

Chapter 6

Dielectrics and Polarization

6.1 Polarization in Dielectric Materials

Dielectric materials can exist in various phases, including gases, liquids, and solids, each with unique properties. These materials may or may not possess intrinsic dipole moments, depending on the molecular structure. For instance, some materials are composed of polar molecules, which inherently have dipole moments, while others consist of non-polar molecules that do not exhibit such moments without external influence. A simple example can be found in gases. Gases like hydrogen (H_2) consist of non-polar molecules, meaning they lack an intrinsic dipole moment under normal conditions. On the other hand, gases like carbon monoxide (CO) are made up of polar molecules, which naturally possess a dipole moment due to the uneven distribution of charges within the molecule.

In the absence of an external electric field and under thermal equilibrium, the dipoles in a dielectric material, whether polar or non-polar, are oriented randomly. This random distribution results in the overall average dipole moment of the system being zero, represented as $\langle \vec{p} \rangle = 0$. However, when an external E-field \vec{E} is applied to the dielectric material, the situation changes. In non-polar molecules, the external field exerts forces on the opposite charges within the molecule, causing a relative displacement between them. This displacement induces a dipole moment, even though the molecule was initially non-polar. In contrast, in polar molecules, which already possess dipole moments, the electric field applies a torque that reorients the dipoles to align with the direction of the field. These effects—inducing dipoles in non-polar molecules and reorienting dipoles in polar molecules—disrupt the random distribution of dipole moments and cause them to align in a particular direction, producing a net dipole moment. As a result, the average dipole moment becomes non-zero, $\langle \vec{p} \rangle \neq 0$, indicating that the material has developed an overall polarization. Therefore, we can define an electric polarization \vec{P} as the total dipole moment per unit volume,

$$\vec{P} = n\langle \vec{p} \rangle, \quad (6.1)$$

where n is the number density of dipoles (the number of dipoles per unit volume). The polarization \vec{P} is a measure of the alignment of dipoles induced by the external electric field \vec{E} , and it reflects how strongly the material responds to the applied field \vec{E} .

If a dielectric medium has multiple different molecules, then the polarization \vec{P} can be written as,

$$\vec{P} = \sum_i n_i \langle \vec{p}_i \rangle, \quad (6.2)$$

where $\langle \vec{p}_i \rangle$ and n_i are the average dipole moment and the number density of dipoles of i th type of molecules.

Also, if each dielectric molecule has a net charge q_i and the entire dielectric materials could also have excessive or free charge, then the charge density of the dielectric material can be expressed as,

$$\rho(\vec{r}) = \sum_i n_i \langle q_i \rangle + \rho_{free}. \quad (6.3)$$

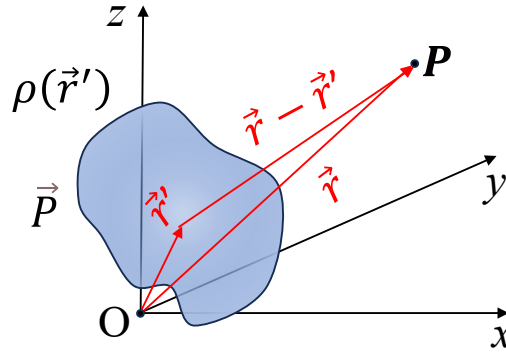


Fig. 6.1 The potential generated by a dielectric material at P .

From a microscopic point of view, for a dielectric material with charge density $\rho(\vec{r})$ and polarization \vec{P} , the electric potential generated at P location far away from the material,

$$\varphi(\vec{r}) = \frac{1}{4\pi\epsilon_0} \iiint_{V'} \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} dV' + \frac{1}{4\pi\epsilon_0} \iiint_{V'} \frac{\vec{P}(\vec{r}') \cdot (\vec{r} - \vec{r}')}{|\vec{r} - \vec{r}'|^3} dV'. \quad (6.4)$$

Thus, the total potential $\varphi(\vec{r}) = \varphi_c(\vec{r}) + \varphi_d(\vec{r})$ is due to the superposition of potential generated by the net charge ($\varphi_c(\vec{r})$) as well as net polarization ($\varphi_d(\vec{r})$) of the dielectric material.

