

## Module 4: Dielectric Ceramics: Basic Principles

### Introduction

Dielectrics are insulating or non-conducting ceramic materials and are used in many applications such as capacitors, memories, sensors and actuators. For the sake of simplicity, we can assume that there is no long range moment of charges. First we will look the simple properties of dielectric materials such as dipole moment, polarization, susceptibility, polarizability and polarization mechanisms. Then we will do analytical treatment of polarizabilities for each of the polarization mechanisms to understand the meaning of these polarizabilities. Subsequently, we will do detailed analysis of dielectric properties for each of the polarization mechanisms under the influence of alternating field, important from the point of understanding the behaviour of these materials in real conditions. Finally, we will look at the breakdown mechanisms which lead to failure of dielectric materials.

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### Suggested Reading:

- [Principles of Electronic Ceramics](#), by L. L. Hench and J. K. West, Wiley
- [Dielectrics and Waves](#), by Arthur R. von Hippel, John Wiley and Sons Inc.

Electroceramics: Materials, Properties, Applications, by A. J. Moulson and J. M. Herbert, Wiley

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## Module 4: Dielectric Ceramics: Basic Principles

### Basic Properties: Dielectrics in DC Electric Field

#### 4.1 Basic Properties: Dielectrics in DC Electric Field

Upon application of a dc or static electric field, there is a long range migration of charges. However, there is a limited movement of charges leading to the formation of charge dipoles and the material, in this state, is considered as polarized. These dipoles are aligned in the direction of the applied field.

The applied field can also align the dipoles that were already present in the material i.e. material containing dipoles without application of the field.

Of course, both these effects may be present in a single material i.e. dipoles can be aligned as well as be induced by the applied field.

The net effect is called Polarization of the material.



### 4.1.1 Electric Dipole

An electric dipole comprises of two equal and opposite point charges that are separated by a distance  $d$ . The resulting dipole moment,  $\mu$  is expressed as

$$\mu = q \cdot \delta \quad (4.1)$$

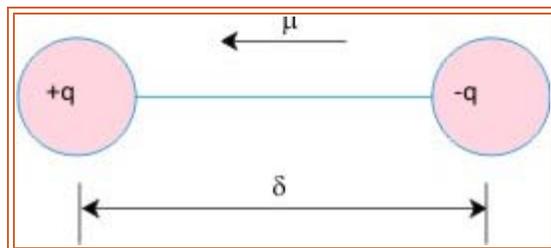


Figure 4.1 Schematic of a dipole

Dipole moment is a vector and  $\mu$  points from  $-ve$  to  $+ve$  charge. It has units of C.m.

Total dipole moment per unit volume is defined as Polarization,  $P$  i.e.

$$P = \frac{\Sigma \mu}{V} \quad (4.2)$$

Units of  $P$  are  $C.m^{-2}$  i.e. charge per unit area.

In the most simplistic way when all the dipole are aligned in one direction,  $P$  can be written as  $N.m$  where  $N$  is the number of dipole per unit volume.

You should note that  $P=0$  does not mean that the material does not necessarily have dipole moments rather it is likely that vector summation of all the dipole moment is equal to 0, which is always the case if dipoles were, vectorially speaking, randomly distributed.

In the subsequent sections, we will replace displacement ' $d$ ' by ' $d$ ' to avoid duplication by other symbols.



### 4.1.2 Polarization and Surface Charge

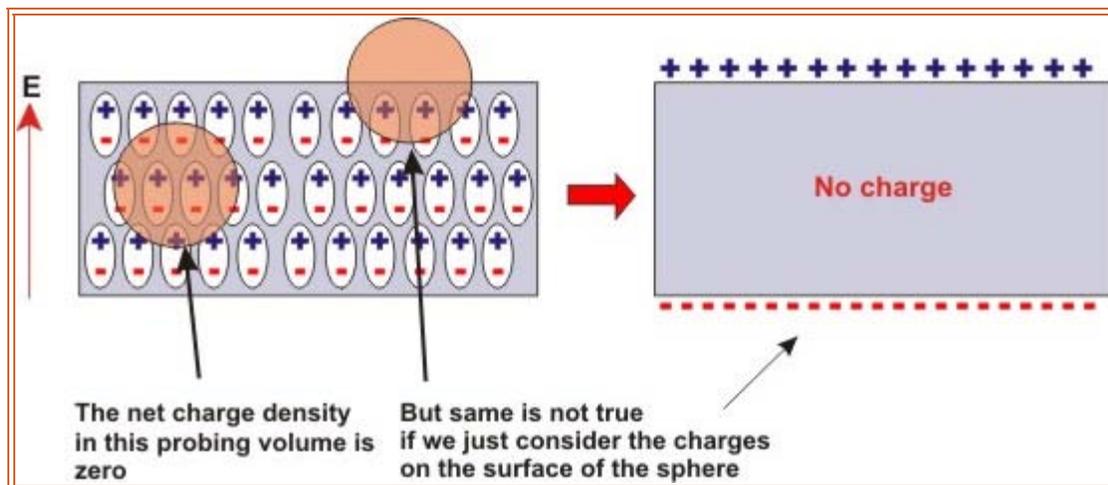


Figure 4.2 Schematic of a dielectric between two plates

Imagine a parallel plate capacitor with homogeneously distributed polarized material between the plates.

Assume that all the dipole moments are aligned in the same direction. Now, if we look at the charge density in a small volume of the material (circle inside the capacitor), then it is clearly zero since both positive and negative charges are equal.

While at the surface, there is a finite charge as shown by the small circle. On both surfaces, the charges move out by a tiny distance,  $dx$ , which is nothing but surface polarization charge which can be calculated.

The number of charges,  $n_c$ , on the surface area  $A$  is equal to the number of dipoles contained within a surface volume ( $V=A \cdot dx$ ) times the charge of the dipole,  $q$  which is nothing but equivalent to one layer of the surface charge.

Assuming homogeneous distribution of the dipoles, polarization can be written as

$$P = \frac{\sum \mu_s}{V_s}$$

where the subscript 's' implies the surface. Hence

$$P = \frac{dx \cdot \sum_s q}{V_s} = \frac{dx \cdot \sum_s q}{dx \cdot A} = \frac{\sum_s q}{A} \quad (4.3)$$

where  $\sum_s$  implies sum over the surface volume. Hence

$$n_c = \sum_s q = P \cdot A \quad (4.4)$$

So the surface charge density  $s$  is

$$\sigma = \frac{n_c}{A} = |P| \quad (4.5)$$

$\sigma$  is a scalar quantity if  $P \cdot A$  is scalar.

If polarization is not normal to the surface then

$$\sigma = n \cdot P \quad (4.6)$$

where  $n$  is the outward pointing unit vector normal to the surface of the polarized material.



## 4.1.3 Dielectric Displacement and Susceptibility

Consider a vacuum plate capacitor configuration as shown below:

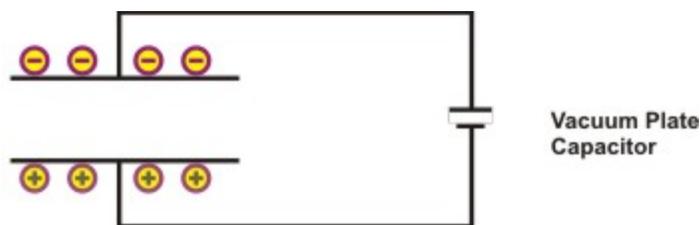


Figure 4.3 Parallel plate vacuum capacitor

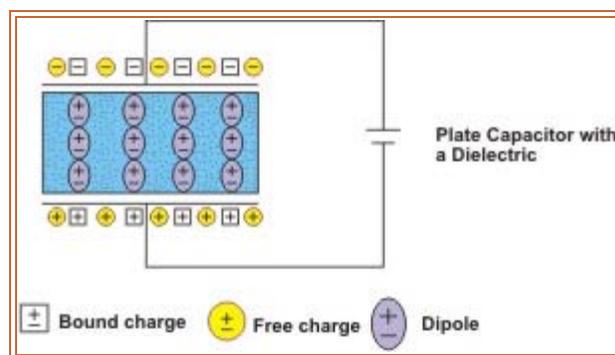


Figure 4.4 Parallel plate capacitor with a dielectric

For a vacuum capacitor

$$Q = \int I \cdot dt$$

OR

$$Q = CV \quad (4.7)$$

where capacitance of the vacuum is given as  $C_{vac} = (\epsilon_0 A)/d$  where  $\epsilon_0$  is the permittivity of free space and is equal to  $8.85 \times 10^{-12}$  F/m.

If one inserts a dielectric between plates, then capacitance gets modified as

$$C = \frac{\epsilon A}{d} = \frac{\epsilon_r \epsilon_0 A}{d} \quad (4.8)$$

Where  $\epsilon_r$  is dielectric permittivity or more commonly (but not accurately) as relative dielectric constant with value greater than 1.

$$C = \frac{\epsilon_r \epsilon_0 A}{d}$$

OR

$$C = \epsilon_r C_{\text{vac}} \quad (4.9)$$

(4.9)

Thus, inserting a dielectric leads to an increase in the stored charge in the capacitor as shown below.

Basically,  $\epsilon_r$  signified some sort of interaction between the material and electromagnetic field.

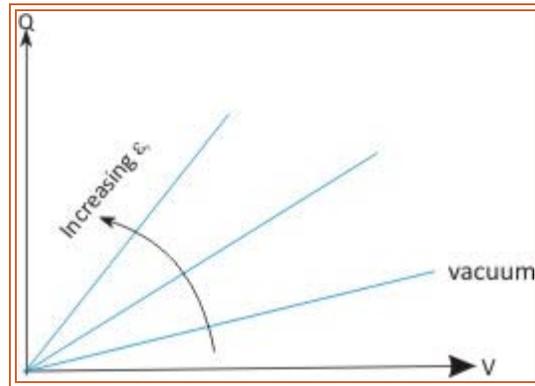


Figure 4.5 Q-V plot with effect of  $\epsilon_r$

Now the question is: Why does inserting a dielectric increases the capacitance of a capacitor?

We will see this in the following sections.

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#### 4.1.4 Polarization Charges

In a parallel plate capacitor without any dielectric, the surface charge in vacuum  $s_s$  is

$$\sigma_s = \left[ \frac{Q}{A} \right]_{\text{vac}} = \left[ \frac{CV}{A} \right]_{\text{vac}} = \left[ \frac{\epsilon_0 V}{d} \right]_{\text{vac}} = \epsilon_0 E \quad (4.10)$$

where  $E$  is the applied field due to the potential  $V$  between the plates.

In the presence of a dielectric, the net charge density now becomes

$$\sigma_{\text{net}} = \left[ \frac{Q}{A} \right]_{\text{dielec}} = \frac{\epsilon_r \epsilon_0 V}{d} = \sigma_s + \sigma_{\text{external}} \quad (4.11)$$

$s_{\text{external}}$  is nothing but due to presence of dielectric and due to polarization of charges and can be written as  $s_{\text{pol}}$ . Hence,

$$\sigma_{\text{net}} = \sigma_{\text{vac}} + \sigma_{\text{pol}} = \sigma_{\text{vac}} + \rho \quad (4.12)$$

where  $\rho$  is the extra charge resulting from the polarization of the dielectric.

According to the electromagnetic theory, the surface charges on the plates can be defined as dielectric displacement,  $D$ , such as

$$D = Q/A$$

OR

$$D = \sigma_{\text{vac}} + P$$

OR

$$D = \epsilon_0 E + P \quad (4.13)$$

The equation shows that the total charge on the plates of a capacitor with dielectric inserted between the plates is now the sum of the surface charge present in a vacuum capacitor ( $\epsilon_0 \cdot E$ ) and extra charge resulting from polarization of the dielectric material,  $\rho$ .

Hence, we can now write dielectric displacement as,

$$D = \epsilon_0 \epsilon_r E = \epsilon_0 E + P \quad (4.14)$$

OR

$$P = \epsilon_0 E (\epsilon_r - 1) = \chi \cdot \epsilon_0 \cdot E \quad (4.15)$$

where  $\chi$  is called dielectric susceptibility and is expressed as

$$(4.16)$$

$$\chi = \epsilon_r - 1 = \frac{P}{\epsilon_0 E}$$

This implies that susceptibility is nothing but the ratio of polarized charge or excess charge to the surface charge in a vacuum capacitor.

Now the question arises: What is the reason for polarization? It can be said that it is basically due to short range movement of masses i.e. electrons, or atoms or molecules under applied electric field. Such a movement is not likely to occur arbitrarily fast, rather it is a function of the frequency of the applied field. This also implies that the dielectric properties are also a function of the frequency. These properties are also a function of material structure and temperature. But for now, we will turn our attention to the understanding of basics of mechanisms of polarization and qualitatively what it means in terms of applied frequency.

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## Module 4: Dielectric Ceramics: Basic Principles

### Summary

#### Summary

So far, we have learnt that the effect of an applied field on a dielectric material is to polarize it which is quantified by parameters such as dielectric constant,  $\epsilon_r$  ; polarization,  $P$ ; and dielectric susceptibility,  $\chi$ . Next we will learn about the polarization mechanisms and local field inside a dielectric.

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## 4.2 Mechanisms of Polarization

Basically, there are four mechanisms of polarization:

- **Electronic or Atomic Polarization**

This involves the separation of the centre of the electron cloud around an atom with respect to the centre of its nucleus under the application of electric field (see (a) in figure below).

- **Ionic Polarization**

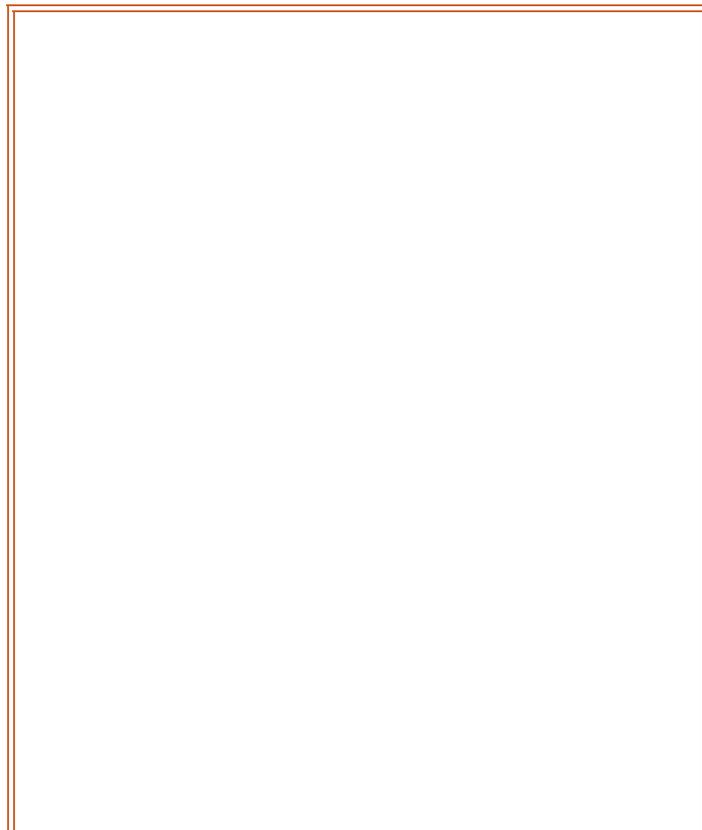
This happens in solids with ionic bonding which automatically have dipoles but which get cancelled due to symmetry of the crystals. Here, external field leads to small displacement of ions from their equilibrium positions and hence inducing a net dipole moment (see (b)).

