General Physics Phenomena

Chapter 1

Physics of Dielectrics

1.1. Definitions

A dielectric material is a more or less insulating material (with high resistivity and with a band gap of a few eV), that is polarizable, i.e. in which electrostatic dipoles exist or form under the influence of an electric field.

Like any material, it is an assembly of ions with positive and negative charges which balance, for a supposedly perfect solid, so as to ensure electrical neutrality. This neutrality is observed at the scale of the elementary structural motifs which constitute solids with ionocovalent bonding (ceramics, for example) and on the molecular scale in molecular solids (polymers and organic solids).

The action of an electric field at the level of these element constituent of solids manifests itself by dielectric polarization effects. Let us remember that the dipole moment of a charge q with respect to a fixed system of reference centered in O is:

$$\vec{m}_t(0) = q\,\vec{r} \qquad\qquad [1.1]$$

where $\vec{r}$ is the vector which connects the point O to the charge's position.

If due to a force (caused, for example, by a magnetic field), the charge moves $\delta\vec{r}$, then the variation of the moment will be:

$$\delta\vec{m}_t(0) = q\,\delta\vec{r} \qquad\qquad [1.2]$$

Chapter written by Guy BLAISE and Daniel TREHEUX.

$\delta \vec{m}_t$ represents *the polarization effect* of the field on the charge. The generalization of expressions [1.1] and [1.2] to a collection of charges occurs by vectorial summation of the moments of each charge. An important case is that of a set of two charges $\pm q$, whose positions are defined by $\vec{r}_1$ and $\vec{r}_2$ (see Figure 1.1). The application of [1.1] to the two charges gives:

$$\vec{m}_t(0) = q\,\vec{r}_1 - q\,\vec{r}_2$$

Setting $\vec{r}_1 = \vec{r}_2 + \vec{\ell}$, we get:

$$\vec{m}_t(0) = q\,\vec{\ell} = \vec{p} \qquad\qquad [1.3]$$

$\vec{p}$ is called the dipole moment formed by the two charges, oriented from the negative charge to the positive charge (see Figure1.1).

The dipole moment appearing in a solid, during the application of a field $\vec{E}$, is (to a first approximation) proportional to it. We can then write:

$$\vec{p} = \varepsilon_0 \alpha\,\vec{E} \qquad\qquad [1.4]$$

In this equation, α characterizes the polarisability of the species which gave the dipole and ε_0 the vacuum permittivity.
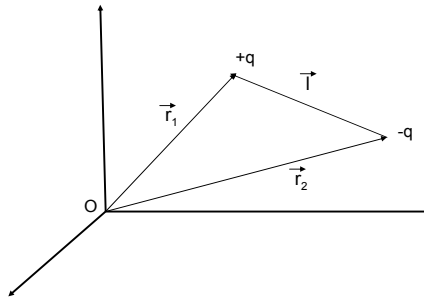

Figure 1.1. *Calculation of the dipole moment formed by 2 charges +q and –q*

1.2. Different types of polarization

To study dielectrics, it is necessary to first of all describe the different types of polarization. In order to do so, we must distinguish two types of solids: polar solids and non-polar solids.

