Ashim Kumar Bain and Prem Chand

Pyroelectric Materials

Physics and Applications

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Preface

Pyroelectricity was probably first observed by the Greeks more than 24 centuries ago. The philosopher Theophrastus wrote that *lyngourion* (most likely the mineral tourmaline) had the property of attracting straws and bits of wood. For two millennia, the peculiar properties of tourmaline were more a part of mythology than of science. In the eighteenth century, pyroelectric studies made a major contribution to the development of our understanding of electrostatics. In the nineteenth, research on pyroelectricity added to our knowledge of mineralogy, thermodynamics, and crystal physics. The field of pyroelectricity flourished in the twentieth century with many applications, particularly in infrared detection and thermal imaging. Pyroelectric sensors have been carried in many space missions and have contributed significantly to our astronomical knowledge.

Recently, pyroelectricity has become one of the most studied phenomena in the scientific community due to the various applications of pyroelectric materials in electronic devices. This book describes the basic physical properties, structure, and applications of pyroelectric materials.

The first chapter of this book deals with the basic concepts of dielectrics. **Chapter 2** describes the basic concepts of pyroelectricity, theory of pyroelectricity, and history of pyroelectricity. C**hapter 3** presents the physical properties, structure, and applications of different pyroelectric materials developed up to the recent time. C**hapter 4** provides up-to-date information on the design and applications of various pyroelectric IR detectors. C**hapter 5** gives an overview of the progress in the development of pyroelectric nanogenerators (PyNGs) for an energy harvesting system that uses environmental or artificial energies such as the sun, body heat, and heaters. **The last chapter** discusses the latest research results on pyroelectric fusion and provides information on newly designed pyroelectric neutron generators and X-ray generators (prototype portable).

I sincerely hope that this book will be very useful for scientific community including students, teachers, and researchers working in this field.

Finally, I would like to thank the Wiley-VCH publishing team for their outstanding support.

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1

Fundamentals of Dielectrics

1.1 Dielectrics

A dielectric material is a substance that is a poor conductor of electricity. On the basis of band structure, the dielectric materials have an energy gap of 3 eV or more. This large magnitude of energy gap precludes the possibility of electrons being excited from the valence band to the conduction band by thermal means. In electromagnetism, a dielectric (or dielectric material or dielectric medium) is an electrical insulator that can be polarized by an applied electric field. When a dielectric material is placed in an electric field, electric charges do not flow through the material as they do in an electrical conductor, but instead only slightly shift from their average equilibrium positions, causing dielectric polarization (Figure 1.1). Because of dielectric polarization, positive charges are displaced in the direction of the field and negative charges shift in the direction opposite to the field (e.g. if the field is moving parallel to the positive x-axis, the negative charges will shift in the negative x-direction). This creates an internal electric field that reduces the overall field within the dielectric itself. If a dielectric is composed of weakly bonded molecules, those molecules not only become polarized but also reorient so that their symmetry axes align to the field.

The study of dielectric properties concerns storage and dissipation of electric and magnetic energy in materials [1, 2]. Dielectrics are important for explaining various phenomena in electronics, optics, solid-state physics, and cell biophysics [3, 4].

Although the term insulator implies low electrical conduction, dielectric typically means materials with a high polarizability. The latter is expressed by a number called the relative permittivity. The term insulator is generally used to indicate electrical obstruction, while the term dielectric is used to indicate the energy-storing capacity of the material (by means of polarization). A common example of a dielectric is the electrically insulating material between the metallic plates of a capacitor. The polarization of the dielectric by the applied electric field increases the capacitor's surface charge for the given electric field strength.

The term dielectric was coined by William Whewell (from *dia* + electric) in response to a request from Michael Faraday [5, 6]. A perfect dielectric is a material with zero electrical conductivity (cf. perfect conductor infinite electrical conductivity), thus exhibiting only a displacement current; therefore, it stores and returns electrical energy as if it were an ideal capacitor.

Charge
+Q   −Q
Dielectric
Electric
field E   Plate
                area A
Plate separation *d*
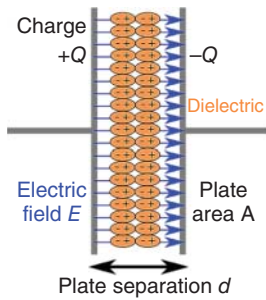
Figure 1.1 A polarized dielectric material.