- **Dipolar or Orientation Polarization**

This is primarily due to orientation of molecular dipoles in the direction of applied field which would otherwise be randomly distributed due to thermal randomization (see (c and d)) and finally

- **Interface or Space Charge Polarization**

This involves limited movement of charges resulting in alignment of charge dipoles under applied field. This usually happens at the grain boundaries or any other interface such as electrode-material interface (see (e and f))



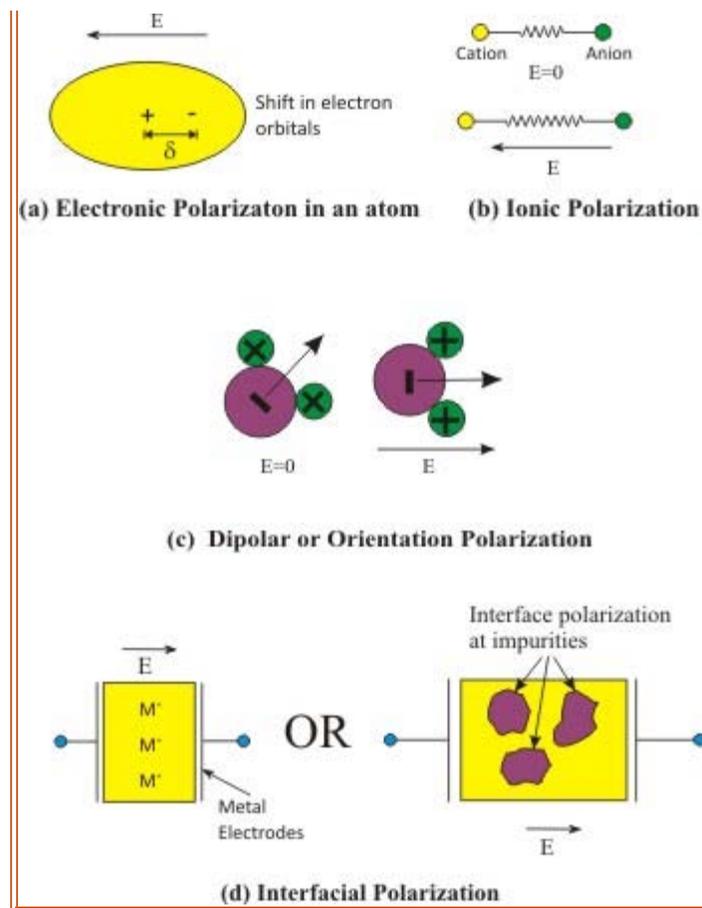


Figure 4.6 Schematic of mechanisms of polarization

Atomic polarization is present in all materials by definition and hence any other mechanism would be an addition.

While mathematical treatment of the first three mechanisms is rather straightforward, interface polarization is not easy to quantify.

Qualitatively, we can see that in the above four mechanisms, the masses of the entities to be displaced are different, with mass getting larger from electronic to ionic to dipolar polarization. This has a direct relation with the frequency of the applied field (see figure below). Intuitively, we can mention that heavier the particular entity, more is the time spent in displacing it. As a result, atomic polarization is the fastest and typically persists at frequencies between  $\sim 10^{13}$ - $10^{15}$  Hz. In contrast, ionic polarization is sluggish and typically occurs at frequencies between  $\sim 10^9$ - $10^{13}$  Hz while dipolar polarization involving movement of molecules happens below  $10^9$  Hz. Interface or space charge polarization occurs at frequencies below 10 Hz.

For non-magnetic dielectrics, Maxwell's electromagnetic theory predicts that the dielectric constant obtained from the electronic contribution is also related to the index of refraction as  $\epsilon_r = n^2$  which is true at very high frequencies, above  $10^{12}$ - $10^{13}$  Hz. Contribution from any other mechanism will be on top of it. So the total dielectric constant for a material would be  $\epsilon_{r\text{-electronic}} (= n^2) + \epsilon_{r\text{-ionic}} + \epsilon_{r\text{-dipolar}}$ .

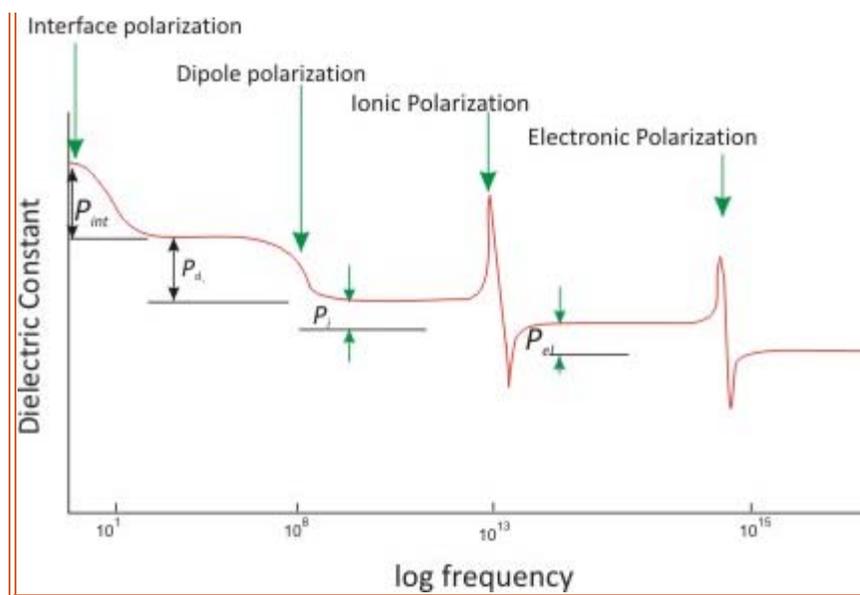


Figure 4.7 Schematic figures between dielectric constant **vs** frequency showing various mechanisms

The following table shows the values of  $\epsilon_r$  and  $n^2$  for a variety of materials and the dominant polarization processes in them:

| Material                 | $\epsilon_r$ | $n^2$ | Dominant mechanisms           |
|--------------------------|--------------|-------|-------------------------------|
| C (Diamond)              | ~5.7         | 5.85  | Electronic                    |
| Ge                       | ~16          | 16.73 | Electronic                    |
| NaCl                     | ~5.9         | 2.37  | Electronic and Ionic          |
| Water (H <sub>2</sub> O) | ~80          | 1.77  | Electronic, Ionic and Dipolar |

So, you can see that while carbon and germanium being single elemental materials show electronic polarization only and as a result their dielectric constants match well with the values of  $n^2$ . However, the same is not the case with NaCl or water which have strong contributions of ionic and ionic and dipolar polarization respectively. We will discuss more about these processes in the latter sections.

### 4.3 Microscopic Approach

Earlier we saw, polarization in a system with  $N$  dipoles per unit volume can be expressed as

$$\mathbf{P} = N \cdot \boldsymbol{\mu}$$

i.e.

$$\mathbf{P} = N q \delta \quad (4.17)$$

This gives

$$\chi = \epsilon_r - 1 = \frac{\mathbf{P}}{\epsilon_0 \mathbf{E}} = \frac{N q \delta}{\epsilon_0 \mathbf{E}} \quad (4.18)$$

Hence, greater is  $d$  greater is  $\chi$  and hence larger is  $\epsilon_r$ , i.e. more polarizable a medium is, more is its dielectric constant.

Further, polarizability of an ion or atom of type,  $i$ , in a dipole is defined as

$$\alpha_i = \frac{\mu_i}{E_{loc}} = \frac{P_i}{N_i E_{loc}} \quad (4.19)$$

where  $E_{loc}$  is the local electric field experienced by an atom or ion or molecule which can be different than the applied field. However, magnitude of local field can be modified quite significantly the polarization of surrounding medium.

As a result  $P$  can expressed as

$$\mathbf{P} = N_i \alpha_i E_{loc} \quad (4.20)$$

Note that equation (4.20) relates a macroscopic parameter,  $P$ , to the microscopic parameters  $N$ ,  $\alpha$  and  $E_{loc}$ .

As a result, in general, susceptibility is

$$\chi = \epsilon_r - 1 = \frac{N \alpha}{\epsilon_0} \quad (4.21)$$

where  $\alpha$  is the sum of all types of polarizabilities due to different mechanisms ( $\alpha_{\text{electronic}} + \alpha_{\text{ionic}} + \alpha_{\text{dipolar}} + \alpha_{\text{interface}}$ ) as we will see later.



## 4.4 Determination of Local Field

The local field,  $E_{loc}$ , experienced by an atom or dipole or molecule usually differs from the applied field,  $E_{ex}$  owing to the polarization of the surrounding medium around a dipole or molecule.

While on a macroscopic scale, the overall field in a material is zero due to the condition of electrical neutrality, when we start looking at the scale of individual atoms and molecules, it is not the case. Although this local field which is nothing but the sum of applied field and some other fields and can, in principle, be solved using Poisson's equation, coupling charge density and potential at each location, the method is far from being simple. Instead, we use a simple approach, by using Lorentz model where we divide the field into different components.

The understanding of this field can be obtained from the figure shown below which shows a sphere of dielectric material, say containing about 10 atoms, removed. The local field at the center of this sphere is composed of two macroscopic fields and two microscopic fields.

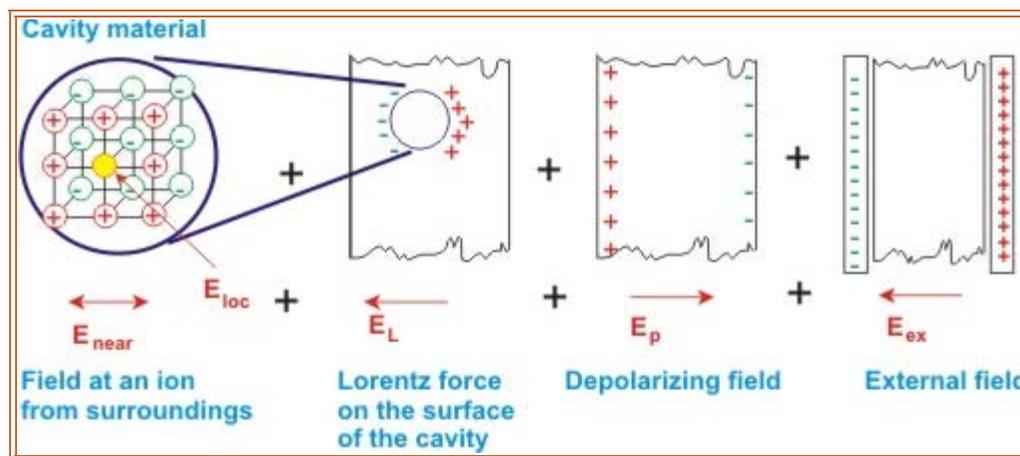


Figure 4.8 Schematic representation of various electric fields when a small cavity is created in a dielectric

The microscopic fields are:

- $E_{center}$ , field at the center of the sphere due to contributions of ions surrounding it with-in the sphere.
- $E_L$ , Lorentz field at the center of the spherical cavity due to charges on the surface of the cavity

(Note the difference between the two: one is talking of a sphere while it is composed of material and another is talking of a material surrounding the spherical cavity from which material has been removed.)

The macroscopic fields considering the dielectric as a continuum are:

- $E_{ex}$ , field due to applied voltage across the capacitor
- $E_p$ , the depolarizing field due to dielectric polarization

d

Hence,  $E_{loc}$  is written as

$$E_{loc} = (E_{ex} - E_d) + E_L + E_{center} \quad (4.22)$$

Now, we know that

$$E_{ex} - E_d = E - \frac{P}{\epsilon_0} \quad \text{if } \epsilon_r = 1 \quad (4.23)$$

Lorentz showed that for isotropic crystals,  $E_{center} = 0$

$E_L$  can be worked out for a cavity as

$$E_L = \frac{P}{3\epsilon_0} \quad (4.24)$$

(Analysis of the Lorentz field in the next slide)

Hence the local field is given as

$$E_{loc} = E + \frac{P}{3\epsilon_0} \quad (4.25)$$

By substituting  $P = \epsilon_0 (\epsilon_r - 1)E$  in (4.25)

$$E_{loc} = \frac{E}{3} (\epsilon_r + 2) \quad (4.26)$$

Now combining equations (4.20) and (4.26), we get

$$P = N_i \alpha_i \frac{E}{3} (\epsilon_r + 2) \quad (4.27)$$

Combining (4.15) and (4.27), we get

$$(\epsilon_r - 1) \epsilon_0 E = N_i \alpha_i \frac{E}{3} (\epsilon_r + 2) \quad \text{OR}$$

$$\frac{N_i \alpha_i}{3 \epsilon_0} = \frac{\epsilon_r - 1}{\epsilon_r + 2} \quad (4.28)$$

The above equation is called Clausius-Mossotti relationship and is valid only for linear dielectrics. The equation is related to a macroscopic quantity on RHS, i.e.  $\epsilon_r$  with a microscopic quantity,  $a$ .

As a result, if one knows the dielectric constant by means to measurement, this form can be used to calculate the polarizabilities of a variety of materials to quite an accurate estimate.

Polarizability,  $a$ , is the sum of polarizabilities from all the contributing mechanisms i.e.  $a_{\text{electronic}}$ ,

$a_{\text{ionic}}$ ,  $a_{\text{dipolar}}$  and  $a_{\text{interfacial}}$ .