1.2.1. *Non-polar solids*

In the case of non-polar solids, the centers of gravity of positive and negative charges coincide, and the dipole moment is therefore null (in the absence of a field). This is the case for solids with metallic bonding, or of numerous ionocovalent solids (ceramic Al_2O_3, ZrO_2, ZnO, SiO_2, etc.). Thus, the tetrahedron SiO_4 which constitutes the motif of quartz has a null dipole moment. It is the distortion of this tetrahedron, under the effect of a mechanical stress, which will make a polarization and the piezoelectric effect appear (see Figure 1.2).
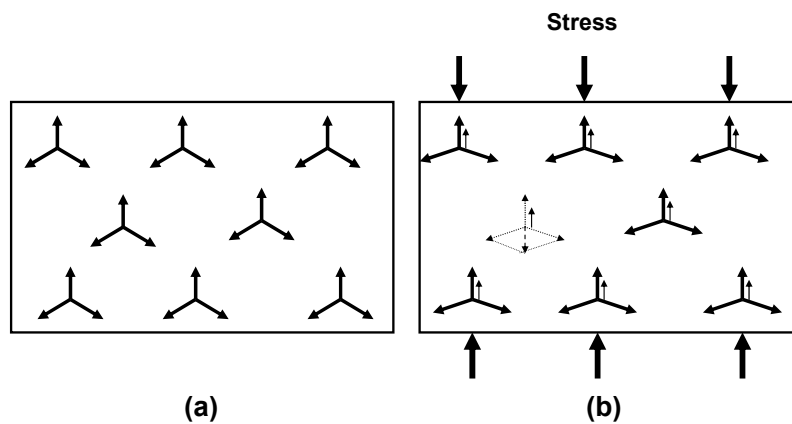
Figure 1.2. *(a) Quartz cristal at rest; it posesses a symmetry axis of order 3. The arrows represent the dipole moments whose resultant is null. (b) Subject to a mechanical stress according to the direction indicated, the network is distorted and the resulting dipole moment (small vertical arrow), is no longer null: an electric field appears*

1.2.2. *Polar solids*

Polar solids are composed of polar molecules for which the centers of gravity of the positive and negative charges do not coincide (for example a water molecule); this is molecular polarization. This is the case for most molecular solids and ferroelectric solids, which present a spontaneous polarization. Figure 1.3 gives, for example, the structure of barium titanate, a typical case of a ferroelectric body (and therefore also piezoelectric).
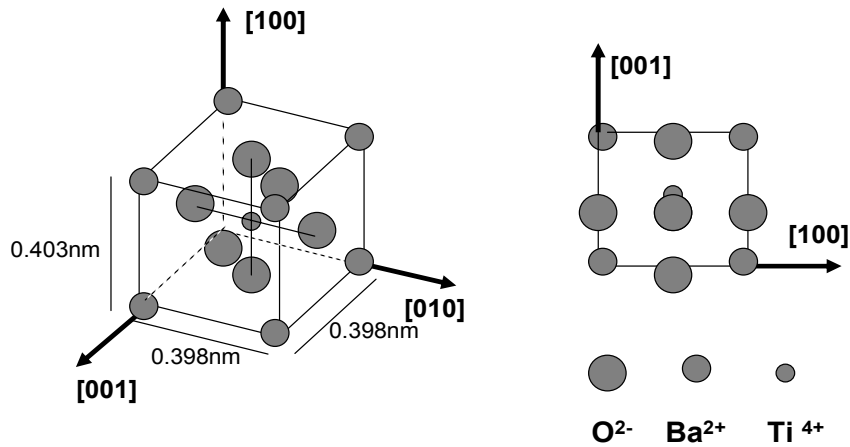
1.2.3. *Electronic polarization*

Let us consider the spherical orbital of an electron. Under the influence of an external electric field $\vec{E}$, the electrons are subject to a force $-e\,\vec{E}$ and the orbital gets

distorted (see Figure 1.4). Consequently, the centers of gravity of the positive and negative charges which were initially merged, no longer are: this is electric polarization, and this leads to the formation of an electrostatic dipole; therefore, a dipole moment internal to the atom is characterized by:

$$\vec{p}_{elect} = \varepsilon_0 \alpha_{elect} \vec{E} \qquad\qquad [1.5]$$

which opposes itself to the field $\vec{E}$. α_{elect} is called the electronic polarisability. The polarization disappears if the field is removed.

Figure 1.3. *Non-centrosymmetric crystalline structure of barium titanate BaTiO$_3$*
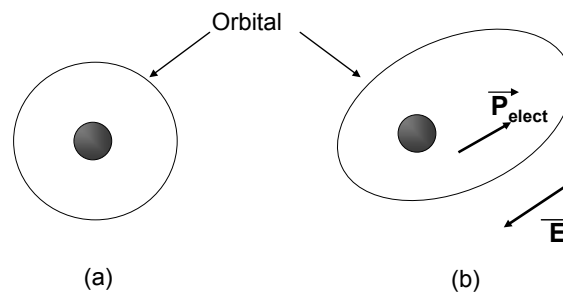
Figure 1.4. *(a) Orbital in the absence of electric field; (b) distortion of the orbital and appearance of electronic polarization $\vec{p}_{elect}$ in the presence of a field $\vec{E}$*