1.1.1 Polarization of Dielectrics

The factors contributing to the polarization of dielectric molecules are as follows: the formation of dipole moments and their orientation relative to the electric field. If, in a dielectric, the molecules forming elementary dipole moments are composed of neutral particles such as atoms, the electric field shifts the electric charge of an atomic shell against the direction of field and the nucleus is moved in with the field. Thus, the center of gravity of the positive and negative charges is displaced from the center of the atom and an "induced dipole moment" is produced, as shown in Figure 1.2a. This part of polarization of molecules is called *electronic* (P_e). The electronic polarization is independent of temperature, but it is directly proportional to the field strength.

If the molecule producing an elementary dipole moment is made of ions of opposite signs, the following process occurs when the dielectric is placed into an electric field: the positive ions leave their equilibrium positions and move in the direction of field, and the negative ions are displaced against the direction of field. This displacement of ions or their groups in a dielectric initiates an *ionic* polarization (P_i) of molecules, as shown in Figure 1.2b. The ionic polarization is also independent of temperature, but it depends on the binding energy of particles in the molecule and in the lattice of the dielectric.
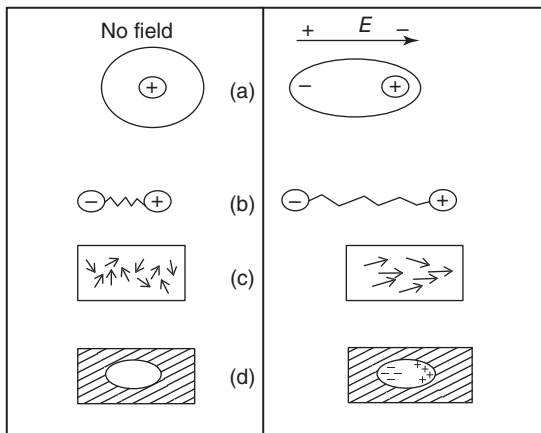
Figure 1.2 Polarization processes: (a) electronic polarization, (b) ionic polarization, (c) orientational polarization, and (d) space charge polarization.

The asymmetric distribution of charge between different atoms in a molecule produces permanent dipole moments in the molecules of a dielectric. Under the action of an electric field, these permanent dipoles are rotated into the direction of the field and thus contribute to polarization. In this case, we speak about the *orientational* polarization (P_o), as shown in Figure 1.2c. The orientational polarization is dependent on temperature. With increasing temperature, the thermal energy tends to randomize the alignment of the permanent dipoles inside the materials.

In real dielectrics, free charges may exist, which, under the action of an electric field, move through the dielectric and are captured by various defects within the dielectric without coming into contact with the electrodes. The free charges then form regions with a surface or a space charge, which in turn produces a dipole moment, also contributing to the polarization of a dielectric. This mechanism initiates a *space (surface)* charge polarization (P_s) inside the dielectric, as shown in Figure 1.2d. Like the orientational polarization, the space charge polarization is also a function of temperature, which, in most cases, increases with temperature.

The total polarization of a dielectric may simultaneously involve all the four mechanisms. If we assume that they are independent, we can write the total polarization of a dielectric material as the sum of the contributions from the four sources described earlier:

$$P_{total} = P_e + P_i + P_o + P_s \tag{1.1}$$

where the subscripts on the right refer to the four types: electronic, ionic, orientational, and space charge polarization, respectively.

1.1.2   Dispersion of Dielectric Polarization

In general, a material cannot polarize instantaneously in response to an applied field. The dielectric polarization process can be expressed as a function of temperature.

$$P(t) = P \left[1 - \exp \left(-\frac{t}{t_r} \right) \right] \tag{1.2}$$

where P is the maximum polarization attained on application of the electric field, and t_r is the relaxation time for the particular polarization process. The relaxation time t_r is the time taken for a polarization process to reach 63% of the maximum value.

The relaxation time varies widely on different polarization processes. There are a number of polarization mechanisms, as shown in Figure 1.3. The most common, starting from high frequencies, are given in the subsequent section.