Special case:

For gases

$$\epsilon_r - 1 \ll 1$$

And hence at low pressures

$$\epsilon_r + 2 \approx 3$$

Thus

$$\frac{N\alpha}{\epsilon_0} = \epsilon_r - 1 = \chi$$

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## 4.4.1 Analysis of the Lorentz Field (newly added)

Here, we are interested in calculating the field from the free ends of dipoles i.e. Lorentz field  $E_l$ , lined along the cavity wall in the direction of applied field, as shown below. This charge density arises from the bound charges and is determined by the normal component of polarization/dielectric displacement vector  $P$  and is written as

$$\vec{P} \cdot \vec{n} \cdot dA = P \cos \theta \cdot dA$$

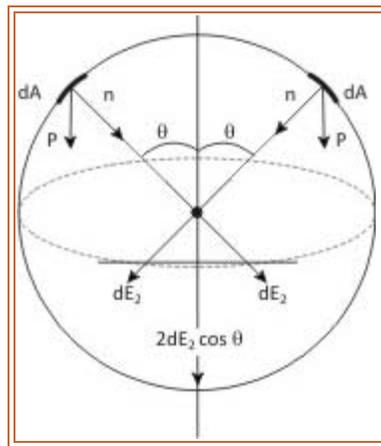


Figure 4.9 Schematic of field components for a spherical cavity

Now, since each element  $dA$  contributes to the field, according to Coulomb's law, the radial field intensity is

$$dE_l = \frac{P \cos \theta}{\epsilon_0 4\pi r^2} dA$$

Each  $dA$ 's angular position is between  $\theta$  and  $\theta+d\theta$  and for each  $dA$  element, there is another  $dA$  element on the other side of the sphere which produces same but opposite horizontal field component.

Horizontal components cancel each other and vertical components  $dE_2 \cos \theta$  survives

So the total field intensity is

$$E_l = \oint_{\text{sphere}} \frac{P \cos^2 \theta}{\epsilon_0 4\pi r^2} dA$$

The field intensity is parallel to the applied field and actually strengthens it. Now we can also rewrite  $dA$  as

$$dA = 2\pi r \sin \theta d\theta$$

SO

$$E_t = \int_0^\pi \frac{P \cos^2 \theta}{\epsilon_0 4\pi r^2} 2\pi r^2 \sin \theta d\theta = \frac{P}{3\epsilon_0}$$

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## Summary

Here, we saw that polarization is caused by the movement of electrons or ions or molecules from their equilibrium positions and is frequency dependent. This is because the mass of each entity is different and hence time scales are different. Basically, there are four polarization mechanisms: electronic, ionic, dipolar or orientation and interface and each of these mechanisms is characterized by different polarizability. The net polarizability of a solid will be sum of these four polarizabilities.

We also learnt that the local field inside a dielectric is not the same as the applied electric field. This field is a result of various microscopic and macroscopic fields inside the dielectric. This leads to derivation of Clausius-Mossotti equation which relates the microscopic dielectric properties to the macroscopic dielectric properties.

Next, we will then calculate the polarizabilities for each polarization mechanisms.

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## 4.5 Analytical Treatment of Polarizability

Here we discuss the simple analytical solutions for determining the polarizability and polarization for each of the above polarization mechanisms. The analysis will shed some light on the dependence of polarizability on the material parameters as well as any external parameters.

### 4.5.1 Electronic Polarization

To achieve this, let us first imagine an atom as a perfect sphere, having  $+Ze$  charge at the center of the nucleus and an equivalent  $-Ze$  charge of electrons around it. Here  $R$  is the radius of the atom.

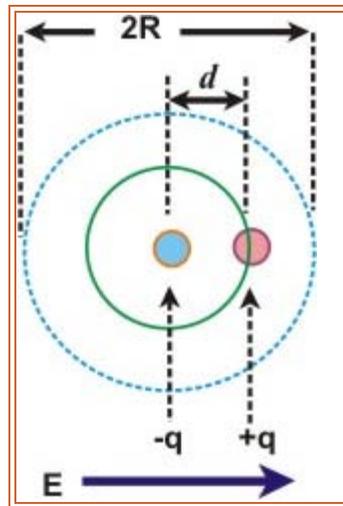


Figure 4.10 Schematic of electronic polarization

Under the application of a electric field,  $E$ , the force  $F_1$ , on the charges is given as

$$F = Ze.E \quad (4.29)$$

As a result, positive and negatives charges experience forces in different direction and their center move away from each other by a distance,  $d$ .

However,  $d$  has to be finite values because this force is balanced by Coulomb force of attraction between opposite charges which can be calculated by simple electrostatics and is given as

$$\begin{aligned} F_2 &= \left( \frac{q(\text{nucleus}) * q(\text{electrons inside the distance } d)}{4 \pi \epsilon_0 \cdot d^2} \right) \\ &= \left( \frac{Ze * Ze \left( \frac{(4/3)\pi d^3}{(4/3)\pi R^3} \right)}{4\pi \epsilon_0 \cdot d^2} \right) = \left( \frac{Z^2 e^2 d}{4\pi \epsilon_0 \cdot R^3} \right) \end{aligned} \quad (4.30)$$

Equating the two forces, gives the equilibrium separation distance  $d_0$ , i.e.

$$d_0 = \frac{4\pi \epsilon_0 \cdot R^3 E}{Ze} \quad (4.31)$$

Induced dipole moment,  $\mu$ , would be

$$\mu = Ze \cdot d_0 \quad \text{OR}$$

$$\mu = 4\pi\epsilon_0 \cdot R^3 E \quad (4.32)$$

If dipole density was  $N$ , the polarization is given as

$$P = 4\pi\epsilon_0 \cdot N \cdot R^3 \cdot E \quad (4.33)$$

Using equation (4.15), we can get electronic susceptibility,  $\chi_e$ , and electronic polarizability,  $\alpha_e$ , as

$$\chi_e = 4\pi N R^3 \quad \text{and} \quad \alpha_e = 4\pi\epsilon_0 R^3 \quad (4.34)$$

This is a very important result as it allows us to work out the electronic contribution to the dielectric constant. This also shows the linear relationship between polarization and electric field for electronic polarization mechanism. Another point to note is that polarizability of atoms with s- and p- atoms i.e. alkali and rare-earth is more than that of transition elements i.e. d-atoms due to higher shielding of nucleus by electrons in d-atoms.

The equation (4.34) also shows that the larger the atom, the larger is the polarization! Moreover, anions are more polarizable than cations as electrons in anions' outer shells are more loosely bound.

The values for atomic polarizability of some atoms are given below:

$\alpha_e (\times 10^{-24}) \text{cm}^{-3}$

| Halogens |     | Alkali |      |
|----------|-----|--------|------|
| F        | 1.2 | Li     | 0.03 |
| Cl       | 3   | Na     | 0.3  |
| Br       | 4.5 | K      | 0.9  |
| I        | 7   | Rb     | 1.7  |

#### 4.5.1.1 Examples

Assume a typical value for dipole density,  $N$ , and atomic radius,  $R$ , for a material made up of atoms with spherical symmetry of orbitals, i.e.  $N = 4 \times 10^{19} \text{ cm}^{-3}$  and  $R \sim 7 \times 10^{-9} \text{ cm}$ , yielding

$$\chi_e = 1.7 \times 10^{-4}$$

which is a very small value and the relative dielectric constant,  $\epsilon_r$ , does not increase by much.

What it says is that the electronic polarization effect is generally very weak and contributes very little to the overall polarization. Having said that, it must be borne in mind that some materials like

Si which are covalently bonded and orbital do not have spherical symmetry and as a result the dielectric constants can be higher (for example Si has about  $\epsilon_r \sim 12$ ). For electronic polarization,  $\epsilon_r$  is also equal to  $n^2$  and hence, if one knows the refractive index, this works as a check for the values calculated.

Values for some materials where electronic polarization is the principle mechanism of polarization are given below (source: "Solid State Physics" by N.W. Ashcroft and N.D. Mermin):

|                  |      |
|------------------|------|
| Carbon (diamond) | 5.7  |
| Ge               | 16.0 |
| GaP              | 8.4  |
| Si               | 12.0 |
| SiC              | 6.7  |
| GaAs             | 10.9 |

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### 4.5.2 Ionic Polarization

The figure below shows that in an ionic solid, in the absence of an external electric field, all the dipoles (formed by each  $\text{Na}^+$  and  $\text{Cl}^-$  pair with an equilibrium separation distance as  $d_0$ ) cancel each other due to crystal symmetry and hence net dipole moment is equal to zero. Remember, in these solids, no dipole rotation is allowed.

However, when a finite field,  $E$ , is applied, the force experienced by the ions leads them to move away from their equilibrium positions, as shown in the figure, giving rise to unequal dipole moments in different directions and as a result, the material will have net dipole moment.

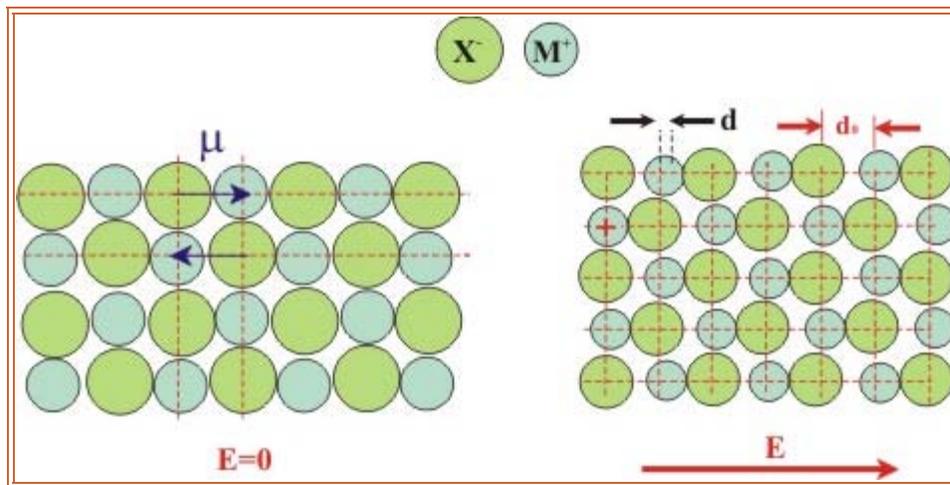


Figure 4.11 Schematic of the ionic polarization

As you can now see, the distance between the ions decreases by 'd' in one direction and increases by 'd' in the opposite direction.

Now we calculate the magnitude of 'd'.

The force,  $F_1$ , which increases the distance between the ions of charge,  $q$ , can be expressed as

$$F_1 = q \cdot E \quad (4.35)$$

However, there is a force,  $F_2$ , in the other direction trying to restore the equilibrium between the ions which is expressed as

$$F_2 = k_1 \cdot E \quad (4.36)$$

Where  $k_1$  can be considered as spring constant of the bond between ions assuming ionic dipoles behave like springs.

The spring constant can be expressed in terms of elastic modulus,  $Y$ , and can be expressed as

$$k_i = Y \cdot d_o \quad (4.37)$$

At equilibrium,  $F_1 = F_2$  and by combining equations (4.35-4.37), we get an estimate of  $d$  i.e.

$$d = \frac{q \cdot E}{Y \cdot d_o} \quad (4.38)$$

Hence, induced 'extra' dipole moment,  $\mu$ , will be

$$\mu = q \cdot d = \frac{q^2 \cdot E}{Y \cdot d_o} = \alpha_i E \quad (4.39)$$

where  $\alpha_i$  is ionic polarizability. Thus the polarization,  $P$ , can be written as

$$P = N \cdot \mu = \frac{N \cdot q^2 \cdot E}{Y \cdot d_o} \quad (4.40)$$

where  $N$  is the dipole density per unit volume.

**Note:** Here we considered the electric field,  $E$ , parallel to the main crystallographic axis. If this is not the case, one needs to take the component of dipole moment in the direction of the field before adding them together.

This is a very a rough guide to the calculation of the ionic polarization and can be more complex in the case of many ionic solids, especially when ions do not have similar charges. **For example**, in calcium fluoride,  $\text{CaF}_2$ , a material used for making lenses for lithography machine, the dielectric constant is approximately equal to  $n^2$ . This enables the lenses to be made of dimensions of about 0.1 mm.

The above expressions also tell us that stronger bonds lead to smaller polarization which seems obvious because then you wouldn't be able to stretch the atoms too far!

The following are the values of the dielectric constant of some materials where ionic polarization contributes (in addition to electronic polarization of course) (**source** : "Solid State Physics" by N.W. Ashcroft and N.D. Mermin):

|      |     |
|------|-----|
| ZnO  | 4.6 |
| ZnS  | 5.1 |
| ZnSe | 5.8 |
| CdSe | 7.0 |
| MgO  | 3.0 |
| CdS  | 5.2 |
| BeO  | 3.0 |



### 4.5.3 Dipolar or Orientation Polarization

In case of dipolar polarization, we have materials where the dipoles are present independent of each other, i.e. they don't interact and they can be rotated freely by an applied field unlike in case of ionic polarization.

One such example is water where each H<sub>2</sub>O molecule has a dipole moment and these dipole moments are free to rotate and can have any orientation with respect to neighbouring molecules. Due to the ability of molecules to move around randomly, liquids like water have very limited dipolar polarization contribution despite having a permanent dipole moment for each molecule.

A two dimensional image of water molecules is shown below which should remain almost similar at any instant. Arrows depict the direction of dipole moment associated with each molecule.

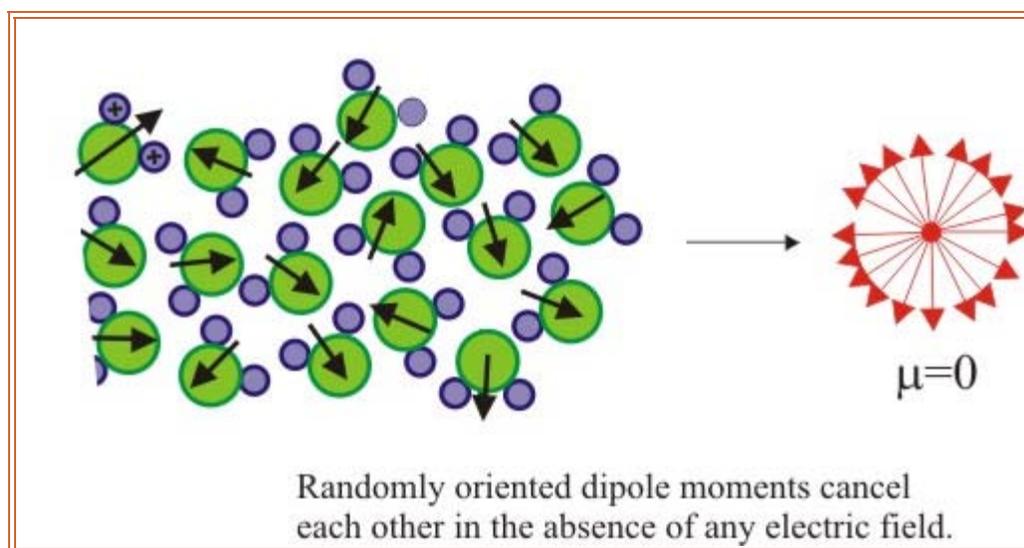


Figure 4.12 Dipoles in a polar material

It is quite obvious by looking at the figure that in the absence of an applied field, all the moments are randomly distributed (huge number for even a small amount of water, say 10 ml) and net dipole moment would be zero.