Considering $\nabla' \frac{1}{|\vec{r} - \vec{r}'|} = \frac{(\vec{r} - \vec{r}')}{|\vec{r} - \vec{r}'|^3}$, the potential $\varphi_d(\vec{r})$ due to polarization can be rewritten as,

$$\varphi_d(\vec{r}) = \frac{1}{4\pi\epsilon_0} \iiint_{V'} \vec{P}(\vec{r}') \cdot \nabla' \frac{1}{|\vec{r} - \vec{r}'|} dV'.$$

Using the equality $\nabla' \cdot (f\vec{C}) = f\nabla' \cdot \vec{C} + \vec{C} \cdot \nabla' f$, we have

$$\vec{P}(\vec{r}') \cdot \nabla' \frac{1}{|\vec{r}-\vec{r}'|} = \nabla' \cdot \frac{\vec{P}(\vec{r}')}{|\vec{r}-\vec{r}'|} - \frac{1}{|\vec{r}-\vec{r}'|} \nabla' \cdot \vec{P}(\vec{r}').$$

Therefore,

$$\begin{aligned} \varphi_d(\vec{r}) &= \frac{1}{4\pi\epsilon_0} \iiint_{V'} \left[\nabla' \cdot \frac{\vec{P}(\vec{r}')}{|\vec{r}-\vec{r}'|} - \frac{1}{|\vec{r}-\vec{r}'|} \nabla' \cdot \vec{P}(\vec{r}') \right] dV' \\ &= \frac{1}{4\pi\epsilon_0} \iiint_{V'} \nabla' \cdot \frac{\vec{P}(\vec{r}')}{|\vec{r}-\vec{r}'|} dV' - \frac{1}{4\pi\epsilon_0} \iiint_{V'} \frac{\nabla' \cdot \vec{P}(\vec{r}')}{|\vec{r}-\vec{r}'|} dV'. \end{aligned} \quad (6.5)$$

By applying the Gauss's theorem for the first volume integration in **Equation 6.5**, we have

$$\varphi_d(\vec{r}) = \frac{1}{4\pi\epsilon_0} \oiint_{S'} \frac{\vec{P}(\vec{r}'_s)}{|\vec{r}-\vec{r}'_s|} \cdot d\vec{S}' - \frac{1}{4\pi\epsilon_0} \iiint_{V'} \frac{\nabla' \cdot \vec{P}(\vec{r}')}{|\vec{r}-\vec{r}'|} dV'. \quad (6.6)$$

There are two contributions to $\varphi_d(\vec{r})$: a surface integration and a volume integration. Compare these expressions to **Equations 3.13** and **3.14**, we find that $\vec{P}(\vec{r}') \cdot \hat{n}$ has the unit of surface charge density, while $\nabla' \cdot \vec{P}(\vec{r}')$ mimics the bulk charge density. Thus, we define surface polarization charge density σ_p as,

$$\sigma_p = \vec{P} \cdot \hat{n}, \quad (6.7)$$

And bulk polarization charge density ρ_p ,

$$\rho_p = -\nabla \cdot \vec{P}. \quad (6.8)$$

Therefore, $\varphi_d(\vec{r})$ can be rewritten as,

$$\varphi_d(\vec{r}) = \frac{1}{4\pi\epsilon_0} \oiint_{S'} \frac{\sigma_p(\vec{r}'_s)}{|\vec{r}-\vec{r}'_s|} \cdot dS' + \frac{1}{4\pi\epsilon_0} \iiint_{V'} \frac{\rho_p(\vec{r}')}{|\vec{r}-\vec{r}'|} dV'. \quad (6.9)$$

Thus, the total potential can be written as,

$$\varphi(\vec{r}) = \frac{1}{4\pi\epsilon_0} \iiint_{V'} \frac{\rho(\vec{r}') + \rho_p(\vec{r}')}{|\vec{r}-\vec{r}'|} dV' + \frac{1}{4\pi\epsilon_0} \oiint_{S'} \frac{\sigma_p(\vec{r}'_s)}{|\vec{r}-\vec{r}'_s|} \cdot dS'. \quad (6.10)$$

The corresponding electric field $\vec{E}(\vec{r})$ generated at P can be expressed as

$$\begin{aligned} \vec{E}(\vec{r}) &= -\nabla\varphi(\vec{r}) \\ &= \frac{1}{4\pi\epsilon_0} \iiint_{V'} \frac{[\rho(\vec{r}') + \rho_p(\vec{r}')](\vec{r}-\vec{r}')}{|\vec{r}-\vec{r}'|^3} dV' + \frac{1}{4\pi\epsilon_0} \oiint_{S'} \frac{\sigma_p(\vec{r}'_s)(\vec{r}-\vec{r}')}{|\vec{r}-\vec{r}'_s|^3} \cdot dS'. \end{aligned} \quad (6.11)$$

There are three contributions to the final electric field: (1) the free/excessive charges of the dielectric material; (2) the bulk polarization charges (or bounded charges) $\rho_p = -\nabla \cdot \vec{P}$; and (3) the surface polarization charges (or bounded surface charges), $\sigma_p = \vec{P} \cdot \hat{n}$.