1.1.2.1   Electronic Polarization
This process occurs in an atom when the electric field displaces the electron density relative to the nucleus it surrounds. Electronic polarization may be understood by assuming an atom as a point nucleus surrounded by spherical electron cloud of uniform charge density. Electrons have very small mass and are therefore able to follow the high-frequency fields up to the optical range. It is an extremely rapid process and is essentially complete at the instant the voltage is applied. Even when the
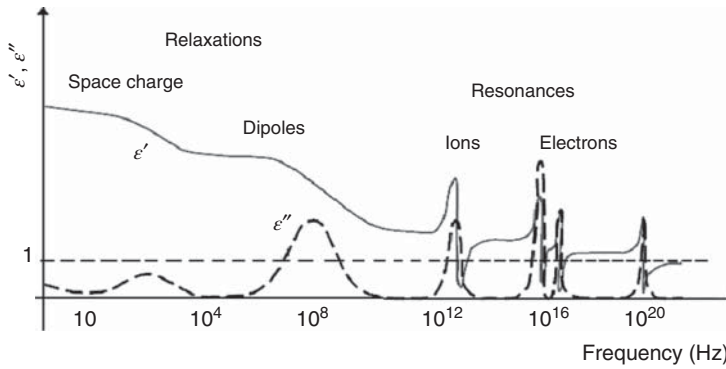
Figure 1.3 Frequency dependence of polarization dispersion.

frequency of the applied voltage is very high in the optical range ($\sim 10^{15}$ Hz), the electronic polarization occurs during every cycle of the applied voltage.

1.1.2.2 Ionic Polarization

This process is associated with the relative motions of cations and anions in an electric field. Ionic polarization is slower than electronic polarization, as the displacement involved here is that of much heavier ion as compared to the electron cloud. The frequency with which ions can be displaced over a small fraction of the interatomic distance will be of the same order as the lattice vibration frequency ($\sim 10^{13}$ Hz). If an electric field of frequency in the optical range ($\sim 10^{15}$ Hz) is applied, the ions do not respond at all, as the time required by an ion for one vibration is 100 times larger than the period of the applied voltage. Therefore, there is no ionic polarization at optical frequencies.

1.1.2.3 Orientation Polarization

It is slower than ionic polarization. Orientation polarization arises from the rotation of molecular dipoles in the field. It is easier for the polar molecules to reorient themselves in a liquid than in solid. Orientation polarization occurs when the frequency of the applied voltage is in the audio range.

1.1.2.4 Space Charge Polarization

It is the slowest process, as it involves the diffusion of ions over several interatomic distances. The relaxation time for this process is related to the frequency of successful jumps of ions under the influence of the applied field. Space charge polarizations often occur in the kilohertz range or even lower.

Referring to Figure 1.3, all the four types of polarization are present at machine frequencies. As the frequency increases, space charge, orientation, and ionic polarization become inoperative in that order. When several polarization processes occur in a material, it follows that the dielectric constant will decrease with increasing frequency of the applied voltage. When the period of the applied voltage is much larger than the relaxation time of a polarization process, the polarization is completed at

any instant during each cycle, and when the period of the applied voltage is much shorter than the relaxation time for a polarization process, the polarization does not occur at all. But when the period of the applied voltage is in the same range as the relaxation time, resonance occurs.

At high frequencies, usually microwave and beyond – the processes that take place are undamped and are called "resonances." Real dielectric materials have several such resonances due to ionic and electronic polarization. At frequencies below microwaves, the polarization processes are heavily damped and are called "relaxations." In physics, dielectric dispersion is the dependence of the permittivity of a dielectric material on the frequency of an applied electric field. This is because there is a lag between changes in polarization and changes in the electric field. The permittivity of the dielectric is a complicated function of frequency of the electric field. Dielectric dispersion is very important for the applications of dielectric materials and for the analysis of polarization systems.

This is one instance of a general phenomenon known as material dispersion: a frequency-dependent response of a medium for wave propagation.

When the frequency becomes higher:

- dipolar polarization can no longer follow the oscillations of the electric field in the microwave region around 10^{10} Hz
- ionic polarization and molecular distortion polarization can no longer track the electric field past the infrared or far-infrared region around 10^{13} Hz
- electronic polarization loses its response in the ultraviolet region around 10^{15} Hz.

In the frequency region above ultraviolet, permittivity approaches the constant ϵ_0 in every substance, where ϵ_0 is the permittivity of the free space. Because permittivity indicates the strength of the relation between an electric field and polarization, if a polarization process loses its response, permittivity decreases.