1.2.4. *Ionic polarization*

In the case of ionic crystals, the average position of positive and negative ions changes under the influence of a field $\vec{E}$. Suppose the ion is perfectly rigid from every angle. The action of the field will be to move it a quantity $\vec{\ell}$ with respect to a fixed mark centered in O; hence a variation of the polar moment:

$$\vec{p}_{\text{ion}} = q\,\vec{\ell} = \varepsilon_0 \alpha_{\text{ion}} \vec{E} \qquad [1.6]$$

This is the induced ionic polarization, proportional to the field (elastic distortions); where α_{ion} is the ionic polarisability.

The total dipole moment attached to the displacement of the ion and to the distortion of the electronic orbitals is, to a first approximation, the sum of [1.5] and [1.6], that is to say:

$$\vec{p}_{\text{t}} = \vec{p}_{\text{ion}} + \vec{p}_{\text{elect}} \qquad [1.7]$$

1.2.5. *Orientation polarization*

When we subject a polar molecule, carrier of a permanent dipole moment $\vec{p}_0$, to an electric field $\vec{E}$, its dipole tends to turn towards the direction of the field, which leads to a distortion of the molecule related to a torque: this is orientation polarization. This distortion is not instantaneous. There is the appearance of a hysteresis, on the one hand because the molecular forces tend to block its motion and, on the other hand, the thermal agitation will tend to disorient the molecules with respect to one another.

If $\vec{p}_0$ makes an angle θ with the direction of the field, the torque is:

$$\vec{\Gamma} = \vec{p}_0 \wedge \vec{E}$$

The application of a field will have the effect on each molecule of producing a polar component in the direction of the field, whose first-order expression is:

$$\vec{p}_{\text{or}} = \varepsilon_0 \alpha_{\text{or}} \vec{E} \qquad [1.8]$$

α_{or} is called orientational polarisability. In general, $\vec{p}_{\text{or}} \ll \vec{p}_{\text{o}}$.

1.2.6. *Interfacial or space-charge polarization*

This type of polarization plays a part when the material possesses different phases or permittivity zones. Subject to a low-frequency electric field (from 10^{-1} to 10^2 Hz), this material will behave as though it contains electric charges with interfaces separating the zones. However, these charges are not real charges, but known as "polarization" charges (see section 1.3.3).

1.2.7. *Comments*

Units: a dipole moment is the product of a charge by a distance; it is therefore measured in C.m. A commonly used unit is the Debye:

$$1 \text{ Debye} = \frac{1}{3} 10^{-29} \text{ C.m} = e \times 2.08 \ 10^{-11} \text{ m (e charge of the electron)}.$$

A dipole moment is measurable, unlike q and l. The dipole moment must be taken as an entity, in the same way as an electric charge.

Polarization vector: this is the dipole moment per unit volume. By analogy with a capacitor, we can write:

$$\vec{P} = \varepsilon_0 \ (\varepsilon_r - 1) \ \vec{E} = \varepsilon_0 \ \chi \ \vec{E} \tag{1.9}$$

where ε_0 is the vacuum permittivity, ε_r is the dielectric constant of the material and $\chi = (\varepsilon_r - 1)$ is its dielectric *susceptibility*.

1.3. Macroscopic aspects of the polarization

1.3.1. *Polarization of solids with metallic bonding*

Rather than address non-conductive materials, it is interesting first of all to describe the polarization phenomena appearing in a metal. In this case, each ion of the solid is neutralized on the scale of the atomic volume by "free" electrons. The ions do not move under the action of the field and subsequently do not introduce any dipole moment. On the other hand, the conduction electrons go up the field (polarisability $\alpha \to \infty$) until they reach the limit of the solid: the electrons accumulate on the surface of the solid by which the field enters, leaving an excess of positive charges on the surface by which it comes out (see Figure 1.5). This giant dipole creates an internal field $\vec{E}_{ch}$ within the solid which opposes itself to the applied field $\vec{E}_a$. The motion of charges takes place until the total field is null:

$$\vec{E}_{internal} = \vec{E}_{ch} + \vec{E}_a = \vec{0} \qquad\qquad [1.10]$$

We say that the free charges come to screen the applied field. The total charge of the solid is null but its surface is positively charged on one side and negatively on the other.
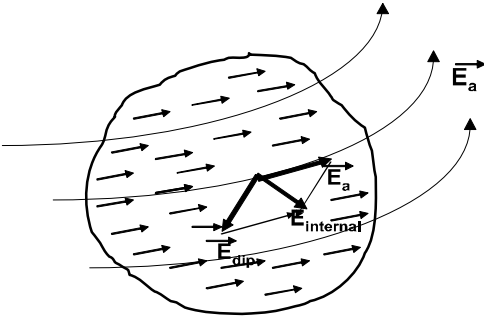
1.3.2. *Polarization of iono-covalent solids*

Unlike metals, there are no free charges in a perfect iono-covalent solid: there is therefore no screen with the applied field. Each ion of the elementary structural motif is subject to a polarization, such that the solid presents a dipolar structure at the atomic or molecular scale (see Figure 1.6). The solid being neutral, the internal field at a point is the sum of the applied field and the field created by all of the dipoles.

$$\vec{E}_{internal} = \vec{E}_{dip} + \vec{E}_a \neq \vec{0} \qquad\qquad [1.11]$$
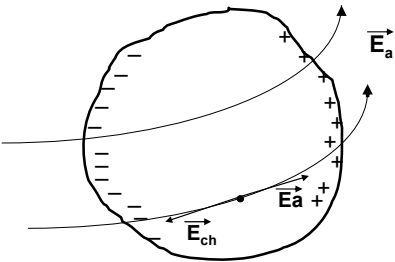
Figure 1.5. *Polarization of a solid with metallic bonding*

Figure 1.6. *Polarization of an iono-covalent solid*

This internal field is called the local field ($\vec{E}_{internal} = \vec{E}_{loc}$). It is this field which is responsible for the polarization of the medium whose description was given in section 1.2.

If each atom, i, of a solid with a cubic lattice of parameter, a, carries a dipolar moment, $\vec{p}_i$, the polarization vector is defined by:

$$\vec{P}_i = \frac{Na}{a^3} \vec{p}_i \qquad\qquad [1.12]$$

where N is the number of atoms per cell.

If $\vec{P}(\vec{r}) \, d^3r$ is the dipole moment at point $\vec{r}$ of an element with continuous volume d^3r, the potential $dV(\vec{R})$ created by this dipole moment at a point $\vec{R}$ (see Figure 1.7) is:

$$dV(\vec{R}) = \frac{1}{4\pi\varepsilon_0} \vec{P}(\vec{r}) \, g\vec{rad} \, \frac{1}{|\vec{r} - \vec{R}|} d^3r \qquad\qquad [1.13]$$

Let us consider a continuous solid of volume $\mathcal{V}$ and surface S, totally neutral (with no excess charges in the medium), subject to an external field $\vec{E}_a$ (see Figure 1.7). It presents a polarization $\vec{P}(\vec{r})$. The potential $V(\vec{R})$ created at point $\vec{R}$ by the dipole moment $\vec{P}(\vec{r}) \, d^3r$ is (from [1.13]):
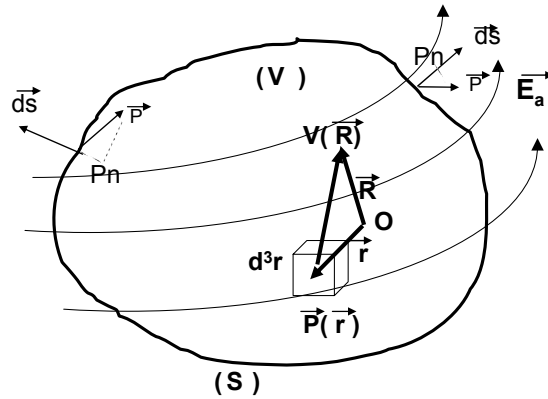
$$V(\vec{R}) = \frac{1}{4\pi\varepsilon_0} \iiint_V \vec{P}(\vec{r}) grad \frac{1}{|\vec{R} - \vec{r}|} d^3r \qquad\qquad [1.14]$$