Now when we apply an external electric field say parallel to the paper along +X- axis as shown below, the dipoles would tend to align with the applied field to lower their electrostatic energy and lead to minimum dipole energy (basically the positive end of the dipole would like to join the negative end of the applied field).

For instance, water does have a pretty large dielectric constant of ~80 which means that there is obviously some orientation along the field.

#### Exercise

You can show it to yourself that this dielectric constant is several orders of magnitude smaller than for fully oriented dipole moments at some normal field strengths (see here for solution).

In reality, the tendency of dipoles to orient along into the field direction will be counteracted by

random collisions between molecules, a process driven by the thermal energy ' $kT$ ' at a temperature ' $T$ '. Moreover, the dipole containing molecules move around at all times due to thermal energy and the associated entropy i.e. **disorder**.

So, basically when we apply an external field, there is a competition between field induced order and thermal driven disorder. The Later prevails in liquids more than in solids. Hence, perfect alignment of dipoles would be possible only at very low temperature and possibly in solid crystals.

As a result of intermolecular collisions and thermally induced random movement, the dipoles do not completely align themselves along the field unless the field is extremely high. So basically, the configuration of dipoles looks something like shown below.

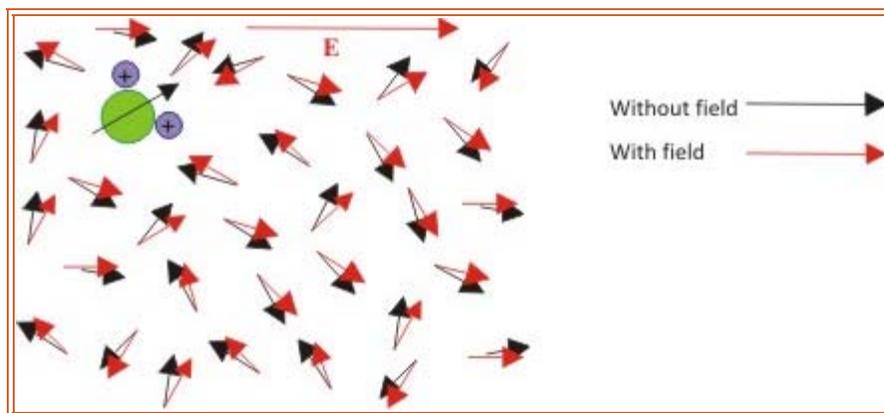


Figure 4.13 Effect of electric field on the dipole orientation

This basically highlights that the orientation of all the dipoles is just a little bit shifted towards the field direction leading to an average non-zero dipole moment in the direction of the applied electric field.

Thermodynamically speaking, we will minimize the free energy,  $G$  which is equal to  $H - TS$  where  $H$  is the internal energy and  $S$  is the entropy. So for this, now we take the following configuration where the charge dipole of an molecule makes an angle,  $\theta$ , to the applied field.

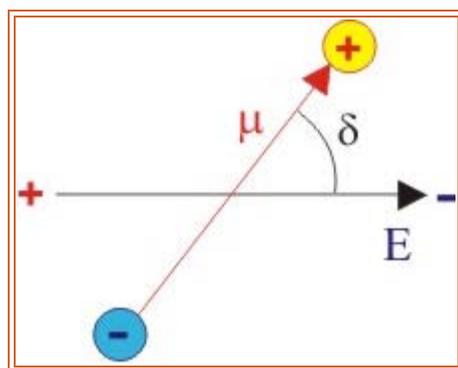


Figure 4.14 2-D schematic diagram of a charge dipole aligned with respect to applied field

The internal energy,  $U$ , of a dipole depends on its orientation with respect to the applied field, i.e. it is function of  $\theta$ .

$U$  is minimum when the dipole is completely aligned with the field i.e.  $\theta = 0$  and maximum if  $\theta = 180^\circ$ .

The energy  $U(\theta)$  of a dipole with dipole moment,  $\mu$  under an applied field,  $E$ , can be written as

$$U(\theta) = \mu \cdot E = |\mu| |E| \cos \theta \quad (4.41)$$

What it means in 3-D world is that we would have a cone of dipoles making an angle  $\theta$  around the applied field  $E$  which points along the axis of the cone as shown below. The total internal energy of the whole material would be the sum of internal energies of all these cones.

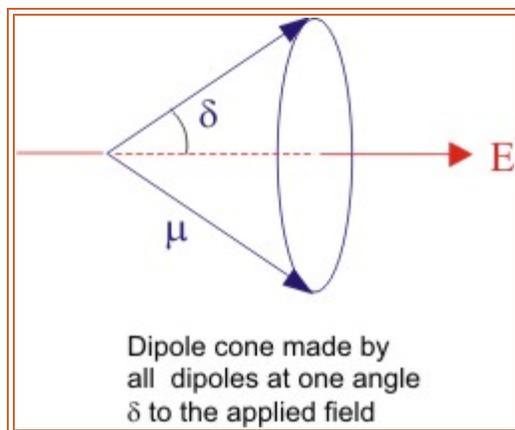


Figure 4.15 Schematic representation of dipoles around the electric field

Now we need to calculate the number of dipoles at an angle  $\theta$ ,  $N(\theta)$  which can then be multiplied with the energy for that  $\theta$  and then be integrated between  $\theta$  ranging from  $0$  to  $180^\circ$  to give us the total internal energy. However, to calculate the free energy, we also need to calculate the entropy,  $S$ , which is not very straightforward.

This is where Boltzmann statistics (from classical thermodynamics) rescues us which allows us to work out the minimum of the free energy using a distribution function.

We treat our system, to a good approximation, as a classical system containing a number of independent entities (the dipoles), occupying various energies as determined by their angle w.r.t. applied field. The distribution of these dipoles at various energies can be expressed by a distribution function in such a manner that it minimizes the free energy of the system.

Now, at a given temperature,  $T$ , the number of dipoles with energy  $U$  can be expressed as

$$N(U(\theta)) = A \exp\left(-\frac{U(\theta)}{k_B T}\right) \quad (4.42)$$

where  $A$  is a constant and  $k_B$  is Boltzmann constant.

Equation (4.42) provides us the number of dipoles in a cone as shown above.

Now, we should calculate the component of the dipole moment parallel to the applied field using the solid angle  $d\Omega$  for a unit sphere in the segment between  $\theta$  and  $\theta + d\theta$ .



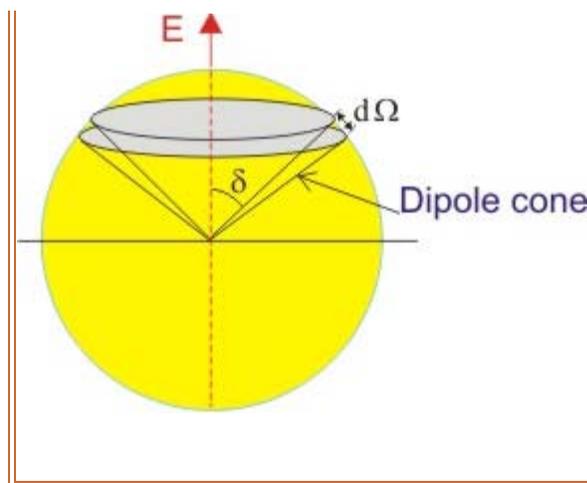


Figure 4.16 Spherical representation of dipoles

This implies that the number of dipoles between  $\theta$  and  $\theta + d\theta$  is equal to  $N(U(\theta)) \cdot d\theta$ .

The total dipole moment is nothing but the sum of the components of the dipole moments in direction of applied field i.e.

$$\mu_E = (Nd\Omega) \times (\mu \cos \theta) \quad (4.43)$$

The average dipole moment,  $\langle \mu_E \rangle$ , is calculated by adding up the contributions from all the solid angles i.e.

$$\langle \mu_E \rangle = \frac{\int_0^\pi N(U(\theta)) \mu \cos \theta d\Omega}{\int_0^\pi N(U(\theta)) d\Omega} \quad (4.44)$$

The incremental solid can be expressed as

$$d\Omega = 2\pi \sin \theta d\theta \quad (4.45)$$

which together with (4.42) yields

$$\langle \mu_E \rangle = \frac{\int_0^\pi \sin \theta \cos \theta \exp\left(\frac{\mu E \cos \theta}{k_B T}\right) d\theta}{\int_0^\pi \sin \theta \exp\left(\frac{\mu E \cos \theta}{k_B T}\right) d\theta} \quad (4.46)$$

To solve this equation, we make substitutions as  $\beta = (\mu E/k_B T)$  and  $x = \cos \theta$  in the above equation which yields

$$\langle \mu_E \rangle = \frac{\mu \int_{+1}^{-1} x \cdot \exp(\beta x) dx}{\int_{+1}^{-1} \exp(\beta x) dx} \quad (4.47)$$

or rather

$$\langle \mu_E \rangle = \mu \cdot L(\beta) \quad (4.48)$$

where  $L(\beta) = \text{Langevin function}$ , named after Paul Langevin, and is defined as

$$L(\beta) = \coth(\beta) - (1/\beta) \quad (4.49)$$

The function  $\coth(x)$  is nothing but  $(e^x + e^{-x}) / (e^x - e^{-x})$ . We won't go into details of  $L(x)$  except that it is not an easy function to deal with and  $L(x)$  values are between 0 and 1 for our purposes.

Langevin function is plotted as shown below.

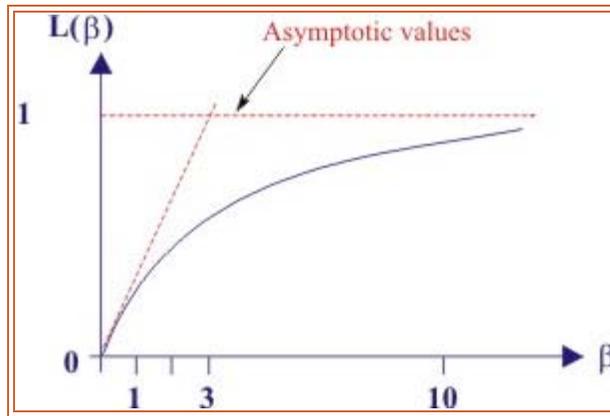


Figure 4.17 Schematic plot of Langevin function

As we can see, for large values of  $\beta$  (i.e. large electric fields or very low temperatures, close to 0 K),

$$L(\beta) \approx 1 \quad (4.50)$$

while for small values of ( $\beta < 1$ ) i.e. nominal fields and higher temperatures, the slope is  $1/3$  for  $\beta \rightarrow 0$  and hence the Langevin function is approximated by

$$L(\beta) = \frac{1}{3}\beta \quad (4.51)$$

In general,  $\beta$  is always much smaller than one i.e.  $\beta \ll 1$ .

As a result, the induced dipole moment, often called as Langevin - Debye equation is given as

$$\langle \mu_E \rangle = \frac{\mu^2 E}{3k_B T} = \alpha_d E \quad (4.52)$$

Where  $\alpha_d$  is dipolar polarizability. Now, the average polarization is

$$P = \frac{N \mu^2 E}{3k_B T} \quad (4.53)$$

These equations hold pretty well for small values of  $\mu$  and  $E$  and/or large enough  $T$  which we can presume as normal conditions.

In fact when fields are very high and temperature is very low (i.e. minimizing the randomization), all

the dipoles would be parallel to the applied field and then the average dipole moment would be equal to the theoretical dipole moment.

Equation (4.52) also shows the temperature dependence of dipolar polarizability as  $\mu = a$ , unlike in the case of electronic and ionic polarization.

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#### 4.5.3.1 Example

Suppose for a system

$$E = 100 \text{ MV/cm}$$

$$\mu = 10^{-29} \text{ cm (large enough dipole moment for a strongly polarized molecule, e.g. HCl, and}$$

$$T = 300 \text{ K.}$$

Using the above equation, we can calculate  $\beta = 0.24$  which validates our analysis.

However, at  $T = 30 \text{ K}$ ,  $\beta = 2.4$  and this may raise doubts about our analysis.

But, at this temperature it is likely to have liquid into solid state and what we see now is only the effect of ionic polarization and no longer at orientation polarization!

Similar analysis is applied to the study of magnetic dipoles (a misnomer) in response to a magnetic field.

Unlike our assumption in the beginning, if there is a dipole-dipole strong interaction, such as in most solids, the dipoles are not free to orient themselves and mostly the contribution in such cases arises from ionic polarization. There are, however, some solids like ferroelectrics where dipoles do interact and can rotate to some extent giving rise to extraordinary effects as we will study later.



## Module 4: Dielectric Ceramics: Basic Principles

### Summary

#### Summary

Here, we calculated the electronic and ionic polarizability and the polarizations of the dielectric using electronic charge dipoles and ionic lattice having charges coupled as springs. In case of electronic polarizability, we see that the larger the ion is, the higher is the polarizability. On the other hand, ionic polarizability is inversely proportional to the elastic modulus which is related to the bond strength. Hence, the higher the bond strength is, the lower is the ionic polarization. Finally we calculated the dipolar polarization using random dipole model and Boltzman statistics. Here, we saw that polarizability is inversely related to the temperature which explains the drop in the polarization of a polar solid upon increasing the temperature.

Next, we will investigate the behavior of dielectric under alternating fields.



## 4.6 Effect of Alternating Field on the Behavior of a Dielectric Material

Here we will examine the behavior of real and ideal dielectric materials under the influence of an alternating electric field, giving an account of the real situations to which dielectric materials are subjected.

### 4.6.1 Behavior of an Ideal Dielectric

While most of the above discussion has been for d.c. or static fields, in most practical applications, dielectrics are used under alternating fields. Hence, it is imperative to work out their characteristics in alternating fields.