The effect of temperature on the relative permittivity of a material can be twofold. In orientation polarization, the randomizing action of thermal energy decreases the tendency for the permanent dipoles to align themselves in the applied field. This results in a decrease in the relative permittivity with increasing temperature. The other effect of temperature is to facilitate the diffusion of ions in space charge polarization. Thermal energy may aid in overcoming the activation barrier for the orientation of relatively large polar molecules in the direction of the field.

1.1.3 Dielectric Relaxation

Dielectric relaxation is the momentary delay (or lag) in the dielectric constant of a material. This is usually caused by the delay in molecular polarization with respect to a changing electric field in a dielectric medium (e.g. inside capacitors or between two large conducting surfaces). Dielectric relaxation in changing electric fields could be considered analogous to hysteresis in changing magnetic fields (e.g. in inductor or transformer cores).

Relaxation in general is a delay or lag in the response of a linear system, and therefore, dielectric relaxation is measured relative to the expected linear steady state

(equilibrium) dielectric values. The time lag between electrical field and polarization implies an irreversible degradation of Gibbs free energy.

In physics, dielectric relaxation refers to the relaxation response of a dielectric medium to an external, oscillating electric field. This relaxation is often described in terms of permittivity as a function of frequency, which can, for ideal systems, be described by the Debye equation. On the other hand, the distortion related to ionic and electronic polarization shows behavior of the resonance or oscillator type. The character of the distortion process depends on the structure, composition, and surroundings of the sample.

1.1.4 Debye Relaxation

Debye relaxation is the dielectric relaxation response of an ideal, noninteracting population of dipoles to an alternating external electric field. It is usually expressed in the complex permittivity ε of a medium as a function of the field's frequency ω:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 - i\omega\tau} \tag{1.3}$$

where ε_∞ is the permittivity at the high-frequency limit (i.e., $\omega \to \infty$), $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ where ε_s is the static, low-frequency (i.e., $\omega \to 0$) permittivity, and τ is the characteristic relaxation time of the medium. Separating into the real part ε' and the imaginary part ε'' of the complex dielectric permittivity yields [7]:

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2\tau^2} \tag{1.4}$$

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + \omega^{2\tau^2}} \tag{1.5}$$

These are the Debye equations, and we find that they are reasonably applicable to most dispersions at electrical frequencies. The dielectric loss is also represented by:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{\varepsilon_s + \varepsilon_\infty\omega^2\tau^2} \tag{1.6}$$

This relaxation model was introduced by and named after the physicist Peter Debye [8]. It is characteristic for dynamic polarization with only one relaxation time.

1.1.5 Molecular Theory of Induced Charges in a Dielectric

A dielectric contains no free charges; then how it is possible for an induced charge to appear on the surface of a dielectric when placed in an electric field? This can be explained by the molecular viewpoint of dielectric. The dielectrics are classified into polar and nonpolar. A nonpolar molecule is one in which the center of gravity of positive and negative charges normally coincides, while a polar molecule is one where they do not coincide. Polar molecules, therefore, have permanent dipole moments. In the absence of an external field, these dipoles are oriented at random. But strong field orients more dipoles in the direction of the field. The charges of a nonpolar molecule suffer a small displacement when placed in an electric field.

Figure 1.4 The depolarization field E_1 is opposite to P. The fictitious surface charges are indicated: the field of these charges is E_1 within the ellipsoid.
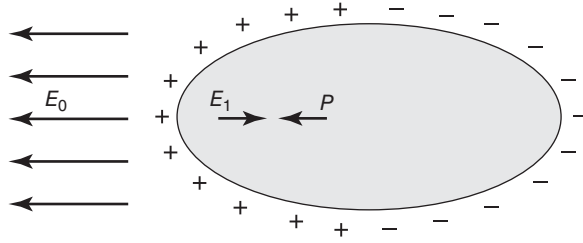
The molecules are said to become polarized by the field and are called induced dipoles. Therefore, the dielectrics, both polar and nonpolar, behave in the same way under the influence of external electric field. We can imagine that these dipoles in the applied electric field can have excess negative charges on one surface and positive charges on the opposite surface, as shown in Figure 1.4.