and the created field has a value of:

$$\vec{E}(\vec{R}) = - g\vec{rad} \, V(\vec{R}) \qquad\qquad [1.15]$$

Using mathematical operations (Ostrogradski and Green), we get:

$$V(\vec{R}) = \frac{1}{4\pi\varepsilon_0} \iiint_V \frac{- div\vec{P}}{|\vec{R} - \vec{r}|} d^3r + \frac{1}{4\pi\varepsilon_0} \iint_S \frac{\vec{P}d\vec{s}}{|\vec{R} - \vec{r}|} \qquad\qquad [1.16]$$

Figure 1.7. *Representation of a solid (V), of surface (S) subject to an external field* $\vec{E}_a$

1.3.3. *Notion of polarization charges*

The two integrals of [1.16] are interpreted as being Coulomb integrals. Indeed, we can write the second integral of [1.16] as: $\vec{P}d\vec{s} = P_n ds$, with P_n being the projection of $\vec{P}$ following the direction of the surface element, directed towards the outside (see Figure 1.7). P_n has the dimension of a surface charge density σ_p. Similarly for the first integral $\rho_p = -\text{div}\vec{P}$ represents a density per unit volume of charges. The densities σ_p and ρ_p are known as *polarization charge* densities.

These polarization charges, in a neutral medium (without excess charges) are not real electric charges; it is a convenient equivalence.

1.3.4. *Average field in a neutral medium*

To the potential $V(\vec{R})$ given by [1.16], due to the polarization, we must add the potential $V_a(\vec{R})$ due to the applied electric field. The potential in $\vec{R}$ is therefore:

$$V_M(\vec{R}) = V(\vec{R}) + V_a(\vec{R}) \tag{1.17}$$

And the field in $\vec{R}$ is given, by using the polarization charges, by:

$$\vec{E}_M(\vec{R}) = \vec{E}_a(\vec{R}) + \vec{E}_{dep}(\vec{R}) + \vec{E}_{\rho_p}(\vec{R}) \tag{1.18}$$

$\vec{E}_{dep}(\vec{R})$ is the field due to surface polarization charges whose effect within the dielectric is to oppose itself to the applied field $\vec{E}_a$. As a result of this, it is called the depolarization field. $\vec{E}_{\rho_p}(\vec{R})$ is the field created by the volume polarization charges.

$\vec{E}_M(\vec{R})$ is the average field. It is the usual macroscopic field defined at all points of the medium and the one that we measure (for capacities, for example). By analogy with [1.9] we can write:

$$\vec{P} = \varepsilon_0\,(\varepsilon_r - 1)\;\vec{E}_M \quad = \varepsilon_0\,\chi\;\vec{E}_M \tag{1.19}$$

where χ is the dielectric susceptibility.

The volume polarization charges ensuing from [1.19] have a density of:

$$\rho_p = -\mathrm{div}\,\vec{P} = -\mathrm{div}(\varepsilon_0\,\chi\;\vec{E}_M) = -\varepsilon_0\,\chi\,\mathrm{div}\,\vec{E}_M\;-\varepsilon_0\,\vec{E}_M\,\mathrm{grad}\,\chi \tag{1.20}$$

with, from [1.18], $\mathrm{div}\,\vec{E}_M = \mathrm{div}\;\vec{E}_a + \mathrm{div}\,\vec{E}_{dep} + \mathrm{div}\,\vec{E}_{\rho_p}$

The sources of the fields $\vec{E}_a$ and $\vec{E}_{dep}$ are either outside, or at the periphery of the medium, subsequently: $\mathrm{div}\;\vec{E}_a = \mathrm{div}\,\vec{E}_{dep} = 0$.

