Dielectric Polarization

Dielectric polarization occurs when a dipole moment is formed in an insulating material because of an externally applied electric field. When a current interacts with a dielectric (insulating) material, the dielectric material will respond with a shift in charge distribution with the positive charges aligning with the electric field and the negative charges aligning against it. By taking advantage of this response, important circuit elements such as capacitors can be made.

Introduction

Dielectric polarization is the term given to describe the behavior of a material when an external electric field is applied on it. A simple picture can be made using a capacitor as an example. The figure below shows an example of a dielectric material in between two conducting parallel plates. The charges in the material will have a response to the electric field caused by the plates.
Figure 1: The bound charges are the charges that are touching the capacitor plates, while the free charges usually float around in the material, but for this case, they are aligned with the bound charges.

Using the capacitor model, it is possible to define the relative permittivity or the dielectric constant of the material by setting its relative permittivity equivalent to the ratio of the measured capacitance and the capacitance of a test capacitor, which is also equal to the absolute permittivity of the material divided by the permittivity of vacuum.

\[ \epsilon_r = \frac{Q}{Q_0} = \frac{C}{C_o} = \frac{\epsilon}{\epsilon_0} \tag{1} \]

The dielectric constant is an important term, because another term known as the electronic polarizability or \( \alpha_e \) can be related to the dielectric constant. The electronic polarizability is a microscopic polarization phenomena that occurs in all materials and is one of the main mechanisms that drives dielectric polarization.

To explain how the dielectric constant relates to the electronic polarizability of a material, the polarization or \( P \) of a material should be determined. The polarization of a material is defined as the total dipole moment per unit volume, and its equation is,

\[ P = N \alpha_e E = \chi_e \epsilon_0 E \tag{2} \]

where the \( \chi \) term is known as the electric susceptibility of the material given by the equation \( \chi = \epsilon_r - 1 \). Then, from substituting \( \epsilon_r - 1 \) for \( \chi \), an equation relating the relative permittivity and the electronic polarizability is determined. \( \epsilon_r = 1 + \frac{N\alpha_e}{\epsilon_0} \) where \( N \) is the number of molecules per unit volume.

While this equation does relate the dielectric constant with the electronic polarizability, it only represents the material as a whole, and does not take into effect the local field, or the field experienced by a molecule in a dielectric. This field is known as the Lorentz field, and the equation to define this is given as,

\[ E_{loc} = E + \frac{1}{3\epsilon_0}P \tag{3} \]

and by substituting this value back for the field used in the previous method, the following equation is determined...
This equation is known as the **Clausius-Mossotti equation** and is the way to interchange between the microscopic property of electronic permittivity and the dielectric constant. In addition to knowing the electronic polarizability of a material, there are also other sub-factors, such as chemical composition and bond type that determine the total dielectric behavior of a material. However, electronic polarization is always inherent in a dielectric material.

### Ionic Polarization

Ionic polarization is a mechanism that contributes to the relative permittivity of a material. This type of polarization typically occurs in ionic crystal elements such as NaCl, KCl, and LiBr. There is no net polarization inside these materials in the absence of an external electric field because the dipole moments of the negative ions are canceled out with the positive ions. However, when an external field is applied, the ions become displaced, which leads to an induced polarization. Figure 2 shows the displacement of ions due to this external electric field.

![Figure 2: The effect of an external electric field on an ionic material. The positive charges will flow with the field and the negative charges will flow against the field, causing a net average dipole moment per ion to form.](https://eng.libretexts.org/Bookshelves/Materials_Science/Supplemental_Modules_(Materials_Science)/Optical_Properties/Diel…)

The equation to describe this effect is given by,

$$P_{av} = \alpha_i E_{loc} \tag{5}$$

Where $P_{av}$ is the induced average dipole moment per ion pair, $\alpha_i$ is the ionic polarizability, and $E$ is the local electric field experienced by the pair of ions. Usually the ionic polarizability is greater than the electronic polarizability by a factor of 10 which leads to ionic substances having high dielectric constants. Similar to electronic polarization, ionic polarization also has a total polarization associated with it. The equation is given by

$$P = N_i P_{av} = N_i \alpha_i E_{loc} \tag{6}$$

which will also lead to a **Clausius-Mossotti equation** for ionic polarization,

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3 \epsilon_0} N_i \alpha_i \tag{7}$$

Note that these equations assume that there is a charge balance inside the ionic material (eg. NaCl) whereas if a charge imbalance is present, such as in materials like CaF$_2$, a different set of equations must be used.
Orientational Polarization

Orientational polarization arises when there is a permanent dipole moment in the material. Materials such as HCl and H₂O will have a net permanent dipole moment because the charge distributions of these molecules are skewed. For example, in a HCl molecule, the chlorine atom will be negatively charged and the hydrogen atoms will be positively charged causing the molecule to be dipolar. The dipolar nature of the molecule should cause a dipole moment in the material, however, in the absence of an electric field, the dipole moment is canceled out by thermal agitation resulting in a net zero dipole moment per molecule. When an electric field is applied however, the molecule will begin to rotate to align the molecule with the field, causing a net average dipole moment per molecule as shown in figure 4.