These charges are not free, but each is bound to a molecule lying in or near the surface. The net charge per unit volume within the rest of the dielectric medium is zero. The electric field E_1 set up by the induced charge always opposes the applied field E_0. The resultant field E is the vector sum of these two. That is,

$$E = E_0 + E_1 \tag{1.7}$$

The field E_1 is called the depolarization field; this is because within the body, it tends to oppose the applied field E_0 as shown in Figure 1.4. The resultant field E points to the same direction as E_0 but is smaller in magnitude. This leads to the conclusion that if a dielectric is placed in an electric field, the induced surface charges appear, which tend to weaken the original field within the dielectric. Thus, we can define the dielectric constant (k) or relative permittivity (ε_r) as the ratio of the magnitude of the applied field E_0 to the resultant field E. Then,

$$\frac{E_0}{E} = \frac{V_0}{V} = k = \varepsilon_r \tag{1.8}$$

where V_0 is the potential difference without any medium and V is the same with a dielectric medium in between the capacitor plates.

Therefore, for same charges Q, the ratio of capacitance with dielectric C and capacitance without dielectric (for free space) C_0 will be

$$\frac{C}{C_0} = \frac{\frac{Q}{V}}{\frac{Q}{V_0}} = \frac{V_0}{V} = \frac{E_0}{E} = k = \varepsilon_r \tag{1.9}$$

From the above definition of k, the dielectric constant or permittivity for free space is unity. Obviously, k is a dimensionless quantity.

1.1.6 Capacitance of a Parallel Plate Capacitor

If a constant voltage V_0 is applied to a plane condenser with a vacuum capacity C_0, a charge Q of density $\sigma = Q/A$ is set up on the condenser with area A and distance of separation d between the plates (Figure 1.4). From the application of Gauss's law, we know that the electric field intensity between two plates with a vacuum is $E = \sigma/\varepsilon_0$.

The potential difference V_0 is the work done in carrying a unit charge from one plate to the other. Hence,

$$V_0 = Ed = \left(\frac{\sigma}{\varepsilon_0}\right) d = \left(\frac{Qd}{\varepsilon_0 A}\right) \tag{1.10}$$

Rearranging the relation (1.9), we can write

$$\frac{Q}{V_0} = \left(\frac{\varepsilon_0 A}{d}\right) \tag{1.11}$$

The capacitance C_0 can be written as:

$$C_0 = \frac{Q}{V_0} = \left(\frac{\varepsilon_0 A}{d}\right) \tag{1.12}$$

The capacitance C of the capacitor with dielectric medium can be written as:

$$C = \varepsilon \frac{A}{d} \tag{1.13}$$

where ε is the permittivity (absolute permittivity) of dielectric medium between the capacitor plates. The permittivity (ε) is often represented by the relative permittivity (ε_r), which is the ratio of the absolute permittivity (ε) and the vacuum permittivity (ε_0).

$$k = \varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \tag{1.14}$$

Rearranging relations (1.13) and (1.14), we can write

$$C = \varepsilon_r \varepsilon_0 \left(\frac{A}{d}\right) = k\varepsilon_0 \left(\frac{A}{d}\right) \tag{1.15}$$

Relation (1.15) can be expressed in the rationalized form in the SI system by the formula:

$$C = \varepsilon_r \varepsilon_0 \left(\frac{A}{d}\right) = \varepsilon_r (8.854 \times 10^{-12}) \left(\frac{A}{d}\right) \text{F} \tag{1.16}$$

where d is in meters and A is in square meters. Normalized units in the *cgs* electrostatic system can be expressed by the formula:

$$C = \varepsilon_r \left(\frac{1}{4\pi}\right) \left(\frac{A}{d}\right) \text{cm} \tag{1.17}$$

where d is in centimeters and A in square centimeters.

Sample Problem 1.1
A parallel-plate capacitor of area $A = 4 \times 10^{-2}$ m^2 and plate separation $d = 2 \times 10^{-2}$ m is raised to a potential difference $V_0 = 100$ V by connecting a battery when there is no dielectric in between the plates.

(a) Calculate the capacitance C_0 of the capacitor. (b) What is the free charge appeared on the plates?