As for the field, $\vec{E}_{\rho_p}$, due to the polarization charges, its divergence has the expression: $\mathrm{div}\,\vec{E}_{\rho_p} = \rho_p/\varepsilon_0$ and, subsequently:

$$\mathrm{div}\,\vec{E}_M = \rho_p/\varepsilon_0 \tag{1.21}$$

Plugging [1.21] into [1.20], the polarization charge is written:

$$\rho_p = -\varepsilon_0\,\frac{E_M}{1+\chi}\,\vec{\mathrm{grad}}\;\chi \tag{1.22}$$

Subsequently, in a neutral medium, the polarization charges are due to the gradient of dielectric susceptibility. In other words, a medium in which susceptibility varies presents volume polarization charges.

The electric induction is defined by:

$$\vec{D} = \varepsilon_0\,\vec{E}_M + \vec{P} \tag{1.23}$$

So, taking into account [1.19]: $\vec{D} = \varepsilon_0 (1 + \chi) \vec{E}_M$, and setting $\varepsilon = \varepsilon_0 (1 + \chi)$:

$$\vec{D} = \varepsilon \vec{E}_M \qquad\qquad\qquad [1.24]$$

where ε is the dielectric permittivity of the material, sometimes called the dielectric constant.

From [1.21] and [1.23], it follows:

$$\text{div}\,\vec{D} = \varepsilon_\Diamond \,\text{div}\,\vec{E}_M + \text{div}\,\vec{P} = \rho_p - \rho_p = 0$$

In a neutral medium the divergence of the induction is null ($\vec{D}$ is at conservative flux). Equally, we can theorize the proportionality between $\vec{P}$ and the depolarization field:

$$\vec{P} = -\varepsilon_0/\lambda \,\vec{E}_{dep} \qquad\qquad\qquad [1.25]$$

The minus sign indicates that $\vec{E}_{dep}$ has an opposite effect to that of $\vec{E}_a$ on the polarization, i.e. it has a depolarizing effect. The fact that $\vec{E}_{dep}$ reduces the polarization produced by $\vec{E}_a$ implies that $\left|\vec{E}\right|_M <. \left|\vec{E}\right|_a$.

1.3.5. *Medium containing excess charges*

Let ρ_a be the charge density of charges and $\vec{E}_{\rho_a}$, the field they produce. This field must be added to the expression [1.18], so:

$$\vec{E}_M(\vec{R}) = \vec{E}_a(\vec{R}) + \vec{E}_{dep}(\vec{R}) + \vec{E}_{\rho_p}(\vec{R}) + \vec{E}_{\rho_a}(\vec{R}) \qquad\qquad [1.26]$$

The presence of charges in the medium imposes $\text{div}\,\vec{D} \neq 0$.

The problem can be tackled in two ways:

– we can treat these excess charges as charges external to the dielectric and associate their field with the applied field $\vec{E}_a$ whose sources are outside the medium. We will therefore set: $\vec{E'}_a = \vec{E}_a + \vec{E}_{\rho_a}$ and subsequently $\text{div}\,\vec{E'}_a = \rho_a / \varepsilon_0$,

− we can also integrate these charges to the medium because, as we will see, these excess charges are generally *trapped charges*, which affect the physical characteristics of the medium considerably. We then set:

$$\vec{E}'_{ch} = \vec{E}_{\rho_a} + \vec{E}_{\rho_p} \text{ et } \text{div}\,\vec{E}'_{ch} = (\rho_p + \rho_a)/\varepsilon_0$$

The final result is identical according to both approaches with:

$$\text{div}\,\vec{E}'_M\,(R) = (\rho_p + \rho_a)+/\varepsilon_0 = \rho/\varepsilon_0$$

where ρ is the total density of charges (polarization charges plus excess charges).

The application of [1.23] gives the expression for the induction:

$$\text{div}\,\vec{D} = \varepsilon_0\,\text{div}\,\vec{E}_M + \text{div}\,\vec{P} = \rho_p + \rho_a - \rho_p = \rho_a$$

Thus, in a charged medium, the divergence of the induction is equal to the density of excess charges.

1.3.6. *Local field*

We have seen (in equation [1.11]) that, within a dielectric subject to an applied field $\vec{E}_a$, an internal field (known as a local field) prevails, such as:

$$\vec{E}_{loc} = \vec{E}_{dip} + \vec{E}_a \neq \vec{0}$$

where $\vec{E}_{dip}$ is the field created by all of the dipoles.