Understanding of the bulk and surface polarization charges

To analyze the concept of bulk and surface polarization charges in a dielectric material, let us first consider a small volume element $\Delta V'$ within the dielectric. At a given location \vec{r}' , there exist two charge densities, ρ^+ and ρ^- . As shown in **Figure 6.2**, in the absence of polarization, the total charge within the volume element is neutral, which can be expressed as:

$$\rho_0^+(\vec{r}') + \rho_0^-(\vec{r}') = 0. \quad (6.12)$$

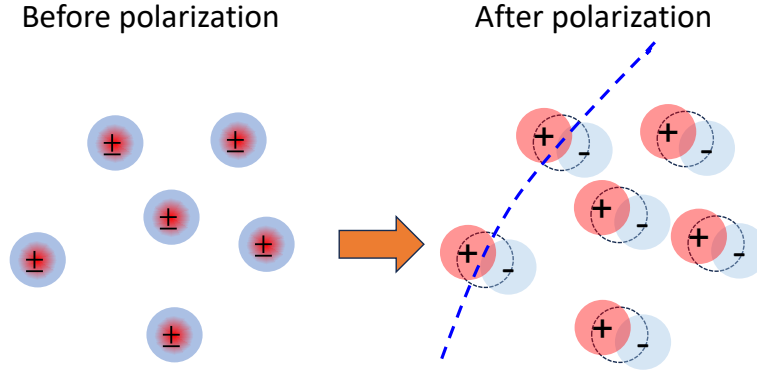


Fig. 6.2 Illustration of non-polar molecules before and after polarization.

This represents the case of non-polarized molecules. When polarization occurs, the positive charges displace by a vector $\vec{\delta}^+$ and the negative charges displace by a vector $\vec{\delta}^-$. These displacements lead to the formation of polarization charges. The positive charge displaced across an elemental surface area dS' is $\rho_0^+ \vec{\delta}^+ \cdot \hat{n} dS'$. Thus, the net gain of positive charge within the volume $\Delta V'$ is,

$$-\iint_{S'} \rho_0^+ \vec{\delta}^+ \cdot \hat{n} dS'$$

Similarly, for negative charges, the gain within the same volume is,

$$-\iint_{S'} \rho_0^- \vec{\delta}^- \cdot \hat{n} dS'$$

Applying Gauss's law, the total charge gained in the volume $\Delta V'$ due to polarization can be written as

$$-\iint_{S'} \rho_0^+ (\vec{\delta}^+ - \vec{\delta}^-) \cdot \hat{n} dS' = -\nabla \cdot [\rho_0^+ (\vec{\delta}^+ - \vec{\delta}^-)] \Delta V', \quad (6.13)$$

Here, the polarization vector \vec{P} is defined as $\vec{P} = \rho_0^+ (\vec{\delta}^+ - \vec{\delta}^-)$. Thus, the polarization charge density ρ_P is given by $\rho_P = -\nabla \cdot \vec{P}$. This indicates that ρ_P is generally non-zero within the dielectric under polarization.

The total polarization charge, including contributions from both bulk and surface regions, can be expressed as,

$$Q_P = \iiint_{V'} (-\nabla \cdot \vec{P}) dV' + \iint_{S'} \vec{P} \cdot \hat{n} dS' = 0. \quad (6.14)$$

Equation 6.14 reveals an essential property: the generation of bulk polarization charge ρ_P is inherently linked to surface polarization. Specifically, any polarization charge appearing within the bulk is balanced by an equal and opposite polarization charge on the surface of the dielectric.

6.2 Electric Displacement Field

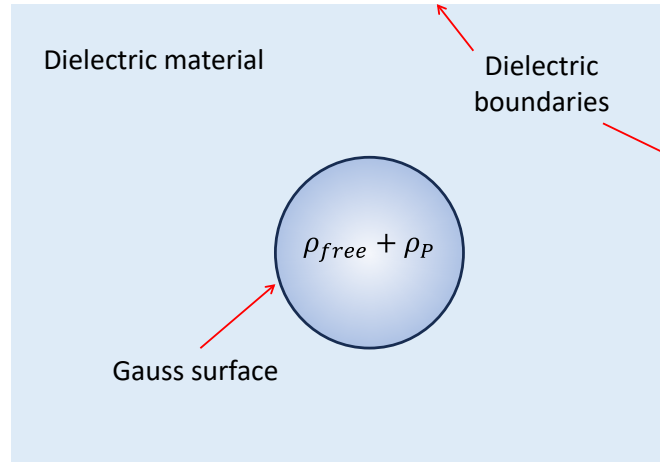


Fig. 6.3 Gauss surface inside a dielectric material.