(a) From Eq. (1.12), the capacitance of the capacitor:

$$C_0 = \frac{\varepsilon_0 A}{d} = \frac{(8.85 \times 10^{-12} \text{ F/m})(4 \times 10^{-2} \text{ m}^2)}{2 \times 10^{-2} \text{ m}}$$
$$= 17.8 \times 10^{-12} \text{ F} = 17.8 \text{ pF (Answer)}.$$

(b) From Eq. (1.12), the free charge:

$$Q = C_0 V_0 = 17.8 \times 10^{-12} \text{ F} \times 100 \text{ V} = 17.8 \times 10^{-10} \text{ C (Answer)}.$$

Sample Problem 1.2

Calculate the dielectric constant of a barium titanate crystal, which when inserted in a parallel plate capacitor of area $A = 10 \text{ mm} \times 10 \text{ mm}$ and distance of separation of $d = 2 \text{ mm}$, gives a capacitance of 10^{-9} F.

From Eq. (1.15), the dielectric constant of the medium between the capacitor plates:

$$k = \frac{C}{\varepsilon_0}\left(\frac{d}{A}\right) = \frac{10^{-9} \text{ F} \times 2 \times 10^{-3} \text{ m}}{8.854 \times 10^{-12} \text{ F/m} \times 10^2 \times 10^{-6} \text{ m}^2} = 2259 \text{ (Answer)}.$$

Sample Problem 1.3

A capacitor of 1 nF is required. If a dielectric material of thickness 0.1 mm and relative permittivity 5.4 is available, determine the required plate area.

From Eq. (1.15), the area of the capacitor plates:

$$A = \frac{Cd}{\varepsilon_0 \varepsilon_r} = \frac{1 \times 10^{-9} \text{ F} \times 0.1 \times 10^{-3} \text{ m}}{8.854 \times 10^{-12} \text{ F/m} \times 5.4} = 0.00209 \text{ m}^2 = 20.9 \text{ cm}^2 \text{ (Answer)}.$$

1.1.7 Electric Displacement Field, Dielectric Constant, and Electric Susceptibility

In physics, the electric displacement field (denoted by D) or electric induction is a vector field that appears in Maxwell's equations. It accounts for the effects of free and bound charge within materials. "D" stands for "displacement," as in the related concept of displacement current in dielectrics. In free space, the electric displacement field is equivalent to flux density, a concept that lends the understanding of Gauss's law.

In a dielectric material, the presence of an electric field E causes the bound charges in the material (atomic nuclei and their electrons) to slightly separate, inducing a local electric dipole moment. The electric displacement field "D" is defined as:

$$D = \varepsilon_0 E + P \tag{1.18}$$

where ε_0 is the vacuum permittivity (also called permittivity of free space), and P is the (macroscopic) density of the permanent and induced electric dipole moments in the material, called the polarization density.

In a linear, homogeneous, isotropic dielectric with instantaneous response to changes in the electric field, P depends linearly on the electric field,

$$P = \varepsilon_0 \chi E \tag{1.19}$$

where the constant of proportionality χ is called the electric susceptibility of the material. Now, rearranging relations (1.18) and (1.19), we can write

$$D = \varepsilon_0(1 + \chi)E = \varepsilon E \tag{1.20}$$

where $\varepsilon = \varepsilon_0 \varepsilon_r$ is the permittivity, and $\varepsilon_r = (1 + \chi)$ is the relative permittivity of the material.

In a linear, homogeneous, and isotropic media, ε is a constant. However, in a linear anisotropic media, it is a tensor, and in nonhomogeneous media, it is a function of position inside the medium. It may also depend upon the electric field (nonlinear materials) and have a time-dependent response. Explicit time dependence can arise if the materials are physically moving or changing in time (e.g. reflections off a moving interface give rise to Doppler shifts). A different form of time dependence can arise in a time-invariant medium, as there can be a time delay between the imposition of the electric field and the resulting polarization of the material. In this case, $\boldsymbol{P}$ is a convolution of the impulse response susceptibility χ and the electric field $\boldsymbol{E}$. Such a convolution takes on a simpler form in the frequency domain: by Fourier transforming the relationship and applying the convolution theorem, one obtains the following relation for a linear time-invariant medium:

$$\boldsymbol{D}(\omega) = \varepsilon(\omega)\boldsymbol{E}(\omega) \tag{1.21}$$

where ω is the frequency of the applied field. The constraint of causality leads to the Kramers–Kronig relations, which place limitations upon the form of the frequency dependence. The phenomenon of a frequency-dependent permittivity is an example of material dispersion. In fact, all physical materials have some material dispersion because they cannot respond instantaneously to applied fields, but for many problems (those concerned with a narrow enough bandwidth), the frequency dependence of ε can be neglected.