Let us apply a sinusoidal field

$$V = V_0 \cdot \exp(i\omega t) \quad (4.54)$$

This leads to the development of a charging current,  $I_c$ , due to a change in the charge with time which is

$$I_c = \frac{dQ}{dt} = C \cdot \frac{dV}{dt} = i\omega CV \quad (4.55)$$

$$= \omega C \cdot V_0 \cdot \exp(i\omega t) \cdot \exp(i\pi/2)$$

$$= \omega C \cdot V_0 \cdot \exp[i(\omega t + \pi/2)] \quad (4.56)$$

The term  $+ \pi/2$  implies that the current leads the voltage by  $90^\circ$  in a perfect dielectric. This current voltage relationship can also be understood from a phasor diagram as shown below.

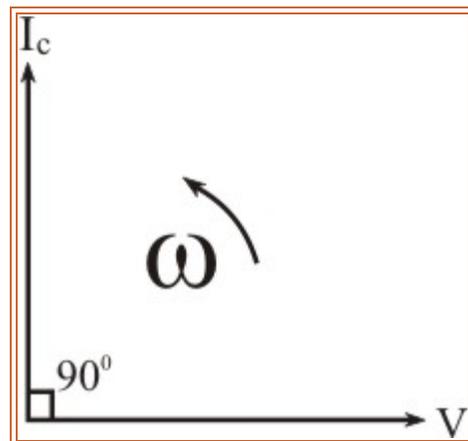


Figure 4.18 Phasor diagram for a perfect dielectric

### 4.6.2 Power Dissipation in an Ideal Dielectric

Since the instantaneous power drawn by the dielectric from the voltage sources is  $I_c V$ , the time-average power dissipated,  $P_{avj}$ , in a dielectric is given as

$$P_{avj} = \frac{1}{T} \int_0^T I_c \cdot V \cdot dt \quad (4.57)$$

where  $T$  is the time period is given as  $(2\pi/\omega)$ .

For an ideal dielectric with no loss of charging current, the power dissipated inside the dielectric must be zero, i.e.

$$P_{avj} = \frac{1}{T} \int_0^T (-\omega C) \cdot V_o^2 \cdot \sin(\omega t) \cos(\omega t) dt \quad (4.58)$$

What it means is that during the first cycle, the capacitor charges completely and during the other cycle it completely discharges without any loss of charge. It is like a mass perfectly oscillating under gravity on a perfect spring.



### 4.6.3 Behavior of Real Dielectrics

However, in real dielectrics, the charging current is also accompanied by a loss current, associated with storage of electric charge by the dipoles. There are two sources of this loss current:

- Long range migration of charges due to ohmic conduction and is frequency independent i.e. d.c. in nature, and
- Dissipation of energy due to dipole rotation or oscillation as there always is certain inertial to their movement due their mass. This contribution is time-dependent i.e. frequency dependent.

Since, both of these current are in phase with the applied field, the loss current,  $I_l$ , can be written as

$$I_l = (G(\omega)_{ac} + G_{dc}) \cdot V \quad (4.59)$$

where  $G$  depicts the conductance in mho or Siemens which is nothing but the inverse of resistance. Hence, the total current,  $I_T$ , is the sum of charging and loss current *i.e*

$$I_T = I_c + I_l = (i\omega C + G(\omega)_{ac} + G_{dc}) \cdot V \quad (4.60)$$

Hence, the current in a real dielectric is a complex quantity that leads voltage by angle  $90^\circ - d$  where  $d$  is defined as the loss angle or dissipation factor. It is made up of two components that are  $90^\circ$  out of phase with respect to each other and have to be added vectorially as shown below. Naturally,  $d$  will be zero if there was no loss current present.

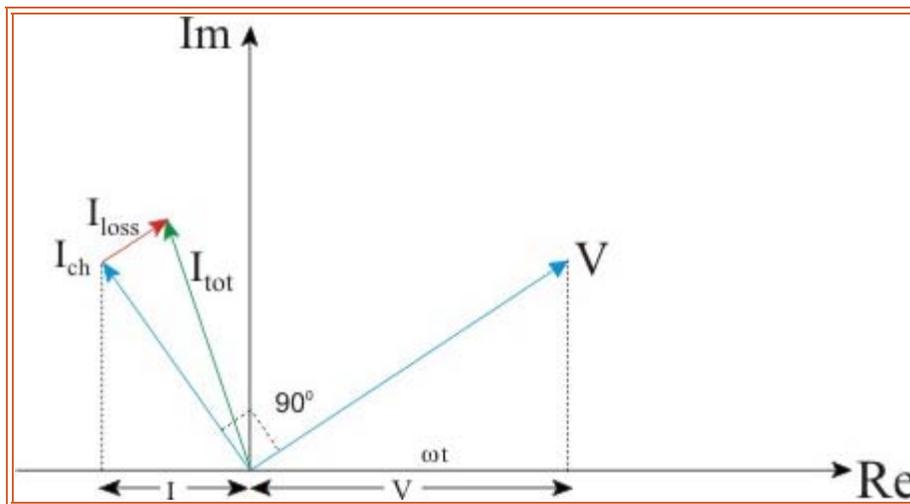


Figure 4.19 Real and Imaginary part of  $I$  and  $V$

When the field applied is static or d.c. i.e.  $\omega = 0$  then

$$I_T = I_l = G_{dc} \cdot V$$

where  $G_{dc} = 1/R$  and  $R$  is the ohmic resistance.

An alternative way to express the real dielectrics passing both charging and loss current is to use complex permittivity.

$$\epsilon = \epsilon' - i \epsilon'' \quad (4.61)$$

and

$$k^* = \epsilon / \epsilon_0 = k' - i k'' \quad (4.62)$$

Total current in a dielectric can now be expressed in terms of a single material parameter,  $k$ , since capacitance and charge are

$$C = k^* C_0 \text{ and } Q = C V = k C_0 V \quad (4.63)$$

Using equation (4.54), the total current can be expressed as

$$\begin{aligned} I_c &= I_T - I(\omega) \\ &= I_T - I(\omega = 0) = \frac{dQ}{dt} \\ I_T - I(\omega = 0) &= \frac{dQ}{dt} = k^* \cdot C_0 \cdot i \omega V \\ &= (k' - i k'') \cdot C_0 \cdot i \omega V \end{aligned} \quad (4.64)$$

i.e.

$$I_T = i \omega C_0 k' V + \omega k'' C_0 V + G_{dc} V \quad (4.65)$$

Here

$$I(\omega = 0) = G_{dc} \cdot V \quad (4.66)$$

The first term in (4.65) is the out-of-phase charging current term and last two terms are in-phase loss current terms.

Comparing equation (4.65) with (4.60) yields overall conductance,  $G$ , as

$$G = G_{dc} + G(\omega)_{ac} \quad (4.67)$$

where  $G(\omega)_{ac} = \omega k'' C_0 V$

Loss tangent,  $\tan \delta$ , is expressed as

$$\tan \delta = \frac{I_L}{I_c} = \left( \frac{G_{dc} + \omega k'' C_0}{\omega k' C_0} \right) \quad (4.68)$$

If  $G_{dc} \ll \omega k'' C_0$  then

|                          |        |
|--------------------------|--------|
| $\tan \delta = k'' / k'$ | (4.69) |
|--------------------------|--------|

The values of dielectric constant and loss tangent for selected materials are shown below.

|  |  |  |
|--|--|--|
|  |  |  |
|--|--|--|

| Material           | Dielectric Constant ( $\epsilon_r'$ ) | Loss Tangent ( $\tan\delta \cdot 10^{-4}$ ) |
|--------------------|---------------------------------------|---|
| Alumina            | 10                                    | 5-20  |
| SiO <sub>2</sub>   | 3.8                                   | 2   |
| BaTiO <sub>3</sub> | 500                                   | 150   |
| Nylon              | 3.1                                   | 10  |
| Polycarbonate      | ~3                                    | 10  |
| PVC                | 3                                     | 160   |

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## 4.6.4 Power Dissipation in a Real Dielectric

Hence, a.c. conductivity can be expressed as

$$\sigma_{ac} = \sigma_{dc} + \omega k'' \epsilon_0 = \omega \epsilon_0 k' \tan \delta \quad (4.70)$$

If  $\sigma_{dc}$  is very small, then

$$\sigma_{ac} = \omega \epsilon_0 k' \tan \delta \quad (4.71)$$

Now, the time average power loss can be expressed as

$$\begin{aligned} P_{av} &= \frac{1}{T} \int_0^T I_{loss} V dt \\ &= \frac{1}{T} \int_0^T (\omega k'' C_0 + G_{dc}) V_0^2 \cos^2(\omega t) dt \end{aligned} \quad (4.72)$$

If  $G_{dc} \ll \omega k'' C_0$ , then

$$P_{av} = \frac{1}{2} (\omega k'' C_0) \cdot V_0^2 = \frac{1}{2} G_{ac} V_0^2 \quad (4.73)$$

OR

$$P_{av} = \frac{1}{2} (\omega k' \tan \delta C_0) \cdot V_0^2 = \frac{1}{2} V_0^2 \cdot \omega \cdot C \cdot \tan \delta \quad (4.74)$$

Hence, if  $C_0 = (\epsilon_0 A/d)$ ,  $C_0 = (V_0/d)$  and  $V = A \cdot d$ , the dissipated power density in a dielectric would be

$$\frac{P_{av}}{V} = \frac{1}{2} \omega \cdot \epsilon_0 k' \cdot \tan \delta \cdot E_0^2$$

One can now see that for static or d.c. fields,  $\omega = 0$ , *i.e.*

$$G_{ac} = G_{dc} = 1/R \quad (4.75)$$

and hence,

|                  |        |
|------------------|--------|
| $P_{av} = I^2 R$ | (4.76) |
|------------------|--------|

which is the standard equation for power dissipation in a material under dc fields.

## Module 4: Dielectric Ceramics: Basic Principles

### Summary

#### Summary

We have investigated the behavior of dielectric materials in alternating electric fields. We see that for ideal dielectrics, the current leads the voltage by  $90^\circ$  and power dissipation is equal to zero. On the other hand, in real dielectrics, the current leads voltage by an angle  $90^\circ - \delta$  where  $\delta$  is the loss angle. This results in real and imaginary parts of the dielectric constant and the ratio of imaginary to real part is loss tangent, depicting the power loss in a real dielectric.

Next we will look into the frequency dependence of the dielectric properties.

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## 4.7 Frequency Dependence of Dielectric Properties: Resonance

As briefly shown in the earlier section, polarization mechanisms have frequency dependence and that is because of the mass associated with the charge dipoles and hence inherent inertia to movement. This also means that if the frequency of the field is very high, say above  $10^{15}$  Hz, no dipole system will be able to follow the field oscillations and in such a situation, no mechanism will contribute and hence  $\epsilon_r \sim 1$ .

However, at frequencies below  $10^{12}$  Hz, the dielectric properties are affected by the frequency of the field.

In case of electronic and ionic polarization, the charge dipoles can be considered behaving as mechanical oscillators where charges are connected with linear springs whose restoring force balances the force induced via the applied electric field. The characteristic of any such mechanically oscillating system is resonance at a certain frequency.

In case of orientation polarization, there is no direct mechanical restoring force. Instead we have many statistical events, that respond in their average results to the driving forces of electrical fields. In other words, if a driving force is present, there is an equilibrium state with an (average) net dipole moment. If the driving force were to disappear suddenly, the ensemble of dipoles will assume a new equilibrium state (random distribution of the dipoles) within some characteristic time called **relaxation time**. This process does not show any resonance phenomena and is characterized by its relaxation time instead of a resonance frequency.



### 4.7.1 Description of Ionic and Electronic Phenomenon

If we assume charge dipoles behaving like a linear harmonic oscillator, then they also follow the its equation of motion.

The equation of motion describing an oscillating system driven by a sinusoidal force can be written as

$$m_i^* \frac{d^2x}{dt^2} + m_i^* \gamma_i \frac{dx}{dt} + m_i^* \omega_{o,i}^2 x = q_i E \quad (4.77)$$

where  $m_i^*$  is the mass of the particle (i.e. charges or ions containing charges),  $i$ ,  $x$  is the displacement from the equilibrium,  $\gamma_i$  is the friction coefficient on the species and  $\omega_{o,i}$  is the natural frequency of the particle. In this equation, on the left hand side, the first term is the force due to acceleration, the second term is the damping or frictional force, and the third term is the spring restoring force, while the term on the right hand side is the force due to applied electric field.

The field will actually be local field than just the applied field but for the sake of simplicity, we can assume the system to behave like a gas consisting of  $N$  atoms per unit volume for which  $q_i = -Z_i e$ .

Consider two cases:

#### Case I: When the applied field in d.c. and is switched off at a given moment

- Restoring force pulls back the charges to equilibrium.
- If friction is zero, there will be no damping of oscillations.
- If friction is present, then system will have damped oscillations.

#### Case II :

When applied field is sinusoidally varying field i.e.

$$E = E_o \exp(i\omega t) \quad (4.78)$$

The corresponding displacement is given as

$$x = x_o \exp(i\omega t) \quad (4.79)$$

Ignoring transient terms, the solution of equation (4.78) is

$$x(t) = \frac{q_i E_o \exp(i\omega t)}{m[(\omega_{o,i}^2 - \omega^2) + i\gamma_i \omega]} \quad (4.80)$$

The induced dipole moment per particle is

$$\mu_i = q_i \cdot x$$

$$= \frac{q_i^2 E_o \exp(i\omega t)}{m_i [(\omega_{o,i}^2 - \omega^2) + i\gamma_i \omega]} \quad (4.81)$$

$$= \alpha_i \cdot E_o \exp(i\omega t) \quad (4.82)$$

where  $\alpha_i$  is the electronic or ionic polarizability as be the case. If the friction term is neglected, then frequency dependent polarizability is

$$\alpha_i = \frac{q_i^2}{m(\omega_{o,i}^2 - \omega^2)} \quad (4.83)$$

Here mass,  $m_i$ , is either the mass of electrons in atoms or ions in crystals.

In case of ionic polarization, one takes the reduced mass which is given as  $\{M^+ M^- / (M^+ + M^-)\}$  where  $M^+$  and  $M^-$  are cation and anion masses respectively. Similarly  $q_i$  will be charge on the particle as appropriate and  $\omega_{o,i}$  will be natural frequency of electronic or ionic polarization mechanisms.