To understand how Gauss's law is modified in the presence of a dielectric material, consider a polarized dielectric, as illustrated in **Figure 6.3**. Within such a material, the total charge density consists of two components: the free charge density and the polarization charge density. This relationship is expressed as,

$$\rho = \rho_{free} + \rho_P. \quad (6.15)$$

Here ρ_{free} is the free charge density from external sources. With polarization included, Gauss's law becomes

$$\oiint_S \vec{E} \cdot \hat{n} dS' = \frac{Q_{free} + Q_P}{\epsilon_0}. \quad (6.16)$$

In this form, the electric field \vec{E} accounts for the polarization within the dielectric. The total polarization charge Q_P enclosed by the Gauss surface can be expressed as,

$$Q_P = \iiint_{V'} \rho_P dV' = \iiint_{V'} (-\nabla \cdot \vec{P}) dV'. \quad (6.17)$$

his equation differs from earlier treatments (e.g., **Equation 6.14**) because the boundaries of the dielectric material are far away from the Gauss surface considered. Consequently, the boundary surface polarization charge does not need to be considered explicitly. Combining **Equations 6.16** and **6.17**, Gauss's law in a dielectric material becomes

$$\epsilon_0 \nabla \cdot \vec{E} + \nabla \cdot \vec{P} = \rho_{free}. \quad (6.18)$$

To simplify this relationship, we define the electric displacement field \vec{D} as,

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P}. \quad (6.19)$$

Substituting into **Equation 6.18**, we obtain

$$\nabla \cdot \vec{D} = \rho_{free}. \quad (6.20)$$

This equation reveals that the free charge density is the sole source of the displacement field \vec{D} , regardless of the material's polarization.

Since the polarization \vec{P} is induced by the electric field \vec{E} , their relationship is known as the constitutive relationship, which describes how a dielectric material interacts with an external electric field,

$$\vec{P} = \vec{P}(\vec{E}). \quad (6.21)$$

For most materials, this relationship can be expressed as

$$\vec{P} = \varepsilon_0 \chi(\vec{E}) \vec{E}, \quad (6.22)$$

where $\chi(\vec{E})$ is the electric susceptibility of the material, which measures the material's response to an electric field. The displacement field \vec{D} becomes,

$$\vec{D} = \varepsilon(\vec{E}) \vec{E} = \varepsilon_0 [1 + \chi(\vec{E})] \vec{E} = \kappa \varepsilon_0 \vec{E}, \quad (6.23)$$

where $\varepsilon(\vec{E})$ is the permittivity of the material and κ is the dielectric function (relative permittivity). For homogenous, isotropic, and linear materials, $\chi(\vec{E}) = \chi$ is constant. Thus, the Maxwell equations for electric field simplify to

$$\nabla \cdot \vec{D} = \rho_{free} \text{ and } \nabla \times \vec{E} = 0. \quad (6.24)$$

The corresponding boundary conditions at the interface of two materials become,

$$\begin{cases} (\vec{D}_2 - \vec{D}_1) \cdot \hat{n}_2 = \sigma_{free} \\ (\vec{E}_2 - \vec{E}_1) \times \hat{n}_2 = 0 \end{cases} \quad (6.25)$$

These equations ensure continuity of the normal component of \vec{D} (accounting for no free surface charges) and the tangential component of \vec{E} across the interface.

6.3 Microscopic Theory of Dielectrics

The concept of polarization in dielectric materials describes how materials respond to an external E-field by redistributing charges. However, the specific mechanisms underlying polarization depend on the material's microscopic properties. In this section, we explore three distinct microscopic polarization mechanisms, induced displacement of electrons in atoms or molecules, polarization due to displacement of ions in ionic crystals, and orientation change of permanent dipoles.

6.3.1 Displacement polarization

The first mechanism involves the displacement of electrons relative to their nuclei in response to an external electric field. This can be understood through both quantum mechanical and classical mechanical frameworks.

Quantum mechanical picture

Consider a hydrogen atom subjected to an external E-field \vec{E} . The Hamiltonian of the electron in the atom under the influence of the field can be expressed as,

$$H(\vec{r}, t) = H_0(\vec{r}, t) + H'(\vec{r}, t), \quad (6.26)$$

where $H_0(\vec{r}, t)$ is the Hamiltonian of the electron in the absence of the E-field, while

$$H'(\vec{r}, t) = e\vec{E} \cdot \vec{r} = eEz, \quad (6.27)$$

is the perturbation Hamiltonian introduced by the external field. Assuming that the eigen wavefunctions of $H_0(\vec{r}, t)$ can be written as $[nlm]$ [4.1], we denote the

ground state of the hydrogen atom as, $|100\rangle$. Based on perturbation theory, the new eigenstate under the external field becomes,

$$|\varphi\rangle = |100\rangle + \sum_{n \neq 1} \sum_{l,m} |nlm\rangle \frac{\langle nlm|H'|100\rangle}{E_1 - E_n} + \dots \quad (6.28)$$