1.1.8 Local Field in a Dielectric

We now develop an expression for the local field at a general lattice site, not necessarily of cubic symmetry. To evaluate E_{loc}, we must calculate the total field acting on a certain typical dipole; this field is due to the external field as well as all *other* dipoles in the system. This was done by Lorentz as follows: the dipole is imagined to be surrounded by a spherical cavity whose radius R is sufficiently large that the matrix lying outside it may be treated as a continuous medium as far as the dipole is concerned (Figure 1.5a). The interaction of our dipole with the other dipoles lying inside the cavity is, however, to be treated microscopically, which is necessary since the discrete nature of the medium very close to the dipoles should be taken into account. The local field, acting on the central dipole, is thus given by the sum

$$E_{loc} = E_0 + E_1 + E_2 + E_3 \tag{1.22}$$

where $\boldsymbol{E}_0$ is the external field; $\boldsymbol{E}_1$ is the depolarization field, that is, the field due to the polarization charges lying at the external surfaces of the sample; $\boldsymbol{E}_2$ is the field due to the polarization charges lying on the surface of the Lorentz sphere (Figure 1.5b), which is known as Lorentz field; and $\boldsymbol{E}_3$ is the field due to other dipoles lying within the sphere.

It is important to note that the part of the medium between the sphere and the external surface does not contribute anything since the volume polarization charges
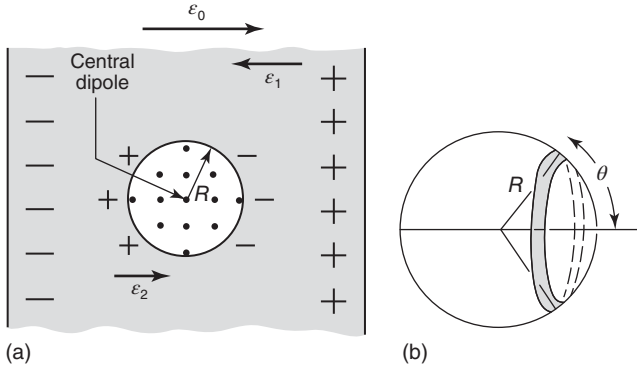
Figure 1.5 (a) The procedure for computing the local field. (b) The procedure for calculating E_2, the field due to the polarization charge on the surface of the Lorentz sphere.

compensate each other, resulting in a zero net charge in this region. The contribution $E_1 + E_2 + E_3$ to the local field is nothing but the total field at one atom caused by the dipole moments of all the other atoms in the specimen. Dipoles at distances greater than perhaps 10 lattice constants from the reference site make a smoothly varying contribution. It is convenient to let the interior surface be spherical.

1.1.8.1 Lorentz Field, E_2

The polarization charges on the surface of the Lorentz cavity may be considered as forming a continuous distribution. The field due to the charge at a point located at the center of the sphere is, according to Coulomb's law, given by

$$E_2 = \frac{P}{3\varepsilon_0} \tag{1.23}$$

1.1.8.2 Field of Dipoles Inside Cavity, E_3

The field E_3 due to the dipoles within the spherical cavity is the only term that depends on the crystal structure. For a reference site with cubic surroundings in a sphere, $E_3 = 0$ if all the atoms may be replaced by point dipoles parallel to each other. The total local field at a cubic site is then,

$$E_{loc} = E_0 + E_1 + \frac{P}{3\varepsilon_0} = E + \frac{P}{3\varepsilon_0} \tag{1.24}$$

This is known as *Lorentz relation*. The difference between the Maxwell's field E and the Lorentz field E_{loc} is as follows: the field E is macroscopic in nature and is an average field. On the other hand, E_{loc} is a microscopic field and is periodic in nature. This is quite large at molecular sites, indicating that the molecules are more effectively polarized than they are under the influence of Maxwell's field E.