Each ion of a solid is therefore solicited by this local field different to the applied field. The dipole moment which appears on a site j of the lattice is therefore expressed by:

$$\vec{P}_j = \varepsilon_0 \alpha_j \vec{E}_{loc}\,(j)$$

where α_j is the induced or orientational polarisability, depending on the material. The field created by all of the dipoles in j is the vectorial sum of the fields of each dipole, that is to say:

$$\vec{E}_{loc}\,(j) = \sum_{i \neq j} \vec{E}_i(j)$$

Each dipole i will create a potential at the point j whose expression is similar to equation [1.13].

1.3.7. *Frequency response of a dielectric*

When the applied field varies over time (harmonic field $E(\omega,t)$), this field induces a polarization $P(\omega,t)$, defined from the expression [1.19]:

$$P(\omega,t) = \varepsilon_0\, \chi\,(\omega)\, \vec{E}\,(\omega,t).$$

This polarization is the sum of each type of polarization. But the reaction of a material to a type of polarization is not instantaneous. Thus, there is a phase difference δ between an alternative electric field ($E = E_0 \sin\omega t$) and the polarization $P = P_0 \sin(\omega t - \delta)$. In complex notation, we can write $P^* = P_0 \exp(i(\omega t - \delta))$ and $E^* = E_0 \exp(i\omega t)$. The values of the polarization and of the dielectric constant depend on the ease with which the dipole moments reorient themselves when the direction of the field varies. The time required for this reorientation to take place is called relaxation time, τ, and its inverse the relaxation frequency, f.

Given that the relaxations are related to thermal agitation, the frequency, f, of the material is a function of the temperature (f increases with T). When the frequency electric field is much stronger than the relaxation frequency of a type of polarization, this polarization cannot be produced. Conversely, if the frequency of a field is much less than the relaxation frequency, the polarization is produced instantaneously and the phase difference between P and E is null. But if the frequency of the field and the relaxation frequency are close, the phase difference, δ, increases to reach a maximum value. In this case, the curves $D = f(E)$ or $P = f(E)$ form a hysteresis buckle. The area of this buckle represents the energy loss per cycle and per unit volume of the material.

Let a solicitation $S = S' + iS''$, in complex notation. The relationship $S''/S' = tg\delta$ allows us to find δ, the "loss angle" or "dissipation coefficient". This coefficient corresponds to all of the energy dissipations in the material during its solicitation.

The most classical solicitations are mechanical or electrical. In the first case, we find the anelasticity phenomenon encountered for the mechanical properties of the materials. We note G' and G'' the real and complex modules which lead to *the mechanical loss angle δ_m.* For a dielectric, we consider the real permittivity ε' and the complex permittivity ε'' and *the dielectric loss angle δ_e.*

Electronic and ionic polarizations, which bring about short-distance rearrangements, persist in a large range of frequencies. On the other hand, for

molecular materials, the orientation polarization imposes reorientations of the dipoles at the molecular scale. It can't take place above a certain frequency, determined by the size of the molecules and by the molecular dipole moments. We must then take into account the variations of the dielectric constant and the loss factor according to the frequency.

From an experimental point of view, the mechanical solicitations have frequencies in the range 10^{-6} and 10^7 hertz, which permits them to act especially on the molecular chains in polymers. The electrical solicitations can have larger ranges of frequencies, up to 10^{15} hertz, which allows ionic and electronic vibrations to be analyzed.

1.4. Bibliography

[JON 83] JONSCHER A.K., *Dielectric Relaxation in Solids*, Chelsea Dielectric Press, London, 1983.

[KEL 89] KELDYSH L.V., KIRZHNITZ D.A., MARADUDIN A.A. (Eds), *The Dielectric Function of Condensed Systems: Modern Problems in Condensed Matter Sciences*, North Holland, Elsevier Science Ltd, 1989.

[LAN 69] LANDAU L., LIFCHITZ E., *Electrodynamique des milieux continus*, éditions MIR, 1969.

[SCA 89] SCAIFE B.K.P., *Principles of Dielectrics*, Clarendon Press, 1989.