The first-order energy perturbation is,

$$E_1^{(2)} = \langle 100|H'|100\rangle = 0. \quad (6.29)$$

The second-order energy perturbation is given by

$$E_1^{(2)} = \sum_{n \neq 1} \sum_{l,m} \frac{\langle 100|H'|nlm\rangle \langle nlm|H'|100\rangle}{E_1 - E_n}. \quad (6.30)$$

After calculation, this becomes,

$$E_1^{(2)} = -\frac{9}{4} E^2 a_B^3, \quad (6.31)$$

where E is the magnitude of the applied E-field and $a_B = \frac{4\pi\epsilon_0\hbar^2}{e^2 m_e}$ is the Bohr radius with e and m_e being the charge and mass of the electron. The induce electric dipole moment is then calculated as,

$$\bar{p}_z = \langle \varphi|(-ez)|\varphi\rangle = -\frac{2}{E} E_1^{(2)} = \frac{9}{2} E a_B^3 = \alpha \epsilon_0 E. \quad (6.32)$$

Thus, the polarizability of the hydrogen atom is,

$$\alpha = \frac{9}{2} \frac{a_B^3}{\epsilon_0}. \quad (6.33)$$

Classic mechanical picture

Alternatively, the displacement of the electron in the hydrogen atom under an external E-field can be treated using classical mechanics. The electron-nucleus system is modeled as a harmonic oscillator. The restoring force acting on the electron when displaced by $\Delta\vec{r}$ from its equilibrium position \vec{r}_0 is,

$$\vec{F} = -m_e \omega_0^2 \Delta\vec{r}, \quad (6.34)$$

where ω_0 is the intrinsic resonant frequency of the harmonic oscillator (in Quantum mechanics, such a resonance is due to the transition between two energy levels of the electron), $\omega_0 = \sqrt{k/m_e}$, with k being the spring constant associated with this resonant frequency. Under the applied E-field, the equilibrium condition requires,

$$m_e \omega_0^2 \Delta\vec{r} = e\vec{E}, \quad (6.35)$$

i.e., the extra electrostatic force on the electron caused by the external E-field is balanced by the restoring force. Therefore, the induced dipole moment \vec{p}_{ind} is then

$$\vec{p}_{ind} = e\Delta\vec{r} = \frac{e^2}{m_e \omega_0} \vec{E}. \quad (6.36)$$

From this, the polarizability is determined to be,

$$\alpha = \frac{e^2}{m_e \omega_0 \epsilon_0}. \quad (6.37)$$

Correspondence between quantum and classical theories

By comparing **Equations 6.33** and **6.37**, we have $\frac{9}{2} \frac{a_B^3}{\epsilon_0} = \frac{e^2}{m_e \omega_0 \epsilon_0}$. Thus, the Bohr radius a_B can be related to classical quantities,

$$\alpha_B = \sqrt[3]{\frac{2e^2}{9m_e\omega_0}}. \quad (6.38)$$

Polarization of a medium with multiple atoms/molecules

For a material composed of various types of atoms or molecules, the total polarization \vec{P} due to induced dipoles is,

$$\vec{P} = \sum_i^N n_i \frac{q_i^2}{m_i\omega_i} \vec{E} = \sum_i^N n_i \alpha_i \epsilon_0 \vec{E}, \quad (6.39)$$

where n_i , m_i , q_i , ω_i , and α_i are the number density, reduced electron mass, electron charge, resonant frequency, and polarizability of the i -th species, respectively. Using **Equation 6.22**, the electric susceptibility $\chi(\vec{E})$ can be expressed as,

$$\chi(\vec{E}) = \sum_i^N n_i \alpha_i. \quad (6.40)$$

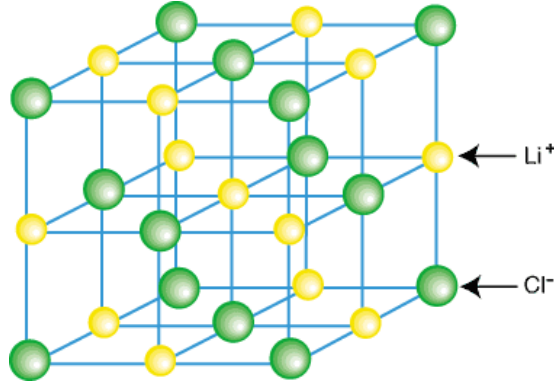


Fig. 6.4 A representative ionic crystal structure.

6.3.2 Induced polarization in an ionic crystal

In ionic crystals, such as NaCl or LiCl, positive and negative ions are arranged in specific lattice sites, forming a repeating crystal structure. The polarization in these materials arises from the displacement of ions under an external electric field. This section explores the mechanisms of induced polarization in ionic crystals and its dependence on electrostatic interactions, lattice structure, and external forces.