The polarization can then be written as

$$P_i^* = N \cdot \mu_i \quad (4.84)$$

Hence using equations (4.15) and (4.16) we get the expressions for the susceptibility and dielectric constant as

$$\chi_{i,\infty}^* = \frac{N \cdot q_i^2}{m_i \epsilon_o} \left\{ \frac{1}{(\omega_{o,i}^2 - \omega^2) + i\gamma\omega} \right\} \quad (4.85)$$

and

$$\epsilon_{r,\infty}^* = 1 + \frac{N \cdot q_i^2}{m_i \epsilon_o} \left\{ \frac{1}{(\omega_{o,i}^2 - \omega^2) + i\gamma\omega} \right\} \quad (4.86)$$

Here \* implies that these are complex quantities which was also mentioned earlier when we discussed power dissipation characteristics in real dielectrics.

The subscript 8 signifies the susceptibility and dielectric constants at frequencies below the resonance frequencies. Resonance for electronic polarization occurs at about  $10^{15} \text{ s}^{-1}$  and for ionic polarization occurs at about  $10^{13} \text{ s}^{-1}$ .

Now, we can separate out the real and imaginary parts of the dielectric constants as following

$$\epsilon'_{r,\infty} = 1 + \frac{N \cdot q_i^2}{m_i \epsilon_o} \left\{ \frac{\omega_{o,i}^2 - \omega^2}{(\omega_{o,i}^2 - \omega^2)^2 + \gamma^2 \omega^2} \right\} \quad (4.87)$$

and

$$\epsilon''_{r,\infty} = \frac{N \cdot q_i^2}{m_i \epsilon_0} \left\{ \frac{\gamma \omega}{(\omega_{o,i}^2 - \omega^2)^2 + \gamma^2 \omega^2} \right\} \quad (4.88)$$

These can be plotted vs frequency as shown below.

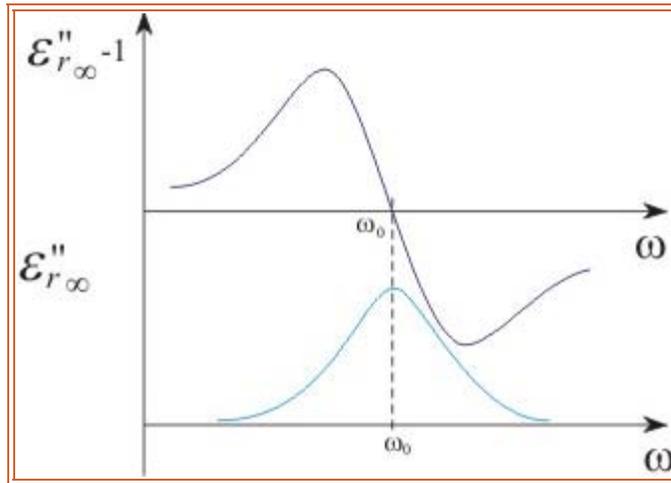


Figure 4.20 Schematic plot of real and imaginary parts of dielectric constant for electronic and ionic polarization

The value of resonance frequency can be determined from the polarizability expressions we determined above in equations (4.34) and (4.39) as we know that  $\omega_0 = \sqrt{k/m}$ . All now you need to do is to balance the force inducing the moment and the restoring force to find out the spring constant. The value of  $\omega_0$  works out to be about  $10^{13}$  Hz for ionic and  $10^{15}$  Hz for electronic polarization mechanism. This makes sense because for ionic polarization, the masses of ions are several thousand times higher than electrons and  $10^{13}$  Hz is very close to the natural frequency of lattice vibrations!

The shape of the plot should also help you understand the far right portion of the dielectric constant versus frequency plot shown earlier when we discussed mechanisms of polarization. For very frequencies when  $\omega \rightarrow \infty$ ,  $\epsilon'_r = 1$  or  $\epsilon' = \epsilon_0$ .

You must remember that the above discussion is valid for gases with non-interacting dipoles for we assumed that local field was equal to the applied field. If we use the local field instead of the applied field *i.e.*  $E_{loc} = E/3(\epsilon_r'' + 2)$ , fortunately we don't change the form of expressions, rather we get only

a shift in the resonance frequency. The changed resonance frequency is  $\omega'_0 = \sqrt{\omega_0^2 - \frac{Ne^2}{3m_e \epsilon_0}}$ .

Naturally for a system with ionic polarization, electronic polarization will be in-built simply because anything is made of atoms.

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## Module 4: Dielectric Ceramics: Basic Principles

### Frequency Dependence of Dielectric Properties: Resonance

#### 4.7.1.1 Electronic polarization vis-à-vis frequency

If  $\omega \ll \omega_{0,e}$  the charges oscillate in phase with the applied field and contribute to dielectric constant.

If  $\omega_{0,e} = \omega$ , i.e. frequency is equal to the natural frequency of vibration, then resonance occurs and  $\epsilon_r'$  attains a maximum. The charges are  $90^\circ$  out of phase with the applied field and do not contribute to  $\epsilon_r'$ . We witness a maximum loss i.e. high  $\epsilon_r''$ .

If  $\omega_{0,e} < \omega$ , then in this region field changes its direction too fast compared to the rate at which electrons can move. Hence, electrons do not respond and no polarization results and  $\epsilon_r'$  is equal to 1, i.e. system behaves as if there was no dielectric was present.

#### 4.7.1.2 Ionic polarization vis-à-vis frequency

If  $\omega \ll \omega_{0,i}$ , the charges oscillate in phase with the applied field and contribute to dielectric constant. The total dielectric constant is now  $\epsilon_{r,e+i}'$  i.e. both due to ionic and electronic contributions.

If  $\omega_0 < \omega$  i.e. frequency is equal to the natural frequency of vibration, then resonance occurs and  $\epsilon_r'$  attains a maximum. The charges are  $90^\circ$  out of phase with applied field and do not contribute to the dielectric constant and we witness maximum loss i.e. high  $\epsilon_r''$ .

If  $\omega_{0,i} < \omega$ , then in this region field changes its direction too fast compared to the rate at which ions can move. Hence, ions don't respond and no ionic polarization results and  $\epsilon_r'$  is  $\epsilon_{r,e}'$ , i.e. the system behaves as if there was no ionic polarization mechanism present.



### 4.7.2 Microscopic Examination of Polarizability

From the equation (4.83), for electronic polarization, we can write the electronic or atomic polarizability as

$$\alpha_e = \frac{(-Ze)^2}{m_e \omega_o^2} \quad \text{if } \omega \ll \omega_o \quad (4.89)$$

Here, we have replaced the subscript i with e for electrons.

We can get an expression for  $\omega_o$  ( = (k (spring constant)/m (mass))<sup>1/2</sup>) by equating the restoring force (k.dx) and the force inducing the displacement. From that the atomic polarizability can be expressed as

$$\alpha_e = 4\pi\epsilon_o \cdot r_o^3 \quad (4.90)$$

which is nothing but equation (4.34) where we worked out the atomic polarizability just from force balance.

A similar analysis can be carried out for ionic polarization as well which is left to you as an exercise.



## 4.8 Dipolar Relaxation i.e. Debye Relaxation in Polar Solids

- Relaxation processes occur in many ceramics and ionic solids, especially glasses and these materials applying damped forced oscillator approach does not work in the low frequency region.
- In such cases, the structure of the solid plays an important role because movement of charges may have to occur over many atomic distances and can be classified as diffusional in nature. These processes can be strongly temperature dependent in nature.
- As a result, it may take considerable amount of time in the distribution of charges.

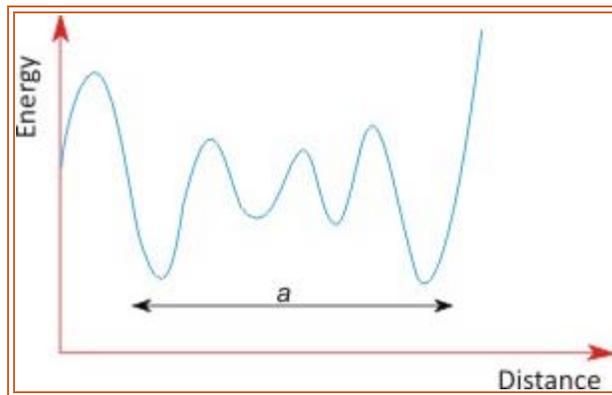


Figure 4.21 Potential energy distribution of ionic sites in a glass

- For instance, in an ionic solid, application of a field leads to first almost instantaneous development of ionic and electronic polarization followed by slow development of dipolar polarization,  $P_d$  to a saturation polarization,  $P_s$ .

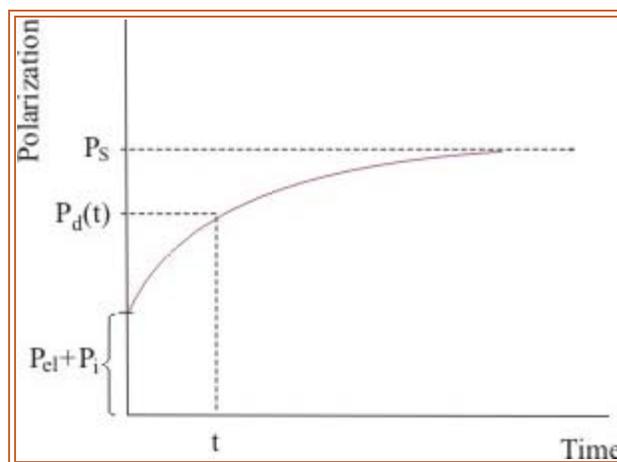


Figure 4.22 Dependence of dipolar polarization on time

- We can approximately express the rate of change of polarization as

$$(4.91)$$

$$\frac{dP}{dt} = \frac{1}{\tau} (P_s - P_d(t))$$

where  $1/\tau$  is the proportionality constant. The above equation is also called Relaxation Equation. This equation can be derived using a simple bi-stable model in a similar fashion to that used in Module 3 (section 3.10) .

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## 4.8.1 Bi-stable model for dipolar relaxation

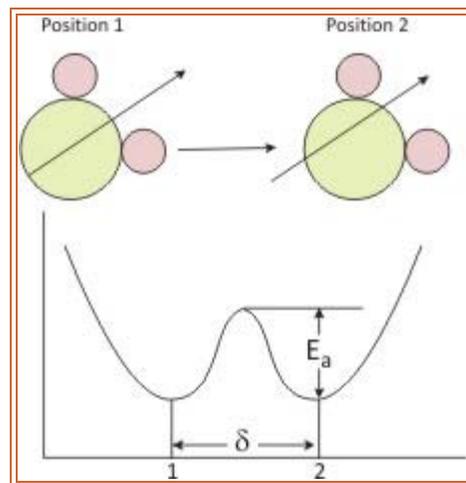


Figure 4.23 Schematic of a polar molecule going one state to another and resulting energy well diagram

In a solid when field is applied to a polar material, the ions hop from ionic position to another as shown above in figure 4.23, e.g.  $\text{Na}^+$  movement in glasses. We consider a bistable dipole model. As the cation moves from left to right, there is a change in the co-ordinates. At any temperature above  $0\text{K}$ , there is random oscillation of cation between these sites.

The probability of jump between sites is given as

$$F = Ae^{-E_a/kT} \quad (4.92)$$

Upon application of field, the wells tilt in the direction of applied field, resulting in unequal probability in two directions resulting a net flow of dipoles

$$F_{12} = F \left( 1 - \frac{\mu E}{kT} \right)$$

$$F_{21} = F \left( 1 + \frac{\mu E}{kT} \right) \quad (4.93)$$

where  $E$  is the applied field.

Under the application of an ac field, the change in the number of dipoles at site 1 = outflow to site 2 – inflow to site 1 i.e.

$$\frac{dN_1}{dt} = -N_1 F_{12} + N_2 F_{21} \quad (4.94)$$

Where  $N_1 + N_2 = N = \text{constant}$

Further, since

$$\begin{aligned}
\frac{dN_1}{dt} + \frac{dN_2}{dt} &= 0 \\
\Rightarrow \frac{dN_1}{dt} &= -\frac{dN_2}{dt} \\
\Rightarrow \frac{d(N_1 + N_2)}{dt} &= 2\frac{dN_1}{dt} = -2\frac{dN_2}{dt}
\end{aligned} \tag{4.95}$$

Replace  $dN_1/dt$  in the above equation, and we get

$$\begin{aligned}
\frac{1}{2} \frac{d(N_1 + N_2)}{dt} &= -N_1 F_{12} + N_2 F_{21} \\
\Rightarrow \frac{1}{2} \frac{d(N_1 + N_2)}{dt} &= -N_1 F \left(1 - \frac{\mu E}{kT}\right) + N_2 F \left(1 + \frac{\mu E}{kT}\right) \\
\frac{1}{2} \frac{d(N_1 + N_2)}{dt} &= -F(N_1 - N_2) + F(N_1 - N_2) \frac{\mu E}{kT}
\end{aligned} \tag{4.96}$$

Now, polarization  $P$  can be expressed as the product of the net ions moved and the dipole moment i.e.

$$\begin{aligned}
P &= (N_1 - N_2)\mu \\
\frac{1}{2\mu} \frac{dP}{dt} &= -\frac{F}{\mu} \vec{p} + \frac{FN\mu E}{kT} \\
\frac{1}{2F} \frac{dP}{dt} + P &= \frac{N\mu^2 E}{kT}
\end{aligned} \tag{4.97}$$

This is a relaxation equation with characteristic relaxation time  $\tau = 1/2F$  where  $F$  is the jump probability in  $s^{-1}$ .

So, the above equation can be written as in the form of "Dipolar Polarization" by substituting  $P$  with  $P_d(t)$  and  $\mu^2/kT$  by dipolar polarizability leading to

$$\begin{aligned}
\tau \frac{dP_d}{dt} + P_d(t) &= N\alpha_s E = P_s \quad \text{OR} \\
\frac{dP_d}{dt} &= \frac{1}{\tau} (P_s - P_d(t))
\end{aligned} \tag{4.98}$$

Similar derivation can also be found in the Section 5.5 of the Chapter 5 of "Principles of Electronic Ceramics" by L.L. Hench and J.K. West.



### 4.8.2 Solution of relaxation equations

The initial and final conditions are

$$\text{At } t = 0, P_d = 0 \text{ and at some reasonably large } t, P = P_s$$

Integrating within these limits yield

$$P_d = P_s \left( 1 - \exp(-t/\tau) \right) \quad (4.99)$$

where  $t$  is defined as relaxation time.

Application of alternating fields to this polarization is not as simple as in the previous analysis

This is because the saturation polarization,  $P_s$ , is dependent on the instantaneous value of field and thus will be time-dependent and the local field is a function of both position and time.