If there are n molecules or atoms per unit volume in a dielectric, then the electric dipole moment per unit volume is $n\alpha E_{loc}$, represented by P, known as polarization. Therefore,

$$P = n\alpha E_{loc} \tag{1.25}$$

where α is a constant and is known as polarizability of the dielectric material. Rearranging relations (1.24) and (1.25), we can write

$$\boldsymbol{P} = n\alpha\boldsymbol{E}_{loc} = n\alpha\left(\boldsymbol{E} + \frac{\boldsymbol{P}}{3\varepsilon_0}\right) \tag{1.26}$$

The polarization is induced by electric field, and therefore, it is a function of electric field. The relationship is written in the following way:

$$\boldsymbol{P} = \varepsilon_0\chi\boldsymbol{E} \tag{1.27}$$

where χ is called the dielectric susceptibility. In general, χ is a tensor and depends on the electric field. The dielectric susceptibility χ is defined in terms of relative permittivity ε_r of the material.

$$\varepsilon_r = (1 + \chi) \tag{1.28}$$

Now, rearranging relations (1.26–1.28), we can write an expression in terms of the relative permittivity:

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{n\alpha}{3\varepsilon_0} \tag{1.29}$$

The above equation is known as *Clausius–Mossotti relation*. This relates the relative permittivity to polarizability of the dielectric material. The total polarizability α can be written as the sum of four terms, representing the most important contributions to the polarization, that is, $\alpha = \alpha_e + \alpha_i + \alpha_o + \alpha_s$, where α_e, α_i, α_o, and α_s are the electronic, ionic, orientational, and space charge polarizabilities, respectively.

Since $\varepsilon_r = k = n^2$, we can rewrite relation (1.29) as follows:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{n\alpha}{3\varepsilon_0} \tag{1.30}$$

This is the *Lorentz–Lorenz* equation. It connects the index of refraction (n) with the polarizability.

1.1.9 Dielectrics Losses

When an electric field acts on any matter, the latter dissipates a certain quantity of electric energy that transforms into heat energy. This phenomenon is known as the loss of power, meaning an average electric power dissipated in matter during a certain interval of time. As a rule, the loss of power in a specimen of a material is directly proportional to the square of the electric voltage applied to the specimen.

If a metal conductor is first connected to direct voltage and then to alternating voltage, the acting magnitude of which is equal to direct voltage, the loss of power P in watts will be the same in both cases in conformity with the Joule–Lenz law and equal to

$$P = \frac{V^2}{R} \tag{1.31}$$

where V is the voltage in volts and R is the resistance of the conductor in ohms.

As distinct from conductors, most of the dielectrics display a characteristic feature: under a given voltage, the dissipation of power in the dielectrics depends on the voltage frequency; the expense of power at an alternating voltage is markedly higher than that at a direct voltage; rapidly grows with an increase in frequency, voltage, and capacitance; and depends on the material of the dielectric.

The power losses in a dielectric under the action of the voltage applied to it are commonly known as *dielectric losses*. This is the general term determining the loss of power in an electrical insulation at both a direct and an alternating voltage. Dielectric losses at a direct voltage can be found from relation (1.31) where R stands for the resistance of the insulation, while the losses under the alternating voltage are determined by more intricate regularities. Actually, the dielectric losses mean the losses of power under an alternating voltage.

1.1.9.1 Dielectric Loss Angle

The phase diagram of currents and voltages in a capacitor energized by an alternating voltage is shown in Figure 1.6. If the power was not dissipated at all in the dielectric of the capacitor (ideal dielectric), the phase of current I through the capacitor would be ahead of the phase of voltage V by 90°, and the current would be purely reactive. In actual fact, the phase angle ϕ is slightly less than 90°. The total current I through the capacitor can be resolved into two components: active I_a and reactive I_r currents.

Thus, the phase angle describes a capacitor from the viewpoint of losses in a dielectric. Since the phase angle ϕ is very close to 90° in a capacitor with a high-quality dielectric, the angle δ (i.e. $\delta = 90° - \phi$) is a more descriptive parameter, which is called the *dielectric loss angle*. The tangent of the angle is equal to the ratio of the active currents to the reactive currents:

$$\tan \delta = I_a/I_r \tag{1.32}$$

or the ratio of active power P (power loss) to the reactive power P_r:

$$\tan \delta = P/P_r \tag{1.33}$$

The dielectric loss angle is an important parameter for the dielectric materials. This parameter is usually described by the loss tangent $\tan \delta$. Sometimes, the quality factor of an insulation portion is determined, that is, the value is reciprocal of the loss tangent:

$$Q = \frac{1}{\tan \delta} = \tan \phi \tag{1.34}$$

Figure 1.6 Phase diagram of current and voltage in a capacitor with a dielectric material.