Each ion in an ionic crystal experiences electrostatic interactions with its surrounding ions. Taking a single ion as a reference point, the interactions include:

- n_1 nearest neighbor with opposite charges,
- n_2 2nd-nearest neighbors with the same charge,
- n_3 3rd-nearest neighbors with opposite charges, and so on.

The electrostatic energy for the reference ion can be written as,

$$u_E = -n_1 \frac{q^2}{4\pi\epsilon_0 r} + n_2 \frac{q^2}{4\pi\epsilon_0 a_2 r} - n_3 \frac{q^2}{4\pi\epsilon_0 a_3 r} + \dots, \quad (6.41)$$

where r is the lattice constant (distance between adjacent ions), $a_i r$ is the distance to the i -th nearest neighbor, and q is the charge of the ion. Simplify **Equation 6.41**, the electrostatic energy becomes

$$u_E = -\frac{q^2}{4\pi\epsilon_0 r} \left[n_1 - \frac{n_2}{a_2} + \frac{n_3}{a_3} - \frac{n_4}{a_4} \dots \right] = -M \frac{q^2}{4\pi\epsilon_0 r}. \quad (6.42)$$

The term $M = n_1 - \frac{n_2}{a_2} + \frac{n_3}{a_3} - \frac{n_4}{a_4} \dots$ is called the Madelung constant [4.2], which depends solely on the crystal structure and geometry of the lattice.

Example: Madelung constant for NaCl

In NaCl, the lattice is cubic, and the values of n_i and i for the first few neighbors are,

- $n_1 = 6, n_2 = 12, n_3 = 8, n_4 = 6, \dots$,
- $a_2 = \sqrt{2}, a_3 = \sqrt{3}, a_4 = 2, \dots$

the Madelung constant for NaCl is $M = 1.748$. **Table 6.1** summarizes the M values for some typical crystal structures.

Table 6.1 A summary of Madelung constant for different lattice structures.

Lattice Structure	Representative Material	M
Cubic	NaCl	1.7475
Cubic	CsCl	1.7626
Zinc Blende	ZnS	1.6838
Wurtzite	FeS	1.6410
Fluorite	CaF ₂	2.5190
Rutile	TiO ₂	2.4080
Corundum	V ₂ O ₃	4.1719

For a lattice with NNN-pairs of ions, the total electrostatic energy is,

$$U_E = Nu_E = -NM \frac{q^2}{4\pi\epsilon_0 r}. \quad (6.43)$$

When the crystal is compressed, the electron clouds of nearby ions overlap, generating a repulsive force due to the Pauli exclusion principle. The corresponding repulsive energy can be expressed as,

$$U_p = \frac{B}{r^n}. \quad (6.44)$$

The total energy of the crystal is then,

$$U(r) = U_E + U_p = \frac{B}{r^n} - NM \frac{q^2}{4\pi\epsilon_0 r}. \quad (6.45)$$

At equilibrium, the total energy $U(r)$ is minimized, which occurs when $\frac{dU(r)}{dr} = 0$. Solving this yields the equilibrium energy,

$$U(r_0) = -NM \frac{q^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right). \quad (6.46)$$

The constant B can also be expressed in terms of equilibrium parameters,

$$B = \frac{NM r_0^{n-1}}{4\pi n \epsilon_0}. \quad (6.47)$$

When an external E-field is applied, the lattice constant deviates slightly from its equilibrium value r_0 . The interaction energy of a single ion becomes,

$$u(r) = \frac{U(r)}{N} = -\frac{Mq^2}{4\pi\epsilon_0} \left(\frac{1}{r} - \frac{r_0^{n-1}}{r^n} \right). \quad (6.48)$$

For small displacements $r = r_0 + \Delta r$, a Taylor expansion yields,

$$u(r) = -\frac{Mq^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n} \right) + \frac{Mq^2(n-1)}{8\pi\epsilon_0 r_0^3} (\Delta r)^2. \quad (6.49)$$

This behavior resembles a harmonic oscillator. Balancing the restoring force with the force due to the external E-field E_{loc} , we have

$$\frac{Mq^2(n-1)}{4\pi\epsilon_0 r_0^3} \Delta r = qE_{loc}.$$

Solving for the displacement Δr ,

$$\Delta r = \frac{4\pi\epsilon_0 r_0^3}{Mq(n-1)} E_{loc}. \quad (6.50)$$

Thus, the induced dipole moment per ion leads to the polarizability,

$$\alpha_{ind} = \frac{4\pi r_0^3}{M(n-1)}. \quad (6.51)$$

The induced polarization of the ionic crystal can be written as

$$\vec{P}_{ind} = 2N \alpha_{ind} \epsilon_0 \vec{E}. \quad (6.52)$$

In reality, ions are not hard spheres, and their electron clouds have anisotropic shapes. When subjected to an external E-field, the electron cloud distribution is distorted. The overall polarizability is then a combination of contributions,

$$\alpha = \alpha^+ + \alpha^- + \alpha_{ind}, \quad (6.53)$$

where α^+ and α^- are the polarizability of the positive and negative ions, respectively. This equation captures the complete polarizability of ionic crystals under an external field.

6.3.3 Orientation polarization

In polar molecules, which possess permanent dipole moments, the dipoles are randomly oriented in the absence of an external E-field. When an external E-field \vec{E}_{loc} is applied, each dipole experiences a torque that tends to align it with the field. The potential energy of a dipole in the field is given by (refer to **Equation 4.11**),

$$u_d = -\vec{p}_0 \cdot \vec{E}_{loc} = -p_0 E_{loc} \cos \theta, \quad (6.54)$$

where \vec{p}_0 is the permanent dipole moment of the molecule and θ is the angle between \vec{p}_0 and \vec{E}_{loc} .

At equilibrium (e.g., at room temperature), the molecular orientation follows the Boltzmann distribution (here we neglect the effect of the induced dipole, i.e., assuming that $p_0 \gg p_{ind}$),

$$n(\theta) = n_0 e^{p_0 E_{loc} \cos \theta / k_B T}, \quad (6.55)$$

where k_B is the Boltzmann constant, T is the temperature, and n_0 is the molecular density at $T = \infty$. For typical conditions, $p_0 \sim 10^{-29}$ Cm, $E_{loc} \sim 10^5$ V/m, $T \sim 300$ K, the factor $p_0 E_{loc} / k_B T \sim 10^{-4}$ is very small. Therefore, a Taylor expansion of the Boltzmann factor yields,

$$n(\theta) \approx n_0 \left(1 + \frac{p_0 E_{loc} \cos \theta}{k_B T} \right). \quad (6.56)$$

The molecular density $n(\theta)$ in a solid angle $d\Omega = 2\pi \sin \theta d\theta$ is used to compute the average dipole moment along the field direction (z),

$$\bar{p}_z = \frac{1}{4\pi n_0} \int_0^\pi n(\theta) p_0 \cos \theta 2\pi \sin \theta d\theta = \frac{p_0^2}{3k_B T} E_{loc}. \quad (6.57)$$

Thus, the polarizability associated with orientation polarization is,

$$\alpha_{ind} = \frac{p_0^2}{3k_B T \epsilon_0}. \quad (6.58)$$

The total induced polarization \vec{P}_{ind} in the material is,

$$\vec{P}_{ind} = N \alpha_{ind} \epsilon_0 \vec{E}_{loc} = \frac{N p_0^2}{3k_B T} \vec{E}_{loc}. \quad (6.59)$$

This equation shows that orientation polarization depends strongly on the temperature, the strength of the external E-field, and the permanent dipole moment of the molecules.

Summary

Polarization in dielectric materials arises from several distinct mechanisms, each contributing differently based on the material type and external conditions. Electronic polarization occurs due to the displacement of electrons relative to their nuclei within an atom or molecule. This mechanism dominates at high frequencies, such as those encountered in optical fields, making it particularly significant in materials exposed to electromagnetic waves at these frequencies. Ionic polarization is another key mechanism, caused by the relative displacement of positive and negative ions in ionic crystals. This type of polarization is prominent in materials with strong ionic bonds, such as NaCl, where the ions shift under the influence of an external electric field, leading to a net polarization. Orientation polarization arises from the alignment of permanent dipole moments in polar molecules when subjected to an external electric field. This mechanism is highly temperature-dependent, as thermal motion competes with the aligning effect of the field. It becomes especially significant at low frequencies or in materials composed of polar molecules.

Understanding these polarization mechanisms is crucial for designing and optimizing materials for various applications, including electronics, optics, and any field that requires precise control over dielectric properties. By tailoring materials to enhance specific polarization effects, researchers and engineers can achieve desired performance characteristics in a wide range of technologies.

6.3 Microscopic and Global Fields

In earlier discussions, the term \vec{E}_{loc} was used to represent the local electric field experienced at a specific microscopic location within a material. This local field is distinct from the global electric field \vec{E} , which is applied uniformly across the entire material. Understanding the relationship between these fields is essential for analyzing dielectric behavior at both macroscopic and microscopic levels.