In any case, if we assume that polarizing field is expressed as  $E^* = E_0 \exp(i\omega t)$  then  $P_s$  can be expressed as

$$P_s = (\epsilon'_{rs} - \epsilon'_{r\infty}) \epsilon_0 E^* \quad (4.100)$$

Here, we can define  $\epsilon'_{rs}$  as static dielectric constant or dielectric constant at very low frequencies and  $\epsilon'_{r\infty}$  is dielectric constant at high frequencies covering electronic and ionic polarization. This kind of makes sense because dipolar polarization occurs between these two ends of the frequency.

Now, substitute  $E^*$  and  $P_s$  into (4.98)

$$\frac{dP_d}{dt} = \frac{1}{\tau} [(\epsilon'_{rs} - \epsilon'_{r\infty}) \epsilon_0 E_0 \exp(i\omega t) - P_d(t)] \quad (4.101)$$

The integration of this equation yields us

$$P_d = C \cdot \exp\left(-\frac{t}{\tau}\right) + \frac{\epsilon'_{rs} - \epsilon'_{r\infty}}{1 + i\omega\tau} \cdot \epsilon_0 E^* \quad (4.102)$$

Here the first term is the transient time dependent term depicting decay of the *d.c.* charges on the capacitor and second term is the *a.c.* behavior of the polarization under an alternating field.

Since, electronic and ionic polarization are approximately frequency independent in this regime of frequencies, we can write

$$\epsilon_r^* - \epsilon'_{r\infty} = \frac{P_d}{\epsilon_0 E^*} \quad (4.103)$$

Now ignoring the transient time dependent term of (4.95) and substituting (4.96) into (4.94), we get

$$\epsilon_r^s = \epsilon_{r\infty}' + \frac{\epsilon_{rs}' - \epsilon_{r\infty}'}{1 + i\omega\tau} \quad (4.104)$$

We also know that  $\epsilon_r^* = \epsilon_r' - i\epsilon_r''$ , hence, now we can separate the real and imaginary parts as

$$\epsilon_r' - i\epsilon_r'' = \epsilon_{r\infty}' + \frac{\epsilon_{rs}' - \epsilon_{r\infty}'}{1 + i\omega\tau} \quad \text{OR}$$

$$\epsilon_r' = \epsilon_{r\infty}' + \frac{\epsilon_{rs}' - \epsilon_{r\infty}'}{1 + \omega^2\tau^2} \quad (4.105a)$$

$$\epsilon_r'' = \frac{\omega\tau}{1 + \omega^2\tau^2} (\epsilon_{rs}' - \epsilon_{r\infty}') \quad (4.105b)$$

and the loss tangent is

$$\tan \delta = \frac{\epsilon_r''}{\epsilon_r'} = \frac{(\epsilon_{rs}' - \epsilon_{r\infty}')\omega\tau}{\epsilon_{rs}' + \epsilon_{r\infty}'\omega^2\tau^2} \quad (4.106)$$

The above equations are called Debye equations.

The graphical representation of these is shown below:

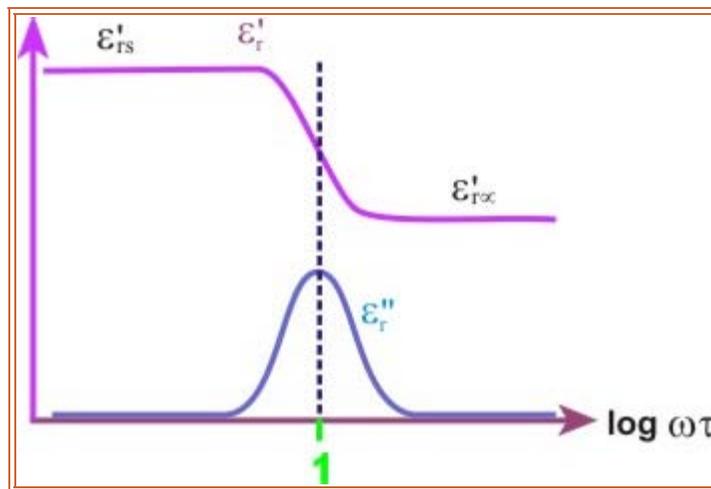


Figure 4.24 Graphical representation of Debye equations

Here, the relaxation frequency  $\omega_r$  is defined as inverse of the relaxation time *i.e.*  $1/\tau$ .

The equation (4.98) and the above figure suggest that  $\epsilon_r'$  is independent of frequency at values corresponding to the sum of three polarizations *i.e.*  $P_d + P_i + P_e$ . As the applied field frequency approaches value  $\omega = 1/\tau$ ,  $\epsilon_r'$  passes an inflection and then drops off to  $\epsilon_{r\infty}'$  which is dependent only on  $(P_i + P_e)$ .

At  $\omega = 1/\tau$ , the oscillating charges are coupled with the applied field and absorb maximum energy

as depicted by the peak in  $\epsilon_r''$  magnitude of  $\epsilon_r''$  peak being  $(\epsilon_{rS}'' - \epsilon_{r8}'')/2$  depending upon the number of oscillating charges and distance of motion.

It is also seen that  $\tan \delta$  is also goes than a maximum, but at higher frequencies with  $\omega = (\epsilon_{rS}' / \epsilon_{r8}')^{1/2} / t$ .

Now since, we have understood that polarization develops by temperature dependent diffusional processes which also give rise to the *d.c.* conductivity, temperature dependence of the relaxation time,  $t$  can be expressed as

$$\tau = \tau_0 \cdot \exp\left(\frac{Q_a}{kT}\right) \quad (4.107)$$

where  $Q_a$  is the activation energy for dipole relaxation and  $t_0$  is the intrinsic relaxation time.

Combining Debye equations with (4.99) we can obtain the frequencies ( $= \omega t$ ) at which maxima for  $\epsilon_r''$  as well as  $\tan \delta$  occur and you will that these frequencies for the maxima change with temperature because  $t$  is temperature dependent. The plots below show this trend for  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  glass ceramic.

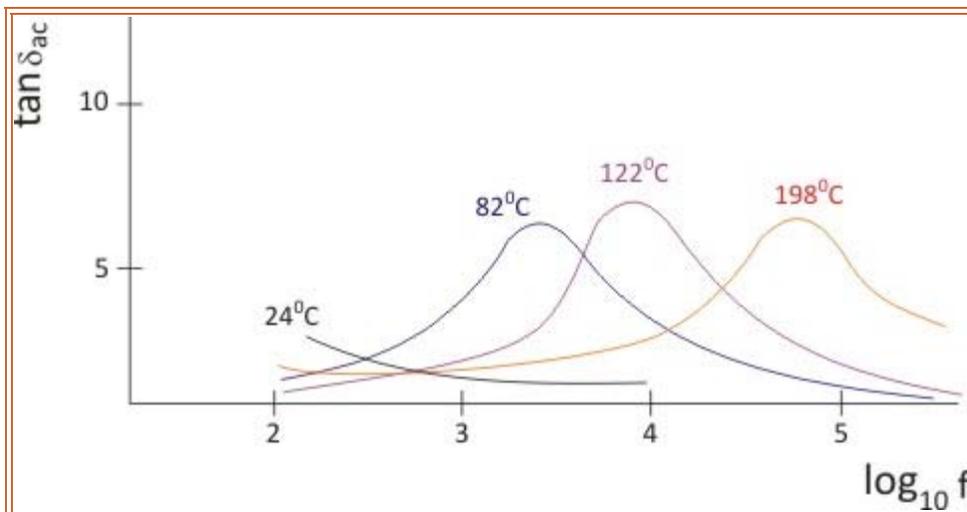


Figure 4.25 Shift of  $\tan \delta$  peak in  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  glass due to increasing temperature (Reproduced from Principle of Electronic Ceramics, L.L. Hench & J.K. West, P206)



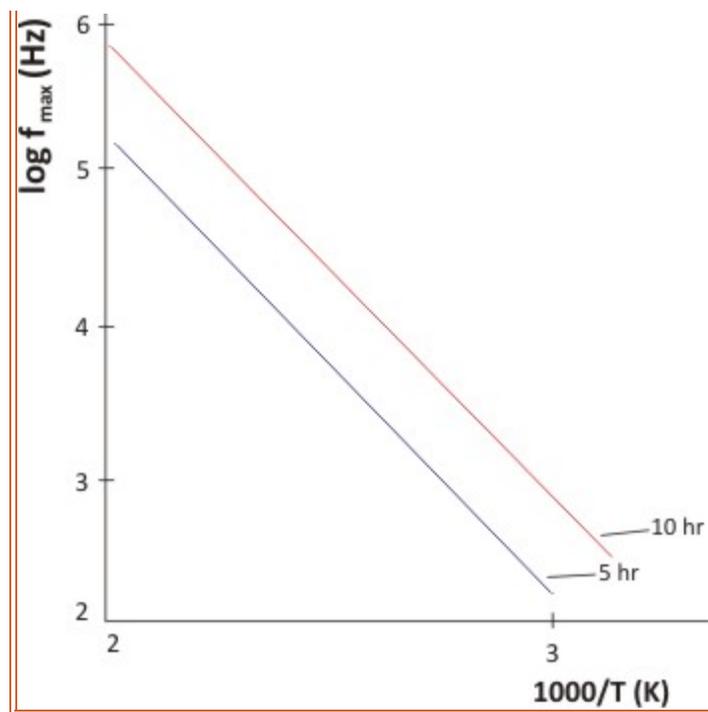


Figure 4.26 Temperature dependence of the frequency maxima **vs** time for  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  glass at  $500^\circ\text{C}$   
(Reproduced from Principle of Electronic Ceramics, L.L. Hench & J.K. West, P207)

### 4.8.3 Complete Picture of Frequency Dependence of the Dielectric Constant

So, now we can plot the contributions to the dielectric constant from all the mechanisms.

In case of an ideal dielectric material exhibiting all four basic mechanisms, we would expect the following curve.

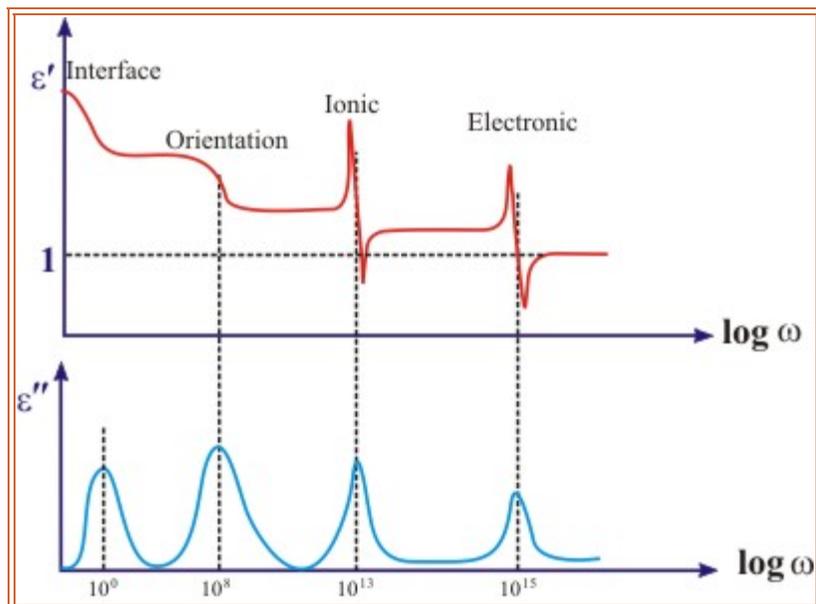


Figure 4.27 Complete plot of frequency dependence of dielectric constant and loss (note that frequency is not to scale)

Although the above plot represents an ideal material, yet the plot gives an idea of what you might expect when you measure dielectric constant of a material as a function of frequency.

Although the real plots may look quite different (look for dielectric constant data for electronic ceramics in journal publications), you can expect a correlation between the real and imaginary part of the curve i.e. we can still clearly see the absorption peak.

As, mentioned earlier, for a non-magnetic dielectric solid, Maxwell's electromagnetic equations predicts that  $\epsilon_r$  be equal to  $n^2$ .

## Module 4: Dielectric Ceramics: Basic Principles

### Summary

#### Summary

We looked at the frequency dependence of all three polarization mechanisms. For electronic and ionic polarizations, we described charges as linear harmonic oscillators and solved the equation of motion in an alternating field. We see that for both these mechanisms, there is a characteristic frequency,  $\omega_0$ , where resonance occurs and the loss is maximum. These mechanisms contribute only when the applied frequency is lower than this characteristic frequency. On the other hand, the scenario for dipolar polarization is depicted by Debye relaxation where inflection in the dielectric constant occurs at a frequency  $\omega = 1/\tau$  which is accompanied by a maxima in  $\epsilon''$ . This maxima is also a function of temperature in many dielectric ceramics.

Next, we will see the circuit representation of dielectric materials which is very important for their characterization and understanding of various phenomena.



## 4.9 Circuit Representation of a Dielectric and Impedance Analysis

Data analysis after dielectric characterization often requires modeling of dielectrics which is helped by their representation as equivalent electrical circuits. Incidentally, a perfect dielectric material can be modeled by an equivalent RC parallel circuit as shown below.

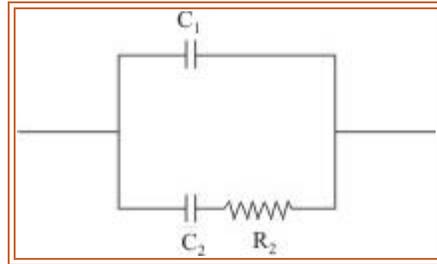


Figure 4.28 Equivalent circuit model of a dielectric

Let us consider the admittance ( $Y$ ) of the material representing the above circuit which is inverse of the impedance ( $Z$ ), and is expressed as

$$Y = \frac{1}{Z} = \frac{1}{Z_1} + \frac{1}{Z_2} \quad (4.108)$$

$$\text{where } Z_1 = \frac{1}{i\omega C_1} \text{ and } Z_2 = \frac{1}{i\omega C_2} + R_2 \quad (4.109)$$

Hence admittance now is

$$Y = i\omega C_1 + \frac{1}{R_2 + \frac{1}{i\omega C_2}} \quad (4.110)$$

Now if we consider time constant for the segment  $R_2C_2$  as  $t_2 = R_2C_2$ , then admittance can be written as

$$\begin{aligned} Y &= i\omega C_1 + \frac{C_2}{\tau_2 + \frac{1}{i\omega}} \\ &= \frac{\omega^2 \tau_2 C_2}{1 + \omega^2 \tau_2^2} + i\omega \left( C_1 + \frac{C_2}{1 + \omega^2 \tau_2^2} \right) \end{aligned} \quad (4.111)$$

Now, since admittance can be related to the dielectric constant as

$$(4.112)$$

$$Y = \frac{1}{Z} = (\varepsilon'' + i\varepsilon') \frac{\omega C_0}{\varepsilon_0} = (\varepsilon_r'' + i\varepsilon_r') \omega C_0$$

This gives

$$\varepsilon_r'' = \frac{C_2}{C_0} \cdot \frac{\omega\tau_2}{1 + \omega^2\tau_2^2} \text{ and } \varepsilon_r' = \frac{C_1}{C_0} + \frac{C_2}{C_0} \cdot \frac{1}{(1 + \omega^2\tau_2^2)} \quad (4.113)$$

which have the same form as Debye equations with  $C_2 = (\varepsilon_s - \varepsilon_\infty) C_0$  and  $C_1 = \varepsilon_\infty$ .