Figure 3: The effect of an electric field on a typical dipolar molecule. P₀ symbolizes the dipole moment, a is the distance away from the body center of the molecule and F is the force, which is the charge Q, times the electric field, E.

Figure 4: The figure shows how thermally agitated molecules (left) can be made to produce a net dipole moment per ion in the material with an externally applied field (right).

To determine if the induced average dipole moment along the electric field, the average potential energy of the dipole must be calculated and compared to the the average thermal energy \(\frac{1}{5} kT\), as determined by thermodynamics for five degrees of freedom. To accomplish this, Force F on figure 3 can be seen as a torque \(\tau\) acting on the rigid body of the dipolar molecule. Using this model, the equation for the torque is given by

\[
\tau = (F \sin \theta) a = EP_0 \sin(\theta) \tag{8}
\]

where \(P_0\) is given by \(P_0 = aQ\). From this equation the maximum potential energy can be calculated by taking the integral at the instant of maximum torque. This maximum potential energy is calculated out to be \(2P_0 E\) which then means that the average dipole potential energy is \(\frac{1}{2} E_{max}\) or \(\frac{1}{2} P_0E\). Once knowing the average dipole...
potential energy, it is then possible to calculate the average dipole moment $P_{av}$ through Boltzmann's statistics, which would lead to the answer,

$$P_{av} = \frac{P_0^2 E}{3kT} \tag{9}$$

This then, leads to the dipolar orientational polarizability, $\alpha_d$ per molecule, which is shown by the equation,

$$\alpha_d = \frac{P_0^2}{3kt}$$

The equation for orientational polarizability shows, that unlike electronic polarizability and ionic polarizability, orientational polarizability is temperature dependent. This is an important factor to consider when choosing a dielectric material for electronic and optical applications.

### Interfacial Polarization

Interfacial or space charge polarization occurs when there is an accumulation of charge at an interface between two materials or between two regions within a material because of an external field. This can occur when there is a compound dielectric, or when there are two electrodes connected to a dielectric material. This type of electric polarization is different from orientational and ionic polarization because instead of affecting bound positive and negative charges i.e. ionic and covalent bonded structures, interfacial polarization also affects free charges as well. As a result interfacial polarization is usually observed in amorphous or polycrystalline solids. Figure 5 shows an example of how free charges can accumulate in a field, causing interfacial polarization. The electric field will cause a charge imbalance because of the dielectric material’s insulating properties. However, the mobile charges in the dielectric will migrate over maintain charge neutrality. This then causes interfacial polarization.

![Figure 5: This shows how the free positive charges inside the dielectric material migrate towards the negative charge build-up on the right, caused by the external electric field.](image)

The equation to show the space charge polarizability constant is $\alpha_c = \alpha - \alpha_{\infty} - \alpha_0$ where $\alpha_{\infty}$ is the space charge polarizability and $\alpha_0$, $\alpha_{\infty}$, and $\alpha_0$ refer to the total, electronic, and orientational polarizations respectively. It is important to note that because the charges are free charges, defects such as grain boundaries or other interfaces can serve as a medium for interfacial polarizability to form.
From the equation of space charge polarization, it is then determined that the total amount of dielectric polarization in a material is the sum of the electronic, orientational, and interfacial polarizabilities, or \( \alpha = \alpha_c + \alpha_{\infty} + \alpha_0 \).

Questions

1. What is a stronger contributor to total polarization in a balanced ionic material (i.e. KCl). ionic polarization or electronic polarization?
2. What is the absolute permittivity of Teflon when it has a dielectric constant of 2.1 at room temperature under 1kHz?
3. Calculate the total polarizability in a material when the ionic polarizability is 0, the orientational polarizability is 15 cm\(^2\), and the interfacial polarization is 3 cm\(^2\)?

Answers

1. Ionic polarization is stronger by about factor of 10 compared to electronic polarization for balanced ionic structures.
2. \( \varepsilon_r = \varepsilon/\varepsilon_0 \) so the answer is 2.1.
3. \( 5 + 3 = 18 \), so 18 cm\(^2\).

Additional Links

- [1] http://chemwiki.ucdavis.edu/Physical...Polarizability

References


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