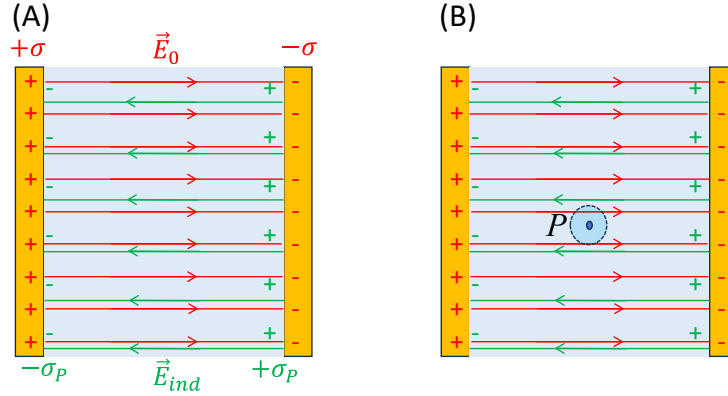


Fig. 6.5 (A) Global field in a dielectric between two parallel plates; (B) the local field around a location P .

Consider a dielectric placed between the plates of a parallel-plate capacitor. When an external field \vec{E}_0 is applied, dipoles within the dielectric align and induce a surface polarization charge density σ_p , as shown in **Figure 6.5A**. This polarization generates an opposing induced field \vec{E}_{ind} , also known as the depolarizing field, which reduces the net field within the material. The total macroscopic field \vec{E} can be expressed as,

$$\vec{E} = \vec{E}_0 + \vec{E}_{ind} = (1 - \chi)\vec{E}_0. \quad (6.60)$$

This global field \vec{E} is the macroscopic field that represents the average field throughout the material.

At a specific location P within the dielectric, the local electric field \vec{E}_{loc} may differ significantly from the global field \vec{E} due to additional microscopic contributions. As shown in **Figure 6.5B**, consider a small local volume surrounding P , the local field can be written as,

$$\vec{E}_{loc} = \vec{E}_0 + \vec{E}_{ind} + \vec{E}_2 + \vec{E}_3, \quad (6.61)$$

where \vec{E}_2 is the Lorentzian cavity field, arising from polarization near the chosen location, and \vec{E}_3 is the field generated by dipoles within the cavity. In most cases, $\vec{E}_3 = 0$ due to symmetry, leaving the primary contribution from \vec{E}_2 .

To calculate \vec{E}_2 , consider a spherical cavity around location P within the dielectric. The surface polarization charge density at the cavity is,

$$\sigma_p = -P_n, \quad (6.62)$$

where P_n is the normal component of the polarization at the surface. Over a solid angle $d\theta$, the total surface polarized charge is,

$$dq = -P \cos \theta 2\pi r \sin \theta r d\theta,$$

At the center of the cavity, the field contribution from this charge is,

$$dE_2 = -\frac{1}{4\pi\epsilon_0} \frac{dq}{a^2} \cos \theta.$$

Integrating over all angles gives the total Lorentzian cavity field

$$E_2 = \frac{P}{2\epsilon_0} \int_0^\pi \cos^2 \theta \sin \theta d\theta = \frac{1}{3\epsilon_0} P, \quad (6.63)$$

i.e.,

$$\vec{E}_2 = \frac{1}{3\epsilon_0} \vec{P}. \quad (6.64)$$

Combining the macroscopic field \vec{E} and the Lorentzian cavity field \vec{E}_2 , the local field \vec{E}_{loc} at P can be written as

$$\vec{E}_{loc} = \vec{E} + \frac{1}{3\epsilon_0} \vec{P}. \quad (6.65)$$

Clausius-Mossotti relationship

In the case of molecular polarization, each molecule within the dielectric acquires an induced dipole moment \vec{p}_{ind} , which is proportional to the local field

$$\vec{p}_{ind} = \alpha \epsilon_0 \vec{E}_{loc}$$

The polarization \vec{P} is then,

$$\vec{P} = N \vec{p}_{ind} = N \alpha \epsilon_0 \left(\vec{E} + \frac{1}{3\epsilon_0} \vec{P} \right). \quad (6.66)$$

Rearranging to solve for \vec{P} ,

$$\left(1 - \frac{N\alpha}{3} \right) \vec{P} = N \alpha \epsilon_0 \vec{E}. \quad (6.67)$$

Substituting $\vec{P} = (\kappa - 1) \epsilon_0 \vec{E}$, yields the Clausius-Mossotti relationship

$$\alpha = \frac{3}{N} \frac{\kappa - 1}{\kappa + 2}. \quad (6.68)$$

This equation links the polarizability α of individual molecules to the macroscopic dielectric constant κ .

In a summary, the distinction between microscopic and macroscopic fields is critical for understanding dielectric behavior. The macroscopic field \vec{E} describes the average field across the material, while the local field \vec{E}_{loc} includes additional contributions from polarization at microscopic scales. The Clausius-Mossotti relationship provides a bridge between these scales, connecting molecular properties like polarizability to bulk dielectric properties such as the dielectric constant. This framework is fundamental for designing and analyzing dielectric materials in applications ranging from capacitors to optical devices.

References

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2. Charles Kittel, *Introduction to Solid State Physics*, 8th Edition, John Wiley & Sons, Inc. (2005).