In 1941, K.S. Cole and R.H. Cole explained the behavior of dielectrics in alternating fields in which they plotted the electrical response of dielectric materials to the alternating fields as a function of frequency.

By this technique, they were able to identify and relate the observed relaxation effect with the atomic and microstructural features of the materials.

However, Cole and Cole used modified Debye equation which is

$$\frac{\varepsilon_r'' - \varepsilon_{r\infty}''}{\varepsilon_r' - \varepsilon_{r\infty}'} = \frac{1}{(1 + i\omega\tau)^{1-\alpha}} \quad (4.114)$$

where  $\alpha$  is a parameter which describes the distribution of relaxation times in the material.

For an ideal dielectric with well defined relaxation time i.e.  $\alpha = 0$ , the system would be represented by the Debye equations i.e. equations (4.104-4.106).

As a result, if we plot  $\varepsilon_r''(\omega)$  vs  $\varepsilon_r'(\omega)$  i.e. imaginary vs real part of the dielectric constant on a complex plane, we get a semi-circle.



## 4.10 Impedance Spectroscopy

The frequency response of the impedance of above circuit would also yields a semi-circle in the complex plot between real and imaginary parts of the dielectric constant and such a response represent a capacitor with losses. Such technique of characterizing dielectrics is called Impedance Spectroscopy.

The intercepts of the semi-circle on the x-axis represent high and low frequency dielectric constants or  $\epsilon_{r\infty}'$  and  $\epsilon_{rs}'$  respectively.

The maxima of the semi-circle occurs at

$$\omega\tau = 1 \text{ or } \omega R_2 C_2 \quad (4.115)$$

The semicircle equation turns out to be

$$(\epsilon_r'(\omega) - \frac{1}{2}(\epsilon_{rs}' + \epsilon_{r\infty}')) + \epsilon_r''(\omega)^2 = \frac{1}{4}(\epsilon_{rs}' - \epsilon_{r\infty}')^2$$

which can be obtained by removing  $\omega\tau$  from the equations (4.105a) and (4.105b).

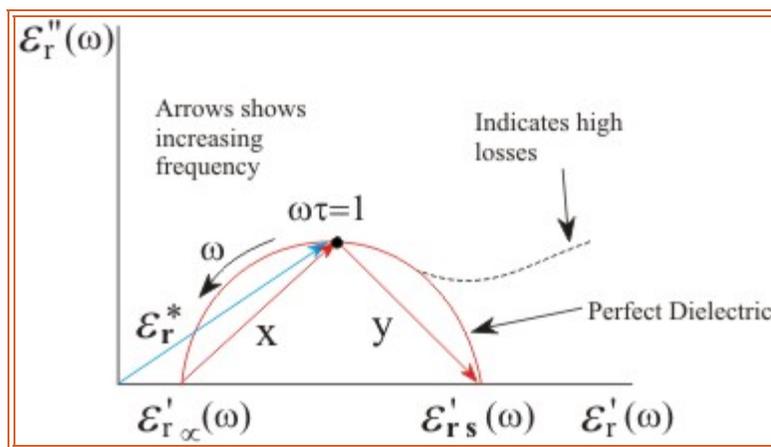


Figure 4.29 Cole-Cole Plot

Alternatively in a semi-circle one can draw two vectors, X and Y which are always perpendicular to each other and are related as  $y = -i\omega t.x$ . This relation can easily be obtained just by using the Debye's equation (4.98) and simple vector additions and subtractions.

Basically any point on the surface of the semi-circle of diameter  $(\epsilon_{rs}' - \epsilon_{r\infty}')$  in this complex plane can be defined by these vectors.

In the figure above, a perfect semicircle represents a narrow distribution of relaxation times indicating only one primary mechanism of polarization.

However, if there is the presence of a tail on the low frequency side, as shown by dashed line i.e.

increasing  $\epsilon_r''$ , indicates large distribution of relaxation times and usually is due to high losses in the material.

In case a material has more than one contribution to the impedance, which is often the case with polycrystalline ceramics where grain, grain boundaries and electrode-ceramic interface have distinct contributions, then one can witness more than one semi-circle, often overlapping each other. An idealized picture of such a scenario can be seen below. One of the ways to model such a behavior may be using three series-parallel RC elements circuit as shown below.

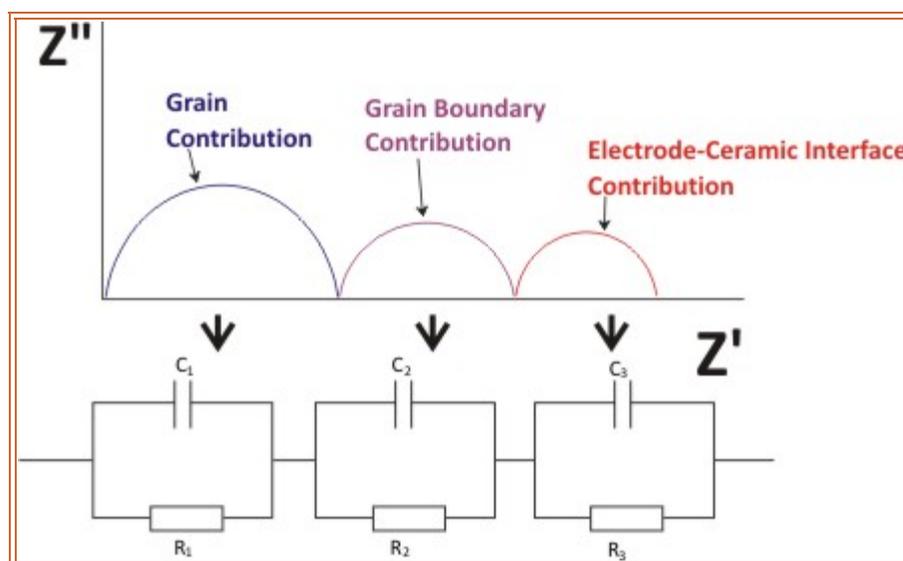


Figure 4.30 Cole-Cole Plot and possible equivalent circuit for a solid with multiple polarization mechanisms

## 4.11 Dielectric Breakdown

Every material is bound to fail or breakdown under certain conditions. Basically, in case of a dielectric it means short circuiting across the dielectric.

Technically speaking, dielectric breakdown occurs when the electron density in the conduction band becomes very high during the application of an electric field such that conductivity increases rapidly resulting in a permanent damage to material. However, it is easier to measure and talk in terms of the electric current which is anyway a representation of electron density.

The most critical parameter is the field strength  $E$  in the dielectric. If it exceeds a critical limit, breakdown occurs. The (DC) current vs. field strength characteristic of a dielectric therefore may look like this:

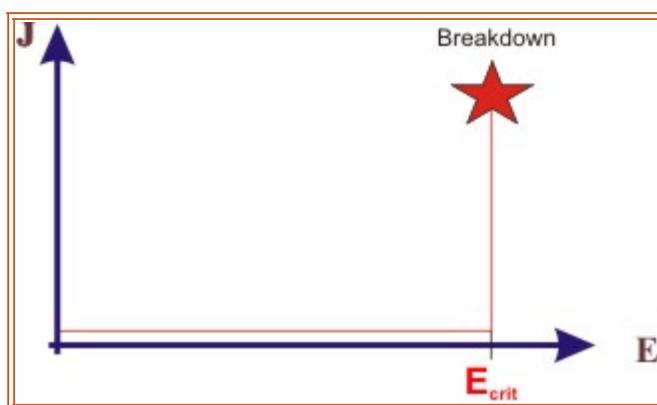


Figure 4.31 Dielectric breakdown I-V Plot

After reaching a critical field or breakdown field,  $E_c$ , a sudden increase in the current may, within a few seconds or even quicker, completely destroy the dielectric resulting in something like a 'burnt' material.

However,  $E_c$  is not a well defined material property, it depends on many parameters such as material thickness (bulk or thin film), temperature, atmosphere, level of porosity, crystalline anisotropy, level of crystallinity and composition.

While electric field plays an important role, dielectric may also break in a gradual time dependent manner and in such cases we would rather call it as 'failure'. In such situation, the field may be well below the nominal breakdown or critical field and material is destroyed in long time. In such cases, normally the breakdown field also decreases with time.

In such cases, the breakdown may not be sudden, rather a leakage current develops which increases over time, and it may develop until it suddenly increases leading to complete failure. You can do this measurement rather easily by letting a small current pass through the samples and then monitor the voltage needed as a function of time. You will notice that the voltage needed to pass this current reduces as time progresses indicating that materials is getting leakier.

A typical voltage-time curve may then look like this:



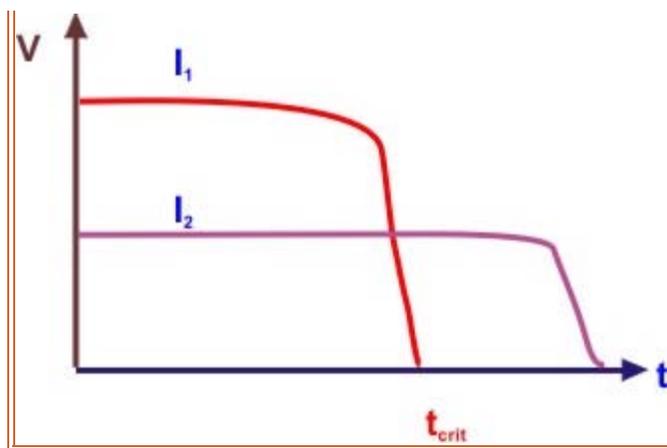


Figure 4.32 Time dependent failure for a dielectric

The values of breakdown fields for some materials are given below:

| Material                                     | Critical Field Strength [kV/cm] |
|--|---------------------------------|
| Oil  | 200                             |
| Glass, ceramics                              | 200-400                         |
| Mica   | 200-700                         |
| Oiled paper                                  | 1800                            |
| Polymers                                     | 50-900                          |
| Al <sub>2</sub> O <sub>3</sub> film (100 nm) | 16,000                          |
| Al <sub>2</sub> O <sub>3</sub> ceramic       | 200-300                         |
| BaTiO <sub>3</sub> (bulk single crystal)     | 300                             |
| BaTiO <sub>3</sub> (Polycrystalline ceramic) | 120                             |
| SiO <sub>2</sub> (in Integrated circuits)    | > 10,000                        |

#### Example:

For example, in thin film memory devices, SiO<sub>2</sub> is used as a gate dielectric and has a thickness of a few nanometers say 5 nm. The voltages at which these devices operate are about 5 V which translates into a field of 10 MV/cm which is a very large field when compared to break down fields of most of the bulk materials. This explains the importance of material form on the breakdown field.

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## 4.12 Basic mechanisms of breakdown

- Intrinsic breakdown
- Thermal breakdown
- Avalanche breakdown

### 4.12.1 Intrinsic Breakdown

- This mechanism is based on lattice ionization and subsequent increase in the electron temperature.
- Actual breakdown field is larger than critical breakdown field,  $E_c$ , needed to cause a critical breakdown electron temperature,  $T_c$ .
- This mechanism is field dependent and here applied field determines the electron temperature to reach critical level for breakdown
- The break time is very short, smaller than ms, suggesting that the process is electronic in nature.
- It is independent of sample or its geometry or waveform type.
- It is a purely material dependent process.

### 4.12.2 Thermal Breakdown:

- It occurs due to heat dissipation in the sample due to current flowing through defective parts of the sample which in turn further increase the ionic defect concentration leading to subsequent increase in the conductivity and then failure.
- It is a very common process in most of the bulk materials.
- It depends on the speed of application of field.
- It is observed between room temperature and 300°C.
- Ambient temperature determines the electron temperature and not the electric field strength.
- Rate of application of field is an important factor.
- The process can be quite slow, from minutes to ms, and is dependent on sample geometry
- The shorter the pulse time is, the higher is the breakdown voltage.

### 4.12.3 Avalanche Breakdown

- Large electric field in the samples lead to energetic electrons which can further lead to a multiplication process *i.e.* a few electrons knock out more and more electrons leading to a large increase in the conductivity.

- There is a gradual build up of charge rather than sudden change in conductivity even though charge build up can be quite fast.
- Quite often it occurs in thin films.
- It occurs at low temperature and in short time.

## Other or Pseudo breakdown mechanisms are

- Dielectric discharge
- Electrochemical and/or mechanical breakdown

### Dielectric discharge

- In small pores which are always present in sintered dielectric ceramics, the field strength is higher than the average field and as a result, microscopic arc discharge in the pores may be initiated.
- Electrons and ions from the discharge bombard the inner surface and erode it. As the pores grow, the current in the arc increases leading to an increased sample temperature eventually leading to failure.

### Electrochemical breakdown

- This occurs due to transport of conducting material due to the presence of local electrochemical current paths or defect into the interior of the dielectric leading to overall increase in the sample conductivity and then failure.
- It is assisted by suitable atmospheric conditions such as humidity and pH.



## Summary

A dielectric material is characterized by parameters such as dielectric constant or dielectric permittivity which is greater than 1. Other parameters which define dielectric behaviour are dielectric susceptibility and polarization where the former shows the response of a dielectric material upon application of electric field. Polarization in dielectrics happens because of variety of reasons and is a frequency dependent phenomenon as characterized by electronic, ionic and dipolar or orientation polarizations. Application of an alternating field on real dielectrics results in real and imaginary part of dielectric constant and in a loss tangent which define the quality of a dielectric. Frequency dependence of dielectric constant is also characterized by the presence of resonance phenomenon for electronic and ionic polarization mechanisms, occurring at frequencies typically above  $10^{12}$  Hz and relaxation phenomenon for orientation or dipolar polarization in polar materials which is a typically low frequency mechanism. The frequency dependence can also be modeled by impedance spectroscopy and Cole-Cole plots which give an insight into various relaxation mechanisms in a dielectric material arising due to various microstructural features.

