see that no simple relation between  $\bar{P}$  and  $\bar{E}$  exists – it is in fact (highly) non-linear and depends on previous history of sample of material!

**Piezo-electricity**

Piezo-electricity (= “pressure” electricity) is the capability (or ability) of certain crystalline materials to change their dimensions when subjected to an externally-applied electric field; or conversely, the ability to produce electrical signals (i.e. voltages) when mechanically deformed!

Examples of Piezo-Electric materials:

- Quartz crystals (discovered by Pierre & Jacques Curie in 1880’s)
- Rochelle Salts
- Tourmaline
- Kynar ® Piezo-Electric Film (PVDF film)
- Some Barium Salts (e.g. Barium Titanate – BaTiO<sub>3</sub>)
- Human & other mammal bones!!! (crucial for remodeling of bones, esp. after breaking one – evolution at work!!!)

$\vec{S}(\vec{r}) = d \vec{E}(\vec{r})$ <p>Resultant stress From applied <math>\vec{E}_{ext}</math> field (meters/meter)</p>	$\leftarrow$	$\vec{E}(\vec{r}) = g \vec{x}(\vec{r})$	$\leftarrow$	<p>Piezo strain constant of material ((m/m)/(Volt/m))</p> <p>Piezo-Electric voltage constant ((V/m)/(N/m<sup>2</sup>))</p> <p>stress (N/m<sup>2</sup>)</p>
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Piezo-Electricity arises from the electrical polarization produced by mechanical strains in crystals (belonging to certain classes of symmetries). The polarization  $\vec{P}$  is proportional to strain. If a crystal is centro-symmetric, it cannot be Piezo-Electric.

The existence of a polar axis in a crystal gives rise to an inherent, spontaneous polarization  $\vec{P}$ .

**Pyro-Electricity**

Pyro-Electricity (= “heat” electricity) is the ability (or capability) of certain crystalline materials to produce electrical signals (i.e. voltages) when exposed to changes in temperature (i.e. changes in internal thermal energy). This phenomenon is due to electric polarization  $\vec{P}$  induced by thermal energy absorption in certain crystals. The amount of polarization  $\Delta\vec{P}$  is proportional to the change in the thermal energy  $\Delta U_{thermal}$  and hence is proportional to the change in the temperature  $\Delta T$ .

Examples of Pyro-Electric materials:

- Kynar ® (PVDF) film
- Tri-glycerine sulfate (TGS)
- Lead-zirconate-titanate (PZT)

$\Delta Q_B =$  (bound) charge produced by a change in Temperature  $\Delta T$

$$\underbrace{\Delta Q_B}_{\substack{\text{charge} \\ \text{(coulombs)}}} = \underbrace{\rho}_{\substack{\text{pyro-electric} \\ \text{coefficient} \\ \text{(coul/m}^2 \text{ }^\circ\text{K)}}} \underbrace{\Delta T}_{\substack{\text{Temp} \\ \text{change}}} \underbrace{A}_{\substack{\text{cross-sectional} \\ \text{area}}}$$

$\leftarrow$  Nano Coulombs =  $10^{-9}$  Coulombs

For Kynar <sup>®</sup> film,  $\rho \approx 170 \text{ nC/(cm}^2/\text{K)}$

**The Relationship Between the Index of Refraction  $n$  and the Dielectric Constant  $K_e$**

In free space / vacuum, the speed of propagation of electromagnetic radiation (real photons) is  $c = 3 \times 10^8 \text{ m/s}$ , which is related to the macroscopic parameters of the vacuum -  $\epsilon_o$  and  $\mu_o$  by:

$$c = \frac{1}{\sqrt{\epsilon_o \mu_o}}$$

$\epsilon_o = 8.85 \times 10^{-12} \text{ Farads/m}$  = electric permittivity of free space

$\mu_o = 4\pi \times 10^{-7} \text{ Henrys/m}$  = magnetic permeability of free space

$\epsilon_o$  and  $\mu_o$  are macroscopic electric and magnetic properties (respectively) of the (physical) QED vacuum {QED = Quantum Electro-Dynamics} At the microscopic level, the (physical) QED vacuum consists of electrically-charged, virtual fermion-antifermion pairs flitting in/out of existence, as allowed by the Heisenberg uncertainty principle,  $\Delta E \Delta t \leq \hbar$ .

The vacuum is relativistically Lorentz invariant (i.e. no absolute origin exists), thus  $\epsilon_o$  and  $\mu_o$  cannot/do not/must not have any frequency dependence - i.e.  $\epsilon_o \neq \epsilon_o(f)$  and  $\mu_o \neq \mu_o(f)$  because any frequency dependence of the vacuum is forbidden by Lorentz invariance.

In physical matter, electromagnetic waves propagate through physical matter in a manner analogous to that of EM waves propagating through the QED vacuum. One major difference: physical matter is made up of composite atoms-bound states of electrons and nuclei – thus,  $\exists$  resonances at certain frequencies of EM radiation – whenever:

$$E_\gamma = hf = \text{energy of (real) photon} \approx \Delta E_{n,m}^{atom} = E_m^{atom} - E_n^{atom}$$

As a consequence of this, in matter, electromagnetic radiation travels at speed  $v \leq c$ :

For non-conductors – e.g. dielectric media:

$$v(f) = \frac{1}{\sqrt{\epsilon(f)\mu(f)}} \leftarrow \text{Frequency dependent!!!}$$

Frequency dependence of  $v$  is e.g. responsible for rainbows!!!

Because of/due to frequency-dependence of:  
 $\epsilon = \epsilon(f)$  = electric permittivity of medium  
 $\mu = \mu(f)$  = magnetic permeability of medium

$$\text{Compare: } v(f) = \frac{1}{\sqrt{\epsilon(f)\mu(f)}} \text{ (matter) vs: } c = \frac{1}{\sqrt{\epsilon_0\mu_0}} \text{ (vacuum)}$$

$$\text{But } v(f) = \frac{c}{n(f)} \text{ in a dielectric material, i.e. } n(f) = \frac{c}{v(f)} = \sqrt{\frac{\epsilon(f)\mu(f)}{\epsilon_0\mu_0}} = \text{index of refraction}$$

Many dielectric materials have no magnetic properties – i.e. their  $\mu(f) = \mu_0$  to a high degree.

$$\text{Thus for many dielectric materials } n(f) = \sqrt{\frac{\epsilon(f)}{\epsilon_0}} = \sqrt{K_e(f)} \text{ since (for linear dielectrics)}$$

$$K_e(f) \equiv \frac{\epsilon(f)}{\epsilon_0} = 1 + \chi_e(f)$$

$$\text{In general: } v(f) = \frac{1}{\sqrt{\epsilon(f)\mu(f)}} = \frac{c}{\sqrt{K_e(f)K_m(f)}} \text{ where (for linear magnetic materials)}$$

$$K_m \equiv \frac{\mu(f)}{\mu_0} = 1 + \chi_m(f). \text{ In dielectric materials that are non-magnetic, } K_m \approx 1 \text{ because}$$

$$\mu(f) \approx \mu_0, \text{ then } v(f) \approx \frac{1}{\sqrt{\epsilon(f)\mu_0}} = \frac{c}{\sqrt{K_e(f)}